was found to be 2.0 g/mL (observed density for hot pressed B_4C, 2.5 g/mL) and compares favorably with the density of B_4C (1.6–1.8 g/mL) prepared from pyrolysis of poly(carborane-siloxanes).[4] Crystalline B_4C, as determined by X-ray diffraction, of higher density (2.3 g/mL) was obtained by heating the amorphous material at 1450 °C for 2 days.

These initial studies clearly demonstrate that oligomeric vinylpentaborane compounds can be prepared in high yield and are excellent low-temperature precursors to B_4C. Furthermore, the fact that polymer I appears to undergo cross-linking at low temperatures indicates that it might be useful for applications where thermosetting behavior is desired. For example, possible applications might involve the synthesis of composite[14] materials or the generation of thin films of B_4C for use as high temperature thermoelectric materials.[15]

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Diastereoselective Synthesis of the First 2,3,4-Trisubstituted Platina(IV)cyclobutanes

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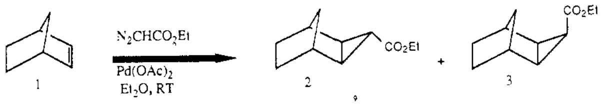
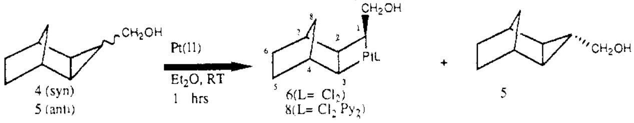
Metallacyclobutane complexes range from proposed transition states to stable entities and are considered to be important pathway components to several organic transformations. Platinacyclobutanes are among the most stable and thus provide a unique opportunity to study metal–carbon ring chemistry. However, until recently the ring-bearing substitutions were simple alkyl and aryl substituents—mostly mono and cis–trans disubstituted.[1-5] There was one trisubstituted example known previously, that being 2,2,3-trimethylplatinacyclobutane.[6] Thus, to explore this area more completely, it seemed reasonable to attempt to expand this group of complexes to more highly substituted examples with more functionality.

We now wish to report (1) the diastereoselective preparation of the first two 2,3,4-trisubstituted platina(IV)cyclobutanes, (2) the crystal structure for one isomer, and (3) the reaction of each diastereomeric cyclobutane complex with diazomethane leading to a *highly stereoselective* preparation of a 1,3-divinylcyclopentane derivative.

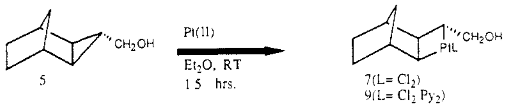
Trisubstituted Platinacyclobutanes. Reaction of ethyl diazoacetate with norbornene (**1**) affords the epimeric mixture of cyclopropyl derivatives **2** and **3** in a ratio of 1.7:1, respectively (eq 1).



(1)



(2)



(3)

Reduction with LAH and subsequent treatment of this alcohol mixture (**4** and **5**) with Zeise's dimer, $(C_2H_4)_2Pt_2Cl_4$, in a molar amount equal to or slightly greater than the minor isomer, yields **6** (L = Cl), selectively, as the precipitated complex (eq 2).[5] Filtration of the solid and reaction of the remaining solution with more Pt(II) yields the diastereomeric isomer **7** (eq 3). Subsequent reaction of **6** and **7** with 2 equiv of pyridine gave **8** and **9**, respectively. The yields of platinum insertion are virtually quantitative.

Carbon NMR spectral data for **8** and **9** are listed in Table I. The key features present which typically describe platinacyclobutane structures are the chemical shifts and $J_{\mathrm{Pt,C}}$ constants for C(1), C(2), and C(3).[1,4,5] The values for C(9) are also consistent with structures **8** and **9**.

Although **9** is less stable thermally than **8**, it readily formed quality crystals from chloroform–heptane solutions for X-ray analysis (Figure 1).[7] This result establishes unambiguously that **9** is the correctly assigned isomer of the trisubstituted platinacyclobutane complexes. The pucker angle in the cyclobutane moiety (i.e., the angle generated by the platinum atom being out of the C_1–C_2–C_3 plane) is 17°.

Reactions of 8 and 9. The reason for synthesizing **8** and **9** was to determine the stereochemical result of reacting each with diazomethane. Previous work in our laboratory had revealed the results shown in eq 4.[8] Thus, for extending the future synthetic advantages of this reaction, we wanted to know (a) if we could

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[7] X-ray structure determination of complex **9**: tan-colored crystals of **9** were grown by allowing heptane to diffuse into a chloroform solution. A specimen suitable for X-ray analysis (approximately 0.22 × 0.48 × 0.63 mm) was mounted on a glass fiber and coated with a drop of a 3:1 mixture of Paratone-N and mineral oil. Uncoated crystals gradually turned opaque when exposed to air, presumably from loss of lattice solvent, and gave powder diffraction patterns. Data collection was carried out at 25 °C on a Nicolet R3mE automated diffractometer with 96-step ω scans with graphite monochromated Mo Kα radiation (g = 0.71069 Å). Unit cell constants of a = 9.421 (2) Å, b = 11.085 (2) Å, c = 11.399 Å, α = 81.98 (2)°, β = 74.40 (2)°, and q = 73.04 (2)° were determined by least-squares refinement by 25 centered reflections in the range 21° < 2R < 30°. Data reduction, including corrections for Lorentz and polarization effects, gave 7894 unique reflections in the range 3° < 2R < 65°, of which 5197 with $I > 3s(I)$ were used for structure refinement. The space group was assumed to be $P\bar{1}$, on the basis of cell volume and was confirmed by a successful structure solution and refinement. Poor refinement behavior was found in the alternative space group $P1$. The platinum position was obtained from a Patterson synthesis, and difference maps gave the remaining non-hydrogen positions, including one chloroform molecule per two units of complex **9**. The chloroform molecule is disordered between two half-occupied orientations, related by an inversion center halfway between two chlorine atom positions that are shared by both orientations. Calculated density for $C_{19}H_{24}N_2OCl_2Pt\cdot{}^1/_2CHCl_3$, z = 2, is 1.89 g/cm^3. Empirical corrections for absorption were based on azimuthal scans collected for 16 reflections with a transmission factor range of 0.34–0.96 (m = 69.2 cm^{-1}, Mo Kα). All atoms were refined with anisotropic thermal parameters, except hydrogens which were assigned to idealized positions with a common refined isotropic thermal parameter. Statistical weighting was used, and one reflection was excluded from the data set based on evidence of strong extinction. The structure refined to an R value of 0.041 (R_w = 0.040). All crystallographic calculations were performed on a Data General Eclipse computer with the SHELXTL program package by G. M. Sheldrick, Nicolet Instrument Corp., Madison, WI.

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Table I. ^{13}C NMR Data for the New Platinacycles and the Two Divinylcyclopentane Analogues

C no.	**8**	**9**	**13**	**14**
	$\delta = (J_{Pt-C})$	$\delta = (J_{Pt-C})$		
1	6.36 (370) d	4.05 (370)	43.8	44.8
2	56.7 (98) d	59 (98)	32.8	32.8
3	13.0 (394) d	14.4 (398)	40.7	41.3
4	40.1 (10) d	41.3 (28)	31.9	31.9
5	28.6[b] t	29.2 (41)	29.2	29.5
6	28.9 t	27.4	142.9	142.9
7	37.8 d	40.7	112.5	112.5
8	37.5 t	35.6	127.2	127.2
9	63.7 (24) t	67.0 (28)	138.1	138.3
10			65.9	65.8

[a] Three singlet but broad pyridine resonances were also observed: ortho, 149.8; para, 138.4; and meta, 125.2 ppm. [b] Pt coupling not resolved.

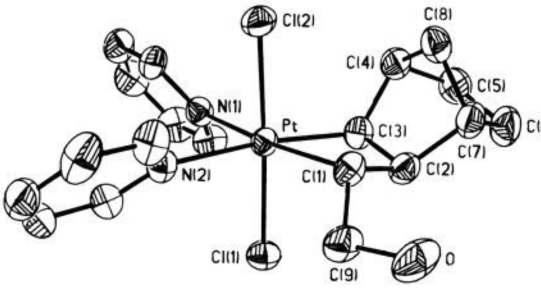
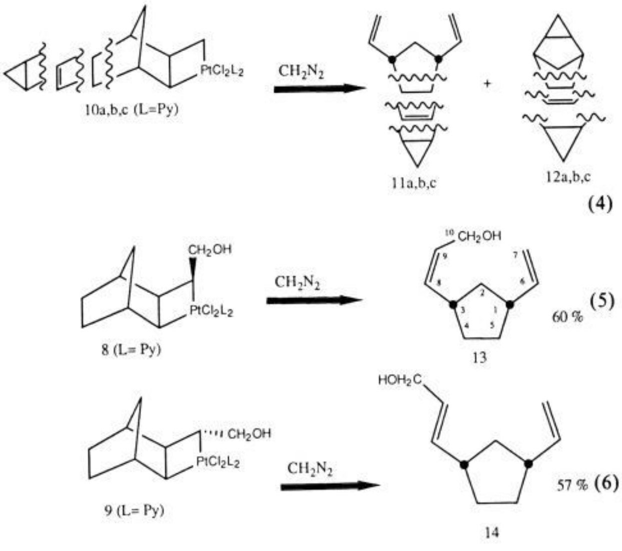


Figure 1. Thermal ellipsoid drawing (at 50% probability) of structure **9** with labeling scheme.

differentiate the two olefinic residues by arranging to have one substituted and (b) if some stereochemical preference could be achieved on the substituted side.



The results are shown in eq 5 and 6. This reaction not only differentiates the olefinic residues but also simultaneously leads to retention of relative stereochemistry at one double bond and yields stereospecificity at the two allylic centers. ^{13}C NMR data for **13** and **14** are listed in Table I and are consistent with the carbon framework.[8] Further, by using homonuclear J resolved ^1H 2D NMR and 1D selective decoupling results, the vicinyl coupling constant for the disubstituted double bond of each isomer was obtained.[9] A value of 10.6 Hz was obtained for **13** and 15.3 Hz was found for **14**. Further, upon adding the shift reagent, $Eu(Fod)_3$, to **13** and decoupling the C(9) methylene, a vicinyl coupling constant of 10.6 Hz was again observed. It is important to note that the protons on C(8) and C(9) are a complex AB multiplet between 5.39 and 5.58 ppm. In **13**, proton 8 is upfield of 9, whereas in **14**, they are reversed.

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Supplementary Material Available: Listings of atomic coordinates, bond lengths and angles, and thermal parameters (3 pages). Ordering information is given on any current masthead page.

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(9) These data were gathered during NMR vendor demonstrations at General Electric (Fremont) and Bruker (Billerica).

Luminescent Organometallic Compounds with Relativistic Metal–Metal Bonds. Synthesis and Characterization of $AuTl[Ph_2P(CH_2)S]_2$, a One-Dimensional Metal–Metal Bonded Polymer in the Solid State

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Several compounds containing short metal–metal distances between relativistic heavy atoms[1,2] such as Au, Pt, Tl, Pb, etc. have been shown to display luminescent properties.[3-7] An important example is the complex $Tl_2Pt(CN)_4$ reported by Nagle, Balch, and Olmstead[5] which has a Pt–Tl bond of 3.140 (1) Å that is shorter than found in columnar structures.[6] Although studies of the luminescence properties of organometallic complexes is a rapidly growing area of interest,[3] much of the work to date has focused on metal carbonyls and on binuclear or polynuclear transition-metal complexes with at least one metal ion in a d^8 electronic configuration.[3,4] The luminescent, trinuclear, bimetallic Ir_2Tl complex with mixed d^8 and s^2 electronic configurations is one recent example.[7]

Very few luminescent binuclear complexes with d^{10} or s^2 electronic configurations are known. We report here the synthesis[8] and characterization of the bimetallic binuclear complex $AuTl(MTP)_2$, (MTP = $Ph_2P(CH_2)S$). This material forms a one-dimensional polymer, Figure 1, with short (2.9–3.0 Å) relativistic Tl–Au bonds[9] and is luminescent in the solid state at 298 K.

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(9) Bruce and Duffy[10a] noted recently that close Au⋯Au separations can be caused by a relativistic contraction of s orbitals.[1,2] Rundle[10b] described this weak Au⋯Au bonding (3.26 Å) without considering relativistic effects in a communication on the structure of $Au(DMG)_2AuCl_2$ (HDMG = dimethylglyoxime). However, the relativistic contraction of the 6s orbital leads to enhanced 5d,6s orbital mixing and the observed bonding. The filled d_{z^2} orbital on Pt^{II} (in $Tl_2Pt(CN)_4$) or Au^I (in the compound reported here) along with the empty 6s orbital mix effectively with the filled 6s orbital on Tl^I to give the bond we are calling a relativistic metal–metal bond. Obviously this same mixing can occur with other heavy atoms which have relativistically contracted s orbitals that are involved in the bonding. Hoffmann et al.[11] have discussed the orbital nature of bonding in binuclear and polynuclear compounds of a similar type.

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