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.

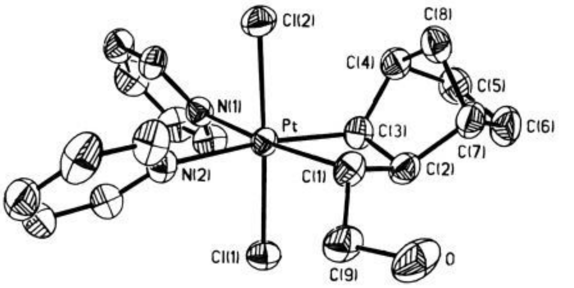
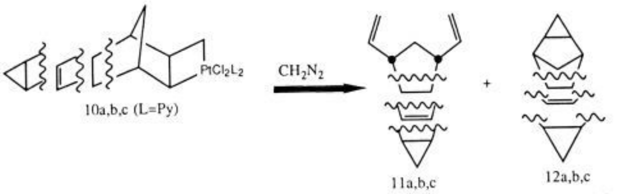


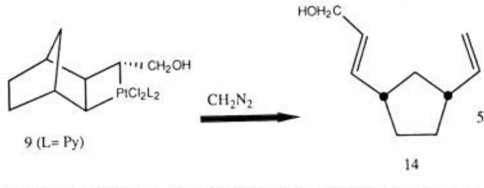
Figure 1. Thermal ellipsoid drawing (at 50% probability) of structure **9** with labeling scheme.

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



(4)

(5)



(6)

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 ^{1}H 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.

Acknowledgment. We thank Montana State University, the National Science Foundation (CHE 7826160, 8115565, 8306254), and the donors of the Petroleum Research Foundation, administered by the American Chemical Society, for support of this research. Also, we wish to acknowledge Johnson-Matthey for their generous loan of platinum.

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$_2$P(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$_2$Pt(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$_2$Tl 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$_2$P(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)$_2$AuCl$_2$ (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$_2$Pt(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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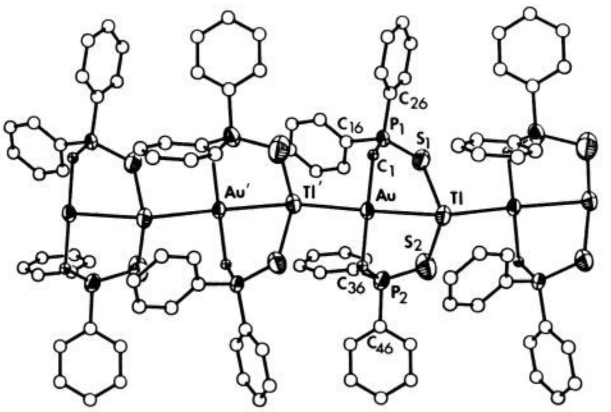

Figure 1. The repeat structure of AuTl(MTP)$_2$, **2**, showing 50% thermal ellipsoids. Selected bond distances and angles are as follows: Tl–Au = 2.959 (2) Å, Tl–Au′ = 3.003 (2) Å, Tl–S(1) = 3.06 (1) Å, Tl–S(2) = 2.91 (1) Å, Au–C(1) = 2.17 (2) Å, Au–C(2) = 2.13 (2) Å, P(1)–S(1) = 19.6 (1) Å, P(1)–C(1) = 1.85 (3) Å, P(2)–S(2) = 1.94 (2) Å, P(2)–C(2) = 1.89 (3) Å, Au–Tl–Au′ = 162.7 (1)°, Tl–Au–Tl′ = 162.9 (1)°, Au–Tl–S(1) = 75.6 (2)°, Au–Tl–S(2) = 83.9 (2)°, Tl–Au–C(1) 88.1 (9)°, Tl–Au–C(2) = 91.6 (7)°, S(1)–Tl–S(2) = 90.5 (4)°, C(1)–Au–C(2) = 173 (1)°, S(1)–P(1)–C(1) = 115.1 (9)°, S(2)–P(2)–C(2) = 120 (1)°, Tl–S(1)–P(1) = 101.7 (5)°, Tl–S(2)–P(2) = 101.7 (6)°, Au–C(1)–P(1) = 104 (1)°, Au–C(2)–P(2) = 110 (1)°.

The AuTl(MTP)$_2$ complex, **2**, is formed[12] by reacting Tl^{I} with the complex [PPN]Au(MTP)$_2$, **1** (PPN = $[(C_6H_5)_3P]_2N^+$), which contains a linear two-coordinate Au^{I} center.[8] The Au(MTP)$_2^-$ anion binds to other metal ions to form binuclear or trinuclear complexes through a bonding of the MTP sulfur atoms to the second metal center.[8,13] **1** reacts readily with Pb^{II} ions to yield[14] Au$_2$Pb(MTP)$_4$.

The structure of **2** was determined by single-crystal X-ray diffraction.[15] As found[8] in **1** and Au$_2$Pt(MTP)$_4$, the Au^{I} center of **2** is coordinated to two carbon atoms. The Tl^{I} center is bonded to two sulfur atoms with the distances of Tl–S(1) = 3.05 (1) Å, Tl–S(2) = 2.91 (1) Å, typical for Tl–S bonds.[16] This molecule forms a one-dimensional polymer along the unique crystallographic *b*-axis of the lattice, with nearly equal Tl–Au spacings, Tl–Au(intramolecular) = 2.959 (2) Å, Tl–Au′(intermolecular) = 3.003 (2) Å.

The Tl–Au separations in **2** are shorter than the Tl–Pt bonds reported by Nagle et al.[5] and less than the sum of Tl–Au metallic radii, 3.034 Å.[17] Significant bonding interaction occurs between the metal centers. Short thallium–transition-metal bonds also have been observed in the complexes [Ir$_2$Tl(CO)$_2$Cl$_2${μ-(Ph$_2$PCH$_2$)$_2$AsPh}$_2$]NO$_3$ and [18] [{Ru$_6$C(CO)$_{16}$}$_2$Tl]$^+$. Weak Tl···Au interactions with long (3.45 Å) separations have been found in Tl[Au(CN)$_2$].[19] Compound **2** is the first example of bimetallic one-dimensional polymer containing short Tl–Au bonds. The Tl–Au–Tl′ and Au′–Tl–Au angles are nonlinear by ca. 17°. The geometry around the Tl^{I} atom can be described as a distorted trigonal bipyramid with a vacant equatorial coordination site.

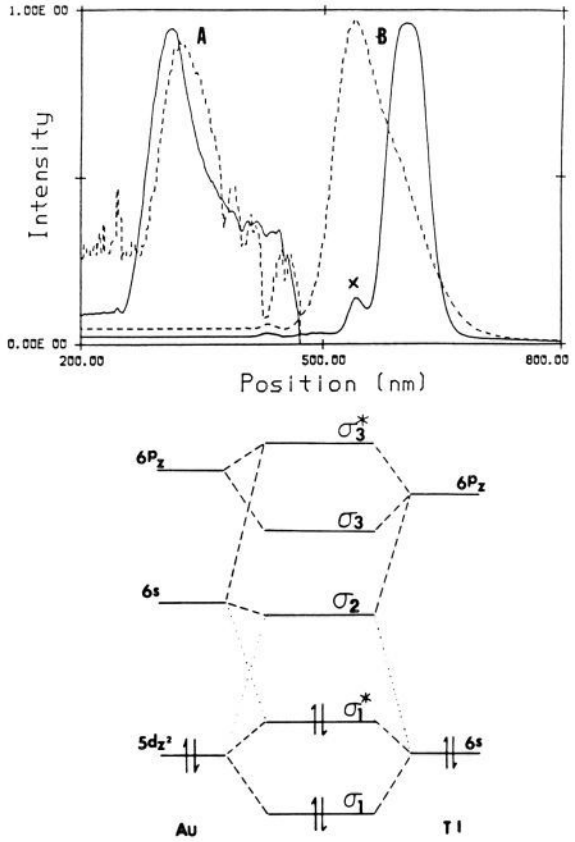

Figure 2. Top: The uncorrected excitation and emission spectra of the frozen solution of **2** in CH$_2$Cl$_2$ (dashed line) and the crystals of **2** (solid line) at 77 K (excitation in curve A, emission in curve B). Bottom: A qualitative molecular orbital diagram for the Au–Tl unit.

A frozen CH$_2$Cl$_2$ solution of **2** shows a strong yellow luminescence, and crystals show an intense yellow-orange luminescence at 298 K when irradiated by UV light. The excitation and emission spectra at 77 K for **2** are shown in Figure 2. The maximum (320 nm) of the excitation spectrum of the solution correlates well with the absorption spectrum of **2** in CH$_2$Cl$_2$ at 298 K, which shows a single maximum at 320 nm (ϵ = 2900 M^{-1} cm^{-1}). The emission band of crystals at 77 K is at lower energy level (602 nm) than that of the frozen solution (536 nm) at 77 K. The energy difference between the emission spectra in the solid and frozen solutions could be caused by the aggregation of AuTl(MTP)$_2$, in the solid being reduced in solution. Molecular weight measurements in solution, however, have failed due to the low solubility of the complex.

The decay of emission at the 575 nm from the solid at 298 K after laser excitation at 355 nm fits reasonably well one single exponential function with a lifetime of 0.98 μs. The long lifetime and large separation between excitation and emission peaks indicates that the luminescence is phosphorescence.

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(12) Addition of a colorless solution of Tl$_2$SO$_4$ in methanol to a CH$_2$Cl$_2$ solution of [PPN]Au(MTP)$_2$ in a 1:1 ratio yields yellow crystalline **2** (53%). The ^{1}H NMR spectrum of **2** shows no coupling of CH$_2$ groups with the Tl nucleus (^{205}Tl, $I = 1/2$). The methylene doublet of the ligand at δ = 1.64 ppm (CH$_2$, J_{P-H} = 12 HZ, in CDCl$_3$) is shifted downfield compared with that of **1** (doublet, δ = 1.52 ppm, J_{P-H} = 15 HZ, in CDCl$_3$), indicating the presence of a bonding interaction of Tl^{I} ion with the Au(MTP)$_2^-$ anion in solution through the two sulfur atoms of the Au(MTP)$_2^-$ anion. Anal. Calcd. for 2: C, 36.14; H 2.78. Found: C, 36.65; H, 2.53. The presence of the Tl^{I} cation in the complex **2** was confirmed by the quantitative precipitation of TlCl upon the addition of [PPN]Cl to the CH$_2$Cl$_2$ solution of **2**.

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(15) Crystal data for **2** (293 K): C$_{26}$H$_{24}$TlAuS$_2$P$_2$, monoclinic, $P2_1/a$, a = 24.368 (4) Å, b = 11.655 (2) Å, c = 9.445 (2) Å, β = 101.13 (2)°, V = 2632.2 (8) Å^3, Z = 4, D_{calcd} = 2.18 g cm^{-3}, μ = 120.19 cm^{-1}. Yellow crystals, grown from CH$_2$Cl$_2$ by slow solvent evaporation, were used for data collection on a Nicolet R3m/E diffractometer. Structure solution and refinements were carried out by using the SHELXTL, 5.1, locating metal atoms by direct methods. Convergence to final R values of R = 0.0625 and R_w = 0.0647 for **2** was obtained by using 1659 reflections [$F^2 \geq 3\sigma(F^2)$] and 111 least-square parameters. Tl, Au, P, and S were refined anisotropically.

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The luminescence properties of **2** are probably the result of Au–Tl interactions. PPNAu(MTP)$_2$ does not possess any strong absorption band at 320 nm. Tl^I ion is luminescent, but its excitation and emission bands appear at much higher energy than those of AuTl(MTP)$_2$.[20] A simple molecular orbital diagram[21] for Au–Tl bonding in **2** is given in Figure 2 (lower part). It is proposed that the absorption band at 320 nm which results in the luminescence of **2** is from the σ_1* to σ_2 transition localized on the Au–Tl bond. The Au–Tl bond may be stabilized by the mixing of the filled 6s level on Tl^I with the empty 6s level on Au(I) and p$_z$ mixing with both levels, a process suggested to occur due to relativistic effects of these heavy metal atoms.

Acknowledgment. We thank the Welch Foundation, the National Science Foundation (CHE 8708625), and the Texas A&M Center for Energy and Minerals Resources for financial support.

Supplementary Material Available: Tables of atomic positional parameters, bond distances, bond angles, anistropic thermal parameters, and data collection parameters for **2** (3 pages); table of observed and calculated structure factors for **2** (20 pages). Ordering information is given on any current masthead page.

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(21) The relative positions of the orbital energies are based on the energies of the atomic orbitals (Herman, F.; Skillman, S.; *Atomic Structure Calculation*; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1963).

Stereochemistry of the Addition of Diarylsilylenes to *cis*- and *trans*-2-Butenes

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The ultraviolet photolysis of linear trisilanes is known to yield silylene. While the reaction of silylenes with olefin has been studied,[1] there seem to be few reports on the stereochemistry of the silylene addition. The scarcity and ambiguity of the stereochemical information are due to the extreme instability of siliranes when attacked by nucleophiles; in such a case they readily give ring-opening products. Ishikawa,[2] Jones,[3] and Seyferth[4] independently reported the stereospecific addition of silylene to olefins. There is general agreement that normal silylene has singlet ground state[5] and reacts with olefin in concerted fashion. However, bulky silylenes might find the concerted pathway more difficult than they do their small substituted one and give nonstereospecific products in either singlet or triplet state. We wish to report the results of recent investigations on bulky diorganosilylene reactions with 2-butenes, leading to the first reported examples of nonstereospecific additions of silylenes.

Photolysis of 2,2-dimesityl-1,1,1,3,3,3-hexamethyltrisilane (**1a**) and a large excess of *cis*-2-butene (1:100) in hexane at −5 °C was carried out with a low-pressure mercury lamp for 10 min to give 99% of *cis*-silirane (**3a**)[6] and only 1% of trans isomer **4a**[7] (Scheme I). Surprisingly, the photolysis of **1a** in *trans*-2-butene gave a considerable amount of the cis isomer **3a** (30%) in addition to **4a** (70%).

2,2-Bis(2,4,6-triisopropylphenyl)-1,1,1,3,3,3-hexamethyltrisilane (**1b**) was synthesized as a precursor of more crowded novel silylene **2b** and irradiated in *trans*-2-butene to afford **3b** (41%) and **4b** (59%); the ratio of nonstereospecific adducts apparently increased.

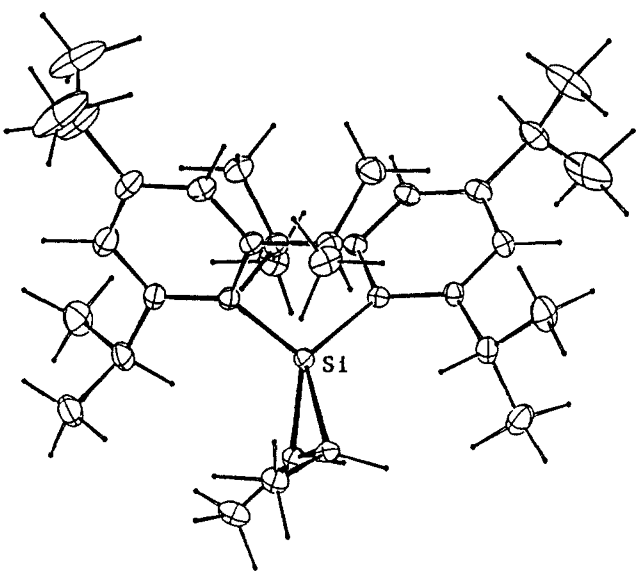
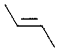


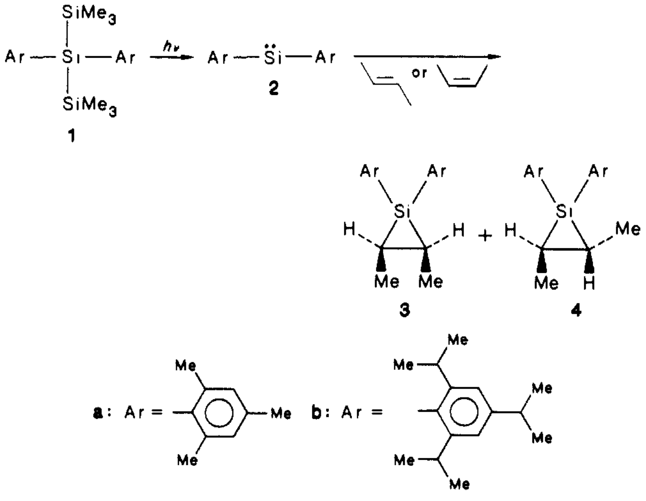
Figure 1. ORTEP drawing of **3b**.

Table I. Product Ratios of Reactions of Dimesitylsilylene and 2-Butene[a]

starting materials	irradtn time[b]	product ratios (%) **3a** (cis)	product ratios (%) **4a** (trans)
1a + 	10 min	30	70
	3 h	23	77
	9 h	34	66
	10 min[c]	55	45
1a + 	10 min	99	1
	3 h	96	4
	9 h	90	10
	10 min[c]	95	5

[a] The product ratios were determined by ^{13}C NMR and HPLC (solvent MeOH:H$_2$O = 9:1). [b] The reaction was carried out at −5 °C. [c] The reaction was carried out at −95 °C.

Scheme I



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(6) Compound **3a**: ^{1}H NMR (CDCl$_3$, 500 MHz) 1.07–1.11 (deformed d, 6 H), 1.19–1.25 (deformed q, 2 H), 2.18 (s, 3 H), 2.20 (s, 3 H), 2.52 (s, 6 H), 2.53 (s, 6 H), 6.77 (s, 2 H), 6.80 (s, 2 H); ^{13}C NMR (CCl$_4$, 125 MHz) 10.5, 13.3, 21.00, 21.03, 24.47, 24.50, 127.1, 128.0, 128.4, 139.2, 139.3, 145.6, 145.8; ^{29}Si NMR (CDCl$_3$, 18 MHz) −83.2; exact MS found 322.2113, calcd for $C_{22}H_{30}Si$ 322.2117.

(7) Compound **4a**: ^{1}H NMR (CDCl$_3$, 500 MHz) 0.77–0.83 (deformed q, 2 H), 1.03–1.07 (deformed d, 6 H), 2.19 (s, 6 H), 2.50 (s, 12 H), 6.77 (s, 4 H); ^{13}C NMR (CCl$_4$, 23 MHz) 16.1, 21.0, 21.4, 24.2, 126.7, 128.1, 138.5, 145.2; ^{29}Si NMR (CDCl$_3$, 18 MHz) −77.4; exact MS found 322.2116, calcd for $C_{22}H_{30}Si$ 322.2117.