subsequently refined with an occupancy factor of 0.5.

Atomic scattering factors were taken from the usual tabulations.[21] Anomalous dispersion terms for W, Ru, Mo, and P atoms were included in F_c.[22] Empirical absorption correction were applied in each instance.[23] The final refinements were conducted by using the SHELX-76 program. All non-hydrogen atoms were allowed to vibrate anisotropically, except carbon atoms of cyclopentadienyl and phenyl rings which were refined as isotropic rigid groups in order to reduce the number of variable parameters (C_5H_5, C–C = 1.420 Å; C_6H_5, C–C = 1.395 Å). Hydrogen atoms, except those attached to the disordered cyclopentadienyl ring in **1a**, were entered in idealized positions (C–H = 0.97 Å) and held fixed during refinements. Scattering factors for the hydrogen atoms were taken from Stewart et al.[24]

Final atomic coordinates and 10^2U_{eq} (or 10^2U_{iso}) for non-hydrogen atoms of compounds **1a** and **4b** are given in Tables IV and V, respectively. Tables S1 and S2 list the thermal parameters ($\times 10^2$) for atoms of **1a** and **4b**, respectively, which were refined anisotropically.[25] Structure amplitudes ($10|F_o|$ vs $10|F_c|$) for the two structures are available in Tables S3 and S4.[25]

Acknowledgment. We thank Johnson-Matthey for generous loan of ruthenium chloride.

Registry No. **1a**, 116698-72-7; **1b**, 116698-74-9; **2a**, 116698-75-0; **2b**, 116698-76-1; **3a**, 116698-78-3; **3b**, 116698-80-7; **4a**, 116698-88-5; **4b**, 116698-90-9; **5a** (isomer 1), 116698-82-9; **5a** (isomer 2), 116698-86-3; **5b**, 116698-84-1; $Ru_3(CO)_{12}$, 15243-33-1; $[PPh_4][CpMo(CO)_3]$, 91463-50-2; $[PPh_4][CpW(CO)_3]$, 91482-94-9; MeC≡CMe, 503-17-3; PhC≡CH, 536-74-3.

Supplementary Material Available: Tables S1 and S2, anisotropic thermal parameters for compounds **1a** and **4b**, respectively (2 pages); Tables S3 and S4, structure factor amplitudes ($\times 10$) for compounds **1a** and **4b**, respectively (51 pages). Ordering information is given on any current masthead page.

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(25) See paragraph at the end of paper regarding supplementary material.

Organometallic Chemistry of Sulfinic Acids. Highly Stereo- and Regioselective Intramolecular Hydroplatinations. X-ray Crystal Structure of $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$

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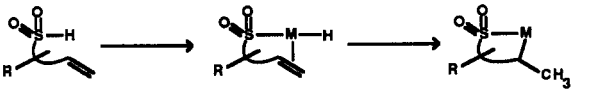
Reactions of sulfinic acids with platinum(0) and platinum(II) complexes are described. *p*-Tolylmethanesulfinic acid reacts with tetrakis(triphenylphosphine)platinum, $(Ph_3P)_4Pt$, to afford *trans*-$(Ph_3P)_2Pt(H)SO_2R$ (R = CH_2-*p*-tolyl) in 70% yield. $(COD)Pt(CH_3)SO_2R$ (COD = 1,5-cyclooctadiene; R = CH_2-*p*-tolyl, 77% yield), $(COD)Pt(CH_3)SO_2R$ (R = *p*-tolyl, 53% yield), and *cis*-$(Ph_3P)_2Pt(CH_3)SO_2R$ (R = *p*-tolyl, 91% yield) were prepared analogously from the corresponding L_2PtMe_2 complexes. Treatment of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ with butene-4-sulfinic acid and pentene-4-sulfinic acid afforded isomerically pure chelates $(Ph_3P)(CH_3)Pt(\eta^3\text{-}SO_2CH(R)CH_2CH_2CH{=}CH_2)$ (R = H, 33% yield; R = CH_3, 31% yield). Reaction of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ with hexene-5-sulfinic acid afforded the unchelated derivative $(Ph_3P)_2(CH_3)Pt(\eta^1\text{-}SO_2CH(CH_3)CH_2CH_2CH_2CH{=}CH_2)$ (22% yield). Intramolecular hydrometalations were observed upon treatment of $(Ph_3P)_4Pt$ with unsaturated sulfinic acids. Butene-4-sulfinic acid was converted to $(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_3)$ (69% yield). Pentene-5-sulfinic acid afforded metallacyclohexane $(Ph_3P)_2PtSO_2CH_2CH_2CH_2CH(CH_3)$ (37% yield), which upon heating, isomerized to a metallacyclopentane, $(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_2CH_3)$, in 27% yield. Pentene-4-sulfinic acid afforded $(Ph_3P)_2Pt[cis\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ (37% yield, >20:1 stereoselectivity), which upon heating afforded $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ in 56% yield and >20:1 stereoselectivity. Hexene-5-sulfinic acid afforded the metallacyclohexane $(Ph_3P)_2PtSO_2CH(CH_3)CH_2CH_2CH(CH_3)$ (47% yield) as a cis/trans mixture of unassigned stereochemistry. Upon heating, both isomers isomerized to $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ in 36% yield and >20:1 stereoselectivity. Stereochemical assignments of all metallacyclopentanes derived from a molecular structure determination of $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$. The metallacycle crystallized in $P2_1/c$ space group with cell parameters a = 10.563 (1) Å, b = 9.733 (17) Å, c = 36.362 (42) Å, β = 94.59°, Z = 4, and R_w = 9.8%. Attempts to deinsert SO_2 from the platinum sulfinates failed to afford the corresponding metal alkyls.

Introduction

The rise of organotransition metals to prominence in organic synthesis has produced a steadily increasing need to understand and control the stereochemistry of substrate functionalizations. We describe herein a study of intramolecular hydrometalations of unsaturated sulfinic acids (eq 1). The observed high and complementary kinetic and



(1)

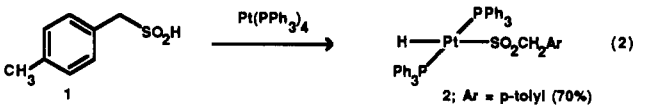
thermodynamic stereoselectivities may shed some light on the stereoselective hydrometallations implicated in internally directed hydrosilylations,[1] hydroacylations,[2] hy-

droformylations,[3] hydrogenations,[4] and hydrocarboalkoxylations.[5,6]

Results

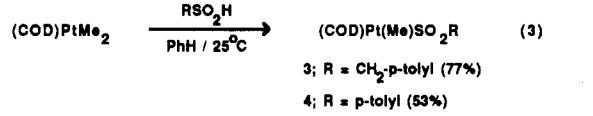
Platinum(II) Hydrido Sulfinates. Due to the paucity of reported reactions of sulfinic acids with transition-metal complexes,[7,8] we began our studies of the internal hydrometalations of sulfinic acids with some simple substitution and addition reactions. In all cases, assignments of the S- rather than O-bound sulfinates[9-12] were supported by well-established infrared absorptions[10,11] as well as large $^{195}Pt-^{13}C$ (two-bond) coupling constants in the Pt–SO_2–C moiety. In general, the reactions proceeded in good yield. The reported yields at times reflect the multiple recrystallizations and chromatographies required to obtain analytically pure samples.

Reaction of 1.2 equiv of *p*-tolylmethanesulfinic acid (**1**) with tetrakis(triphenylphosphine)platinum(0), $(Ph_3P)_4Pt$, in diethyl ether at 25 °C afforded hydride **2** (70% yield) as a colorless precipitate (eq 2). The ^1H NMR spectrum

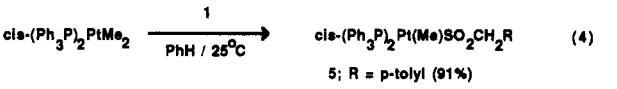


of **2** displayed a hydride resonance at −12.20 ppm with 819 Hz $^{195}Pt-H$ coupling. The absence of $^{31}P-^1H$ coupling in $(R_3P)_2Pt(X)H$ species has been observed previously[27a,b] and ascribed to rapid phosphine exchange. At −80 °C, a sharp singlet in the $^{31}P\{^1H\}$ NMR spectrum at 28.67 ppm with platinum satellites (J_{Pt-P} = 3049 Hz) confirmed the trans stereochemistry of **2**.[13]

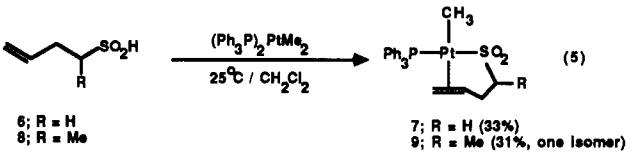
When equimolar quantities of $(COD)Pt(CH_3)_2$[14] (COD = 1,5-cyclooctadiene) and *p*-tolylmethanesulfinic acid (**1**) were combined in benzene solution at 25 °C, effervescence was immediately observed. Colorless microcrystals of **3** could be obtained in 77% yield (eq 3). An analogous



reaction of $(COD)_2Pt(CH_3)_2$ with *p*-toluenesulfinic acid afforded **4** in 53% yield. *cis*-**5** could be prepared isomerically pure in 91% isolated yield by the addition of **1** to *cis*-$(Ph_3P)_2Pt(CH_3)_2$[14] (eq 4).



Chelating Platinum(II) Alkenyl Sulfinates. The reaction of equimolar quantities of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ and butene-4-sulfinic acid (**6**) in dichloromethane at 25 °C (eq 5) resulted in gas evolution and the formation of a



clear, colorless solution. A crude product isolated after 30 min displayed a complex ^1H NMR spectrum containing both free and platinum-coordinated olefin signals. Flash chromatography of the mixture through a long column of silica gel at reduced flow rates provided olefin chelate **7** in 33% yield. (The chromatographic removal of the Ph_3P appeared to drive the equilibrium toward the chelated form.) The ^1H NMR spectrum of **7** displayed upfield shifted olefinic protons[15] with ^{195}Pt satellites. The four aliphatic protons in the butenyl chain were diastereotopic, appearing as well-resolved multiplets. The out-of-plane olefin alignment was assigned based on chemical shift analogies with related chelates.[16,17] Furthermore, the substantial upfield chemical shifts of the olefinic carbon resonances in the ^{13}C NMR spectrum indicated the olefin moiety of **7** to be trans to the methyl group rather than to a phosphine.[18]

Olefin chelate **9** was prepared similarly from pentene-4-sulfinic acid (**8**) in 31% yield (eq 5). The ^1H, $^{31}P\{H\}$, and ^{13}C NMR spectra at 25 and −80 °C were consistent with the formulation of **9** as a single diastereomer. In all other respects the spectroscopic data for **9** were similar to those for **7**. Attempts to obtain X-ray quality crystals for a stereochemical assignment were unsuccessful.

Efforts to prepare the homologous chelate **11** from the reaction of *cis*-$(Ph_3P)_2Pt(CH_3)_2$ and pentene-5-sulfinic acid

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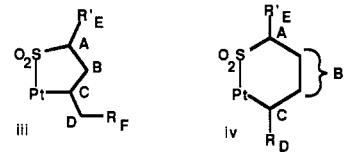
Table I. ^{1}H NMR Data for Platinacycle Sulfinates iii and iv



	chem shift (multiplicity, coupling const)[a]					
	A	B	C	D	E	F
13	3.13 (m) 2.77 (dd, 12, 5)	1.97 (m) 1.17 (bt, 15)	2.25 (br)	0.83 (t, 7.5, 40[b])		
15	2.70 (m)	2.16 (m, 2 H) 1.07 (br) 0.72 (br)	1.76 (br)	1.30 (t, 7.5, 33[b])		
16	3.12 (m) 2.85 (dd, 12, 5)	1.75 (m) 1.08 (m)	2.12 (br)	1.50 (m) ...	...	0.22 (t, 7.1)
18a	...	...	...	1.30 (t, 7.0)	1.41 (d, 7.0)	
18b	...	...	...	1.20 (t, 7.0)	1.01 (d, 7.0)	
trans-**19**	3.13 (m) 1.32 (m)	1.60 (m)	1.91 (br)	1.46 (m)	1.18 (d, 6.5)	0.26 (t, 7.0)
cis-**20**	3.14 (m) 1.32 (m)	1.60 (m)	2.08 (br)	1.05 (td, 7.5, 2.5, 50[b])	1.20 (d, 6.5)	
trans-**20**	3.23 (m)	1.73 (td, 14.5) 1.15 (t, 15)	2.02 (br)	0.97 (t, 7.0, 40[b])	1.22 (d, 6.5)	

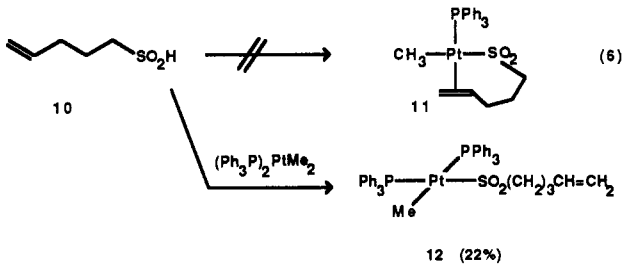
[a] Chemical shifts are reported in parts per million downfield from tetramethylsilane. Coupling constants are reported in hertz. All spectra were recorded in $CDCl_3$ except for **13** (CD_2Cl_2). [b] J_{Pt-H}.

Table II. ^{13}C NMR Data for Platinacyclopentane Sulfinates iii

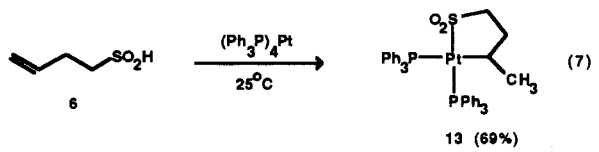
	chem shift (J_{Pt-C}, $J_{P(trans)-C}$, $J_{P(cis)-C}$)[a]						
	solv	A	B	C	D	E	F
13	$CDCl_3$	68.5 (235, 9, 0)	33.3 (0, 0, 0)	44.7 (570, 73, 4)	21.3 (0, 0, 0)		
16	$CDCl_3$	68.0 (235, 8, 0)	26.8 (0, 0, 0)	50.3 (570, 81, 0)	25.7 (0, 0, 0)		12.9 (64, 8, 0)
trans-**19**	$CDCl_3$	70.1 (223, 7, 5)	27.1 (899, 0, 0)	48.3 (564, 71, 4)	35.2 (372, 0, 0)	8.6 (108, 0, 0)	13.7 (64, 0, 0)
cis-**20**	CD_2Cl_2	77.5 (270, 10, 4)	41.4 (97, 0, 0)	42.6 (591, 73, 0)	26.8 (109, 0, 0)	9.0 (111, 0, 0)	
trans-**20**	CD_2Cl_2	70.9 (223, 6, 0)	42.3 (110, 0, 0)	41.5 (563, 71, 0)	23.3 (0, 0, 0)	8.8 (108, 0, 0)	

[a] Chemical shifts are reported in parts per million downfield from TMS and coupling constants are reported in hertz.

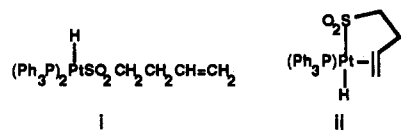
(**10**) afforded only nonchelated adduct *cis*-**12** in 22% yield (eq 6).



Intramolecular Hydrometalations. Admixing $(Ph_3P)_4Pt$ and a small excess of butene-4-sulfinic acid (**6**) suspended in ether/benzene at 25 °C for 9 h afforded metallacycle **13** in 69% yield after flash chromatography and recrystallization (eq 7). The aliphatic region in the



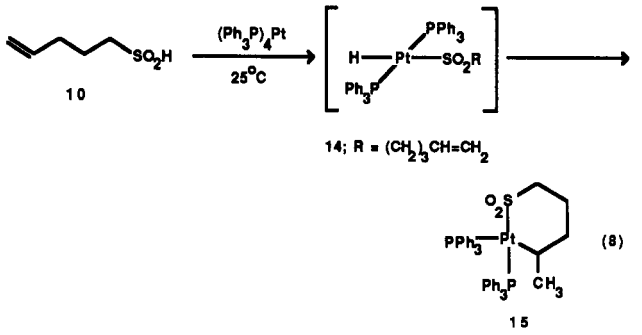
^{1}H NMR spectrum of **13** was rather complicated, with each diastereotopic ring proton displaying a unique chemical shift and coupling pattern (Table I). The methyl protons at 0.83 ppm appeared as a triplet ($^3J_{H-H}$ = 7.5 Hz, $^4J_{P-H}$ = 7.5 Hz) bearing ^{195}Pt satellites ($^3J_{Pt-H}$ = 40 Hz). The ^{31}P{^{1}H} NMR spectrum exhibited a doublet of doublets along with platinum satellites. A DEPT (distortionless enhancement by polarization transfer) ^{13}C NMR spectrum allowed complete assignment of the methyl, methylene, and methine carbons (Table II). Distinct ^{31}P and ^{195}Pt coupling was observed only to the methine and sulfinato methylene carbons, although the methyl carbon signal was broadened substantially. We presume **13** formed by way of hydrido sulfinates such as **i** and **ii**, although spectroscopic analysis of the reaction in progress showed no discernible transient intermediates.[19]



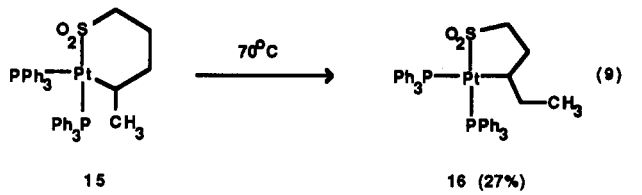
When pentene-5-sulfinic acid (**10**) and $(Ph_3P)_4Pt$ were stirred for several minutes in ether/benzene, a crude semisolid could be precipitated which exhibited ^{1}H and ^{31}P{^{1}H} NMR spectra suggestive of *trans*-hydrido sulfinate **14** (eq 8). The hydride ligand resonated at −11.67 ppm ($^1J_{Pt-H}$ = 794) in the ^{1}H NMR spectrum. When the reaction was allowed to continue at 25 °C, platinacycle **15** precipitated and was isolated as an analytically pure colorless powder in 37% yield.

The ^{1}H NMR spectrum of **15** in $CDCl_3$ at 25 °C displayed a triplet with platinum satellites (J_{Pt-H} = 33 Hz)

(19) The corresponding reaction of **6** with tetrakis(triethylphosphine)platinum at 25 °C afforded an isolable intermediate, whose ^{1}H NMR spectrum displayed a hydride resonance at −12.75 ppm (J_{PtH} = 931 Hz) along with resonances corresponding to uncoordinated olefin. Heating to 100 °C afforded the triethylphosphine analogue of **13**.[6] For a related observation see: Brookes, P. R. *J. Organomet. Chem.* **1973**, *47*, 179.

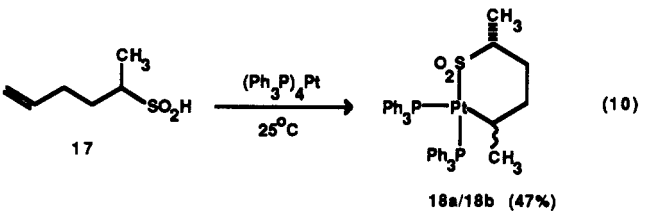


for the methyl group analogous to that seen for platinacycle **13**. The other diastereotopic protons displayed the expected complex coupling patterns. One of the methylene protons displayed a dramatic upfield chemical shift of 0.72 ppm.[20] Upon heating at 70 °C for several hours, **15** was converted completely to metallacycle **16** in 27% yield after chromatography (eq 9). An upfield shifted triplet at 0.22



ppm in the ^1H NMR spectrum of **16** (J_{H-H} = 7 Hz) was assigned to the methyl protons ($PtCHCH_2CH_3$). The unusually large shielding could be rationalized by invoking severe steric interaction with the phenyl rings—a feature that was later confirmed by the X-ray crystal structure of a closely related metallacycle as described below. In the ^{13}C NMR spectrum the carbon α to the sulfonyl group was coupled both to platinum ($^2J_{Pt-C}$ = 64 Hz) and to phosphorus ($^3J_{P-C}$ = 8 Hz). The DEPT spectra confirmed the overall assignment (Table II).

Hexene-5-sulfinic acid (**17**) underwent a reaction at 25 °C with $(Ph_3P)_4Pt$ in diethyl ether to generate a chromatographically inseparable mixture of isomeric metallacyclohexanes **18a** and **18b** in 47% yield (eq 10). The



isomers were readily assigned as six-membered rings from the two pairs of methyl signals in the ^1H NMR spectrum, yet their stereochemistry could not be determined. **18a** displayed a methyl triplet at 1.30 ppm ($^3J_{HH}$ = 7 Hz; $^4J_{PH}$ = 7 Hz) with platinum satellites and a doublet at 1.41 ppm ($^3J_{HH}$ = 7 Hz); **18b** displayed similar resonances at 1.20 and 1.01 ppm. On standing in $CDCl_3$ solution at 25 °C, the initially formed 2.6:1 mixture of **18a** and **18b** slowly isomerized over 48 h, reaching an equilibrium ratio of approximately 1:2 in favor of diastereomer **18b**.

(20) On several occasions, long-range coupling and upfield chemical shifts provided tacit evidence of possible agostic interactions. Metallacyclopentane *trans*-**20**, for example, exhibited temperature-dependent Pt–CH_3 coupling ranging from 40 Hz at 25 °C to 105 Hz at −79 °C. For a discussion and theoretical treatment of agostic interactions in group 10 complexes, see: Koga, N.; Obara, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109. A detailed discussion of the NMR spectroscopy of the metallacycloalkanes described herein can be found in ref 6.

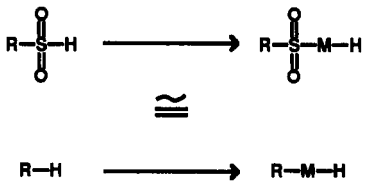


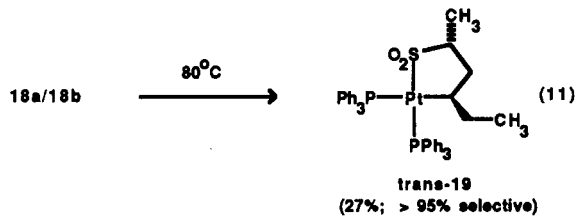
Figure 1.

Table III. Selected Interatomic Distances (Å) for $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ (*trans*-19)[a]

Pt–S	2.316 (32)	P2–C4.1	1.811 (82)
Pt–P1	2.359 (12)	P2–C5.1	1.805 (12)
Pt–P2	2.323 (22)	P2–C6.1	1.833 (98)
Pt–C4	2.093 (10)	C1–C2	1.585 (94)
S–O1	1.439 (90)	C2–C3	1.542 (95)
S–O2	1.424 (77)	C3–C4	1.499 (90)
P1–C1.1	1.819 (10)	C4–C5	1.522 (10)
P1–C2.1	1.804 (61)	C5–C6	1.582 (73)
P1–C3.1	1.826 (81)		

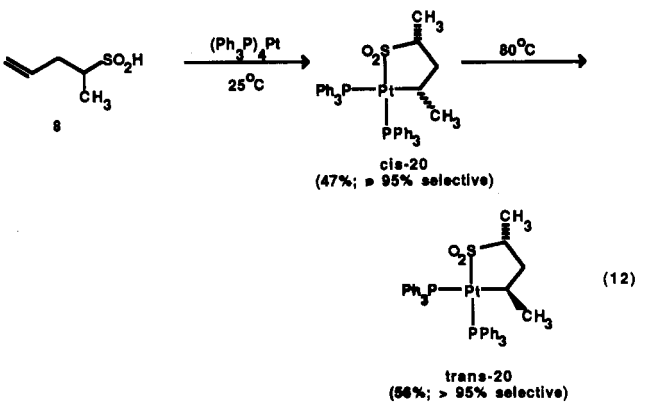
[a] Estimated standard deviations in parentheses.

Heating the **18a**/**18b** mixture at 80 °C for 12 h afforded metallacyclopentane *trans*-**19** as a single stereoisomer (>20:1 selectivity) in 36% yield (eq 11). The ^1H NMR



spectrum of *trans*-**19** displayed a methyl triplet at 0.26 ppm together with complex resonances in the alkyl region. The ^1H, ^{13}C, and DEPT NMR spectra of *trans*-**19** were consistent with the formation of a five-membered ring analogous to **16**. The structure and stereochemistry of *trans*-**19** were shown by X-ray crystallography to be as drawn (vide infra).

Reaction of $(Ph_3P)_4Pt$ with 1.2 equiv of pentene-4-sulfinic acid (**8**) generated metallacycle *cis*-**20** as a single diastereomer (>20:1 selectivity) in 47% yield (eq 12).



Heating *cis*-**20** to 80 °C for several minutes resulted in complete isomerization to stereoisomer *trans*-**20** (56% yield). The isomerization was substantially inhibited by the addition of 1 equiv of triphenylphosphine. The stereochemical assignments followed from analogy with crystallographically characterized ethyl derivative *trans*-**19**, with additional support deriving from the spectroscopic similarities of *trans*-**20** and *trans*-**19**.

Chemical, Thermal, and Photochemical Reactivity of Sulfinates. The chemical reactivity of the platinacycles was briefly explored with two goals in mind: (1) to promote deinsertion of sulfur dioxide as a route to platinum alkyls

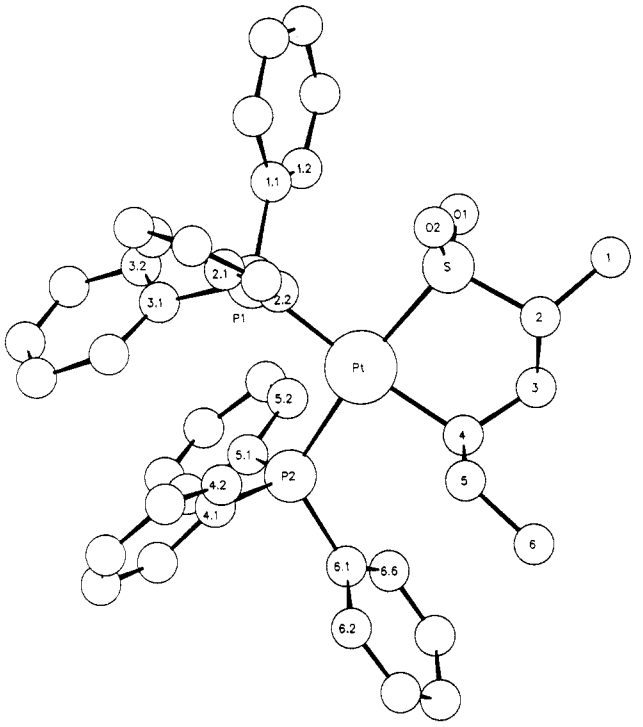


Figure 2. General PLUTO perspective of $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ (*trans*-**19**) showing the metallacyclopentane structure.

and (2) to effect insertion reactions at the Pt–C bonds derived from hydroplatination. Unfortunately, various oxidations, photolyses, and thermolyses failed to provide the primary metal alkyls and metallacycloalkanes derived from deinsertion of SO_2, highlighting the stability of the Pt–SO_2R linkage.[21-23] In a number of instances, forcing conditions provided mixtures of alkenes. Thus, the hopes of using the sulfinic acid moiety as an alkane equivalent (Figure 1) could not be realized in the platinum series.

Molecular Structure of $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CHCH_2CH_3]$ (19). Complex *trans*-**19** crystallizes as discrete molecular units. Figure 2 displays a PLUTO perspective of *trans*-**19** with the atomic numbering scheme used for the calculations. Selected interatomic distances and angles are given in Tables III and IV.

The molecule approximates a square-planar complex of platinum(II). The central platinum atom is bound to two cis phosphorus atoms, a carbon atom, and a sulfur atom. The square-planar geometry is significantly distorted. This distortion can best be visualized from the angles between the four atoms comprising the central plane and the platinum atom: P(1)–Pt–P(2) = 96.9 (5)°, C(4)–Pt–S = 82.5 (5)°, P(1)–Pt–S = 91.6 (5)°, and P(2)–Pt–C(4) = 89.4 (5)°. The former two values agree well with those reported for the analogous P–Pt–P and P–Pt–C angles (98.8° and 80.9°, respectively) in $(Ph_3P)_2Pt(CH_2CH_2CH_2CH_2)$.[24]

The Pt–P(1) and Pt–P(2) bond lengths of 2.359 (1) and 2.323 (2) Å, respectively, are large in comparison with the Pt–P bond lengths of other Pt(II)–PPh_3 derivatives,[25] suggesting that both the alkyl and sulfinate ligands have comparably high trans influences.

Table IV. Selected Interatomic Angles (deg) for $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ (*trans*-19)[a]

S–Pt–P1	91.6 (52)	S–Pt–P2	170.4 (6)
S–Pt–C4	82.5 (50)	P1–Pt–P2	96.9 (51)
P1–Pt–C4	172.4 (9)	P2–Pt–C4	89.4 (50)
Pt–S–O1	109.8 (56)	Pt–S–O2	115.6 (47)
O1–S–O2	114.6 (34)	Pt–P1–C1.1	112.8 (37)
Pt–P1–C2.1	112.9 (55)	Pt–P1–C3.1	120.4 (42)
C1.1–P1–C2.1	105.9 (55)	C1.1–P1–C3.1	99.6 (33)
C2.1–P1–C3.1	103.5 (67)	Pt–P2–C4.1	112.4 (55)
Pt–P2–C5.1	109.6 (48)	Pt–P2–C6.1	117.3 (47)
C4.1–P2–C5.1	111.2 (46)	C4.1–P2–C6.1	105.7 (55)
C5.1–P2–C6.1	99.9 (36)	C1–C2–C3	114.7 (34)
C2–C3–C4	110.2 (34)	Pt–C4–C3	113.2 (52)
Pt–C4–C5	106.6 (35)	Pt–C4–C3	113.2 (52)
C4–C5–C6	113.8 (42)		
P1–C1.1–C1.6	118.3 (35)	P1–C1.1–C1.2	122.8 (60)
P1–C2.1–C2.6	121.6 (47)	P1–C2.1–C2.2	119.7 (64)
P1–C3.1–C3.6	120.1 (49)	P1–C3.1–C3.2	120.5 (53)
P2–C4.1–C4.6	122.1 (57)	P2–C4.1–C4.2	119.6 (26)
P2–C5.1–C5.6	128.0 (49)	P2–C5.1–C5.2	115.6 (43)
P2–C6.1–C6.6	120.2 (60)	P2–C6.1–C6.2	119.7 (28)

[a] Estimated standard deviations in parentheses.

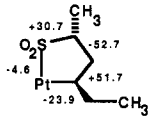


Figure 3.

The platinacycle consists of a five-membered ring connecting atoms C(2), C(3), C(4), Pt, and S, with a methyl substituent at C(2) and an ethyl at C(4). The C–S bond length of 1.784 (9) Å compares favorably with the values 1.76 (2) and 1.73 (2) Å for the same type of bond in a four-membered platinacycle.[26] The C–C bond lengths within the ring average 1.55 (1) Å. The ring exhibits puckering that approximates that of an "envelope" conformation. This can most clearly be seen by examination of the torsional angles for the atoms within the ring (Figure 3). These values indicate that C(2), S, Pt, and C(4) lie in the approximate plane of the envelope while C(3) lies above this plane. The two short C–C bonds of the ring comprise the "flap" of the envelope.

The relative stereochemistry of the methyl and ethyl substituents on the ring of **19** is trans. These substituents are attached to the two ring carbon atoms that define the "fold" of the envelope. The methyl occupies a pseudoequatorial position whereas the ethyl occupies a pseudoaxial position. As to the origin of the high thermodynamic preference for the trans substitution on the metallacyclopentanes, we suspect that it derives from a combination of influences minimizing ethyl–methyl and ethyl–PPh_3 interactions.

Discussion

Despite numerous reports of additions of protic acids to low-valent metal complexes[27] there is little mention in the literature of transition-metal chemistry of sulfinic acids.[7,8] Transition-metal sulfinates have been prepared

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by a variety of other methods, including oxidative addition of sulfonyl chlorides,[11,23,28,29] dispacement reactions at metal halides by sulfinate salts,[10,16,21,28,30] insertion of sulfur dioxide into metal alkyls[11] and metallacycloalkanes,[31] and oxidation of thiolate complexes.[32] We explored the chemistry of sulfinic acids with two goals: (1) to develop a model system that would enable us to isolate and study the stereo- and regiochemistry of internal hydrometalations pivotal to many synthetic applications of transition-metal catalysts and (2) to achieve deinsertion of the SO_2 moiety and develop a mild, general synthesis of metal alkyls and metallacycles usable in inorganic and organic syntheses.

Sulfinic acids were found to undergo a variety of reactions with platinum(II) and platinum(0). Dimethylplatinum(II) complexes readily expelled methane, affording the $L_2Pt(CH_3)SO_2R'$ derivatives in reasonable overall yield. Upon reaction with unsaturated sulfinic acids, 5-$^1/_2$ membered ring chelates could be formed in high (yet unassigned) diastereoselectivity. The corresponding 6-$^1/_2$ membered analogues proved inaccessible. Reaction of saturated sulfinic acids with $Pt(PPh_3)_4$ afforded isolable platinum hydrides. The presumed platinum hydride intermediates generated from unsaturated sulfinic acids underwent intramolecular hydroplatinations to form SO_2-substituted metallacyclopentanes and -hexanes.[31] The kinetic isomers invariably resulted from exocyclic hydrometalation, irrespective of chain length. The kinetic stereoselectivities for the metallacyclohexanes were low (<3:1), whereas the metallacyclopentanes were formed in exceptional (>20:1) selectivities. Thermal equilibration of the metallacyclohexanes or metallacyclopentanes afforded metallacyclopentanes in very high (>20:1) stereoselectivities that were opposite to the kinetic selectivities. All metallacyclopentane stereochemical assignments stemmed from an X-ray crystal structure of *trans*-**19**.

Internal hydrometalations represent the key product-determining steps in a number of synthetically important reactions including internally directed hydrosilylations,[1] hydroacylations,[2] hydroformylations,[3] hydrogenations,[4] and hydrocarboalkoxylations[5] (Chart I). In each instance, however, little is known about the factors that influence the stereo- and regiochemical outcomes. Taken in conjunction with complementary hydrometalations studied by Yamamoto and others,[33,34] sulfinic acids may eventually provide insight into the fundamental principles governing some of the more elusive hydrometalations. However, given the absence of detailed mechanistic data, extensive speculations on the origins of the selectivities are not warranted at this time. Nevertheless, some simple observations are worthy of note. (1) The preference for internal hydrometalation producing the secondary metal alkyl appears to be the direct result of the intramolecularity; hydrometalations of simple alkenes typically produce the opposite regiochemical result.[35] The high effective molarity of the internal alkene was also reflected by the facility of the internal hydrometalations relative to their bimolecular counterparts.[36] (2) The complementary stereo- and regioselectivities observed under kinetic and thermodynamic control illustrate the potential impact that subtle differences in the rates of the discrete steps could have on hydrofunctionalization product distributions. (3) The facile isomerizations provide additional information on the actively studied β-hydride eliminations of platinum(II) alkyls. Whereas Whitesides has found that platinum(II) dialkyls and platinum(II) metallacycloalkanes undergo β-hydride eliminations at 120 °C,[37] Bryndza recently reported that the corresponding $L_2Pt(OR)R$ derivatives β-hydride eliminate at substantially lower temperatures.[38] The results described herein provide further support to Bryndza's contention that electron-withdrawing ancillary ligands (e.g. alkoxide or sulfonyl) dramatically accelerate β-hydride eliminations.

Lastly, we only briefly mentioned extensive attempts to deinsert SO_2 from the metallacyclic metal sulfinates that, in conjunction with the facile oxidative addition of sulfinic acids, could provide versatile syntheses of metal alkyls and metallacycles (Figure 1). Overall, photochemical, thermal, oxidizing, and carbonylating conditions uniformly failed to provide tractable platinum(II) alkyls or all-carbon metallacycloalkanes. Other groups similarly have found platinum(II) sulfinates to be notably robust.[22] Thus, further efforts in this vein would involve metals that have shown a greater propensity to deinsert SO_2.[29,39,40]

Experimental Section

General Data. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer and were calibrated at the 1601 cm^{-1} absorbance of polystyrene. ^1H NMR spectra were recorded on a Varian CFT-20 80 MHz, a Varian XL-200 MHz, a Bruker 300 MHz, or a Varian XL-400 MHz spectrometer with chemical shifts reported in parts per million downfield from tetramethylsilane. $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL

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FX90Q 90 MHz spectrometer operating at 36.23 MHz with chemical shifts reported in parts per million downfield from 85% H_3PO_4 using a secondary reference (PCl_3, 219 ppm). ^{13}C NMR spectra were recorded on a JEOL FX90Q or a Varian XL-400 400 MHz spectrometer operating at 22.49 and 100.572 MHz, respectively, with chemical shifts reported in parts per million downfield from tetramethylsilane using solvent resonances as secondary references. Low-resolution mass spectral data were obtained by using chemical ionization (CI) on a Finnigan Model 3300 mass spectrometer. Microanalyses were performed by Alfred Bernhardt Analytisches Laboratorien, Elbach, West Germany, and Sohwarzkopf Microanalytical Laboratory, Woodside, NY. Manipulations of air- or moisture-sensitive compounds were performed by using standard glovebox and vacuum line techniques. Photolyses were effected under reduced argon atmosphere in a sealed tube with a 275-W sunlamp at a distance of 5–10 cm with forced air cooling. Flash chromatography was performed by the method of Still.[41]

Benzene, benzene-d_6 (C_6D_6), pentanes, hexanes, and diethyl ether were distilled in vacuo from blue to purple solutions containing sodium benzophenone ketyl. The hydrocarbon solvents contained 1% tetraglyme to increase the solubility of the ketyl. Methylene chloride and methylene-d_2 chloride (CD_2Cl_2) were degassed by freeze–pump–thaw cycles and then distilled in vacuo from P_2O_5. Chloroform-d ($CDCl_3$) was degassed by freeze–pump–thaw cycles and then distilled in vacuo after stirring for at least 1 day over activated 6-sieves. p-Toluenesulfinic acid was obtained from Aldrich. Other sulfinic acids were prepared as described below, and all other reagents were handled using standard protocols.

p-Tolylmethanesulfinic Acid (1). A solution of (p-tolylmethyl)magnesium chloride was prepared by treating magnesium turnings (2.19 g, 90.0 mmol) suspended in diethyl ether (63 mL) dropwise with a solution of p-tolylmethyl chloride (12.65 g, 90.0 mmol) in diethyl ether (27 mL). After the reaction was completed, the greenish solution was filtered under an argon atmosphere. The filtrate was then cooled to −78 °C and degassed. An excess of sulfur dioxide, previously condensed and degassed, was added to the Grignard solution by vacuum transfer. The resulting thick white slurry was allowed to warm to 25 °C and the fine white precipitate collected on a Büchner funnel and washed with copious amounts of diethyl ether. The salt was then converted to the acid by dissolving it in 2% aqueous HCl (1000 mL). This suspension was extracted with diethyl ether (3 × 400 mL), and the combined extracts were dried over $MgSO_4$ and filtered. The colorless solution was concentrated to approximately 50 mL, at which point colorless crystals had already begun to form. Cooling the solution to 0 °C provided more crystals. These were collected on a Büchner funnel and air-dried to yield 9.06 g of p-tolylmethanesulfinic acid (59% yield). This compound evidenced no signs of decomposition when stored in a glovebox at 25 °C for several months: ^1H NMR (80 MHz, $CDCl_3$) δ 8.0 (br s, 1 H), 7.2 (s, 4 H), 4.0 (s, 2 H), 2.4 (s, 3 H); $^{13}C\{^1H\}$ NMR (22.49 MHz, $CDCl_3$) δ 138.1, 130.4, 129.4, 125.4, 63.9, 21.1; IR ($CDCl_3$) 3100 (br), 1060 cm^{-1}.

Representative Procedure for the Preparation of Unsaturated Sulfinic Acids 6, 8, 10, and 17. The bromomagnesium sulfinates were prepared in 85–96% yields from the corresponding Grignard reagents in a fashion similar to that employed for 1. 4-Bromobutene, 5-bromopentene, and 5-bromohexene were obtained commercially; 4-bromopentene was prepared by a literature method[42] from the corresponding alcohol. The sulfinic acids could be prepared on gram scales in yields of 75–80% by protonation of the magnesium salts with equimolar quantities of trifluoroacetic acid in dichloromethane; however, due to the instability of these crude oils, fresh batches were usually prepared when needed on a smaller scale in yields of 31–67% as follows: a few hundred milligrams of the bromomagnesium sulfinate were taken up in 3 mL each of water and dichloromethane and shaken with an equimolar quantity of trifluoroacetic acid in a stoppered vial. The aqueous layer was extracted twice with dichloromethane, and the combined organic layers were dried over sodium sulfate. The solvents were removed under high vacuum, and the thermally unstable sulfinic acids were used without further purification.

Butene-4-sulfinic acid (6): ^1H NMR (200 MHz, $CDCl_3$) δ 10.91 (s, 1 H), 5.80 (m, 1 H), 5.08 (m, 2 H), 2.85 (t, J = 7.5 Hz, 2 H), 2.45 (m, 2 H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 134.4, 116.9, 56.3, 25.5; IR (film) 3040 (br), 2600 (br), 1050 (br), 810 (br) cm^{-1}.

Pentene-4-sulfinic acid (8): ^1H NMR (200 MHz, $CDCl_3$) δ 10.21 (s, 1 H), 5.72 (m, 1 H), 5.12 (m, 2 H), 2.63 (br m, 2 H), 2.15 (m, 1 H), 1.20 (d, J = 7 Hz, 3 H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 133.5, 118.3, 59.4, 32.8, 10.4; IR (film) 3040 (br), 2600 (br), 1050 (br), 810 (br) cm^{-1}.

Pentene-5-sulfinic acid (10): ^1H NMR (200 MHz, $CDCl_3$) δ 10.64 (s, 1 H), 5.73 (m, 1 H), 5.02 (m, 2 H), 2.77 (t, J = 7 Hz, 2 H), 2.15 (q, J = 7 Hz, 2 H), 1.77 (m, 2 H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 136.6, 116.0, 56.5, 32.3, 20.4; IR (film) 3040 (br), 2600 (br), 1050 (br), 810 (br) cm^{-1}.

Hexene-5-sulfinic acid (17): ^1H NMR (200 MHz, $CDCl_3$) δ 11.00 (s, 1 H), 5.75 (m, 1 H), 5.04 (dd, J_1 = 13 Hz, J_2 = 1.7 Hz, 1 H), 4.97 (dd, J_1 = 6.5 Hz, J_2 = 1.7 Hz, 1 H), 2.63 (m, 1 H), 2.15 (m, 2 H), 1.93 (m, 1 H), 1.50 (m, 1 H), 1.21 (d, J = 7 Hz, 3 H); ^{13}C NMR (22.49 MHz, $CDCl_3$) δ 137.0, 115.7, 59.1, 30.4, 27.6, 10.4; IR (film) 2950 (br), 2500 (br), 1060 (br), 820 (br) cm^{-1}.

***trans*-Hydrido(p-tolylmethanesulfinato-*S*)bis(triphenylphosphine)platinum(II) (2).** To a stirred suspension of $(Ph_3P)_4Pt$ (311 mg, 0.25 mmol) in diethyl ether (25 mL) at 25 °C was added p-tolylmethanesulfinic acid (51 mg, 0.30 mmol). The reaction mixture was stirred under an argon atmosphere for 1.25 h, during which time a colorless precipitate formed. The suspension was concentrated to approximately 10 mL and filtered. Recrystallization from benzene/hexanes afforded 155 mg of **2** (70% yield) as a fine colorless powder: ^1H NMR (300 MHz, CD_2Cl_2) δ 8.0–7.0 (m, 30 H), 7.20 (d, J = 6 Hz, 2 H), 6.80 (d, J = 6 Hz, 2 H), 2.86 (s, 2 H), 2.33 (s, 3 H), −12.20 (s, J_{Pt-H} = 819 Hz, 1 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) δ 28.67 (s, J_{Pt-P} = 3049 Hz); ^{13}C NMR (22.49 MHz, CD_2Cl_2) δ 136.2–128.5 (m), 68.1 (J_{Pt-P} = 90 Hz), 21.2; IR (C_6D_6) 2100, 1180, 1090, 1040 cm^{-1}. The moderate thermal stability of **2** resulted in an only marginally successful elemental analysis. Anal. Calcd for $C_{44}H_{40}O_2P_2PtS$: C, 59.39; H, 4.53; P, 6.96; S, 3.60. Found: C, 60.78; H, 5.04; P, 6.20; S, 3.06.

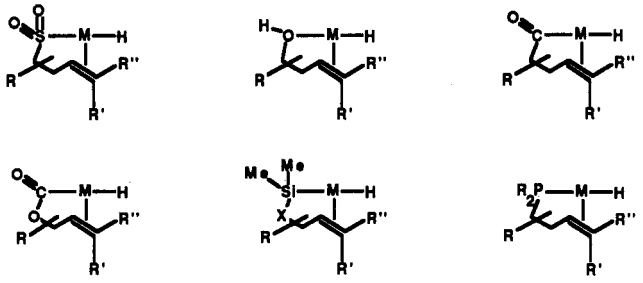
Methyl(p-tolylmethanesulfinato-*S*)(η^4-cyclooctadiene)platinum(II) (3). To a stirred solution of $(COD)Pt(CH_3)_2$ (333 mg, 1.0 mmol) in benzene (25 mL) at 25 °C was added p-tolylmethanesulfinic acid (170 mg, 1.0 mmol). Effervescence was immediately observed. The resulting pale yellow solution was stirred under an argon atmosphere for 15 h, and then the solvent was concentrated to approximately one-third of the original volume. Cooling this solution to 0 °C followed by the addition of a large excess of hexanes by vacuum transfer produced a precipitate of colorless microcrystals. These were filtered from the supernatant, washed with hexanes, and dried under high vacuum to yield 375 mg of **3** (77% yield): ^1H NMR (80 MHz, $CDCl_3$) δ 7.23 (q, J = 7 Hz, 4 H), 5.20 (br, J_{Pt-H} = 30 Hz, 2 H), 4.94 (br, J_{Pt-H} = 20 Hz, 2 H), 4.08 (br s, 2 H), 2.35 (s, 3 H), 2.25 (br, 8 H), 1.10 (s, J_{Pt-H} = 40 Hz, 3 H); $^{13}C\{^1H\}$ NMR (22.49 MHz, CD_2Cl_2) δ 137.3, 131.0, 128.7, 127.8, 109.6 (J_{Pt-C} = 52 Hz), 106.5 (J_{Pt-C} = 79 Hz), 67.2 (J_{Pt-C} = 193 Hz), 29.8 (J_{Pt-C} = 11 Hz), 28.0, 20.9, 5.5 (J_{Pt-C} = 692 Hz); IR ($CDCl_3$) 1195, 1175, 1050 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_2PtS$: C, 41.88; H, 4.96; S, 6.58. Found: C, 41.71; H, 4.91; S, 6.51.

Methyl(p-toluenesulfinato-*S*)(η^4-cyclooctadiene)platinum(II) (4). **4** was prepared from p-toluenesulfinic acid in a 53% yield by a procedure similar to that employed for **3**: ^1H NMR (80 MHz, $CDCl_3$) δ 7.66 (d, J = 8 Hz, 2 H), 7.23 (d, J = 8 Hz, 2 H), 5.75 (br, J_{Pt-H} = 38 Hz, 2 H), 5.25 (br, J_{Pt-H} = 58 Hz, 2 H), 2.48 (br, 8 H), 2.37 (s, 3 H), 0.68 (s, J_{Pt-H} = 75 Hz, 3 H); $^{13}C\{^1H\}$ NMR (22.49 MHz, CD_2Cl_2) δ 148.0 (J_{Pt-C} = 190 Hz), 141.1, 129.0, 126.1, 110.1 (J_{Pt-C} = 50 Hz), 105.9 (J_{Pt-C} = 75 Hz), 30.5, 28.6, 21.3, 6.9 (J_{Pt-C} = 646 Hz); IR ($CDCl_3$) 1190, 1045 cm^{-1}. Anal. Calcd for $C_{16}H_{22}O_2PtS$: C, 40.59; H, 4.68; S, 6.77. Found: C, 40.50; H, 4.68; S, 6.63.

***cis*-Methyl(p-tolylmethanesulfinato-*S*)bis(triphenylphosphine)platinum(II) (5).** To a stirred suspension of *cis*-$(Ph_3P)_2Pt(CH_3)_2$[7] (520 mg, 0.69 mmol) in dichloromethane (7 mL) at 25 °C was added p-tolylmethanesulfinic acid (118 mg, 0.69 mmol). Effervescence was immediately observed. The resulting

(41) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.
(42) Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 291.

Chart I



colorless solution was stirred under an argon atmosphere for 20 min, and then the solvent was concentrated to approximately one-third of the original volume. Cooling this solution to −78 °C followed by the addition of a large excess of hexanes by vacuum transfer produced a copious white precipitate. The mixture was allowed to warm to 25 °C and then filtered. The fine colorless powder was dried under high vacuum to yield 570 mg of **5** (91% yield). An analytically pure sample could be obtained by flash chromatography on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50–6.93 (m, 34 H), 3.98 (s, 2 H), 2.55 (s, 3 H), 0.77 (t, J = 6.5 Hz, J_{Pt-H} = 60 Hz, 3 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 23.80 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 1997 Hz), 18.10 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 2835 Hz); $^{13}C\{^1H\}$ NMR (22.49 MHz, CD_2Cl_2) δ 137.1–127.5 (m), 66.8 (dt, J_{P-C} = 14 Hz, J_{Pt-C} = 174 Hz), 21.5 (s), 10.7 (dd, J_1 = 77 Hz, J_2 = 5 Hz); IR ($CDCl_3$) 1190, 1170, 1040 cm^{-1}. Anal. Calcd for $C_{45}H_{42}O_2P_2PtS$: C, 59.79; H, 4.68; P, 6.85; S, 3.55. Found: C, 59.60; H, 4.69; P, 6.90; S, 3.42.

$(Ph_3P)(CH_3)Pt(\eta^3$-$SO_2CH_2CH_2CH_2CH{=}CH_2)$ (7). To a stirred solution of freshly prepared butene-4-sulfinic acid (**6**; 71 mg, 0.585 mmol) in dichloromethane (20 mL) at 25 °C was added *cis*-$(Ph_3P)_2Pt(CH_3)_2$ (438 mg, 0.585 mmol). Effervescence was immediately observed. The resulting colorless solution was stirred under an argon atmosphere for 48 h after which the solvent was removed. Flash chromatography of the residue on silica gel (3% methanol in dichloromethane) followed by recrystallization from dichloromethane/hexanes afforded 115 mg of **7** (33% yield) as a fine colorless powder: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.7–7.4 (m, 15 H), 4.78 (br m, 1 H), 4.05 (d, J = 15 Hz, J_{Pt-H} = 40 Hz, 1 H), 3.77 (dd, J_1 = 8 Hz, J_2 = 6 Hz, J_{Pt-H} = 43 Hz, 1 H), 3.24 (td, J_1 = 15 Hz, J_2 = 4 Hz, 1 H), 3.03 (br m, 1 H), 2.63 (br tt, J_1 = 15 Hz, J_2 = 4 Hz, 1 H), 2.06 (br d, J = 15 Hz, 1 H), 1.20 (d, J = 5 Hz, J_{Pt-H} = 77 Hz, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 21.5 (J_{Pt-P} = 2732 Hz); $^{13}C\{^1H\}$ NMR (22.49 MHz, $CDCl_3$) δ 133.9 (dt, J_{P-C} = 11 Hz, J_{Pt-C} = 16 Hz), 131.4 (d, J_{P-C} = 1 Hz), 128.9, 128.5, 126.5 (J_{Pt-C} = 28 Hz), 111.0 (J_{Pt-C} = 59 Hz), 78.2 (J_{Pt-C} = 48 Hz), 58.7 (dt, J_{P-C} = 14 Hz, J_{Pt-C} = 129 Hz), 25.9 (J_{Pt-C} = 14 Hz), 8.5 (dt, J_{P-C} = 7 Hz, J_{Pt-C} = 660 Hz); IR ($CDCl_3$) 1185, 1060, 1050 cm^{-1}. Anal. Calcd for $C_{23}H_{25}O_2PPtS$: C, 46.70; H, 4.26; P, 5.24; S, 5.42. Found: C, 64.83; H, 4.28; P, 5.29; S, 5.25.

$(Ph_3P)(CH_3)Pt(\eta^3$-$SO_2CH(CH_3)CH_2CH_2CH{=}CH_2)$ (9). To a stirred solution of freshly prepared pentene-4-sulfinic acid (**8**; 85.5 mg, 0.638 mmol) in dichloromethane (40 mL) at 25 °C was added *cis*-$(Ph_3P)_2Pt(CH_3)_2$ (430 mg, 0.580 mmol). Effervescence was immediately observed. The resulting colorless solution was stirred under an argon atmosphere for 48 h. The solution was concentrated and enriched with hexanes to precipitate a colorless solid that was then washed with hexanes to remove excess triphenylphosphine. Flash chromatography of this material on silica gel (3% methanol in dichloromethane) followed by recrystallization from dichloromethane/pentanes afforded 110 mg of **9** (31% yield) as a fine colorless powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.7–7.4 (m, 15 H), 4.70 (br m, 1 H), 4.16 (d, J = 15 Hz, J_{Pt-H} = 40 Hz, 1 H), 3.75 (dd, J_1 = 8 Hz, J_2 = 6 Hz, J_{Pt-H} = 40 Hz, 1 H), 3.27 (m, 1 H), 2.32 (ddd, J_1 = 17 Hz, J_2 = 13 Hz, J_3 = 5 Hz, 1 H), 2.02 (dd, J_1 = 17 Hz, J_2 = 2 Hz, 1 H), 1.36 (d, J = 6.6 Hz, 3 H), 1.26 (d, J = 5 Hz, J_{Pt-H} = 77 Hz, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 22.1 (J_{Pt-P} = 2708 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.11 (dt, J_{P-C} = 11 Hz, J_{Pt-C} = 24 Hz), 131.44 (d, J_{P-C} = 5 Hz), 128.82 (d, J_{P-C} = 9 Hz), 108.39 (J_{Pt-C} = 59 Hz), 78.60 (J_{Pt-C} = 46 Hz), 61.09 (dt, J_{P-C} = 14 Hz, J_{Pt-C} = 112 Hz), 33.63, 9.23 (dt, J_{P-C} = 7 Hz, J_{Pt-C} and 661 Hz), 8.64; IR ($CDCl_3$) 1170, 1040 cm^{-1}.

***cis*-Methyl(pentene-5-sulfinato-*S*)bis(triphenylphosphine)platinum(II) (12).** To a stirred suspension of freshly prepared pentene-5-sulfinic acid (**10**, 80 mg, 0.54 mmol) in dichloromethane (15 mL) was added *cis*-$(Ph_3P)_2Pt(CH_3)_2$ (390 mg, 0.52 mmol). Effervescence was immediately observed, and the resulting colorless solution was stirred for 10 min under an argon atmosphere. The solution was concentrated and enriched with pentanes to produce a fine precipitate. Flash chromatography on silica gel (4% methanol in dichloromethane) followed by crystallization from dichloromethane/pentanes afforded 100 mg of **12** (22% yield) as a colorless powder: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.80–7.05 (m, 30 H), 5.82 (m, 1 H), 5.00 (m, 2 H), 2.83 (br m, 1 H), 2.36 (br m, 1 H), 2.17 (br m, 1 H), 1.97 (br m, 1 H), 1.39 (br m, 1 H), 1.15 (d, J = 6.7 Hz, 3 H), 0.63 (t, J = 6.5 Hz, J_{Pt-H} = 63 Hz, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 26.02 (dt, J_{P-P} = 8 Hz, J_{Pt-P} = 1960 Hz), 18.01 (dt, J_{P-P} = 8 Hz, J_{Pt-P} = 2761 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 135.1–127.6 (m), 114.28, 59.41 (d, J_{P-C} = 13 Hz), 31.11, 28.18, 11.40, 9.20 (d, J_{P-C} = 75 Hz). Anal. Calcd for $C_{43}H_{43}O_2P_2PtS$: C, 58.56; H, 5.03; P, 7.02; S, 3.64. Found: C, 58.44; H, 5.13; P, 7.18; S, 3.56.

$(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_3)$ (13). To a stirred suspension of freshly prepared butene-4-sulfinic acid (**6**; 53 mg, 0.44 mmol) in diethyl ether/benzene (4:3, 25 mL) at 25 °C was added $(Ph_3P)_4Pt$ (448 mg, 0.36 mmol). The resulting clear yellow solution was stirred under an argon atmosphere. After 10 min a fine colorless precipitate began forming, and after 9 h the supernatant had become almost colorless. The reaction mixture was filtered and the filtrate washed with diethyl ether and dried under high vacuum to yield 267 mg of **13** (88% yield) that was greater than 95% pure by ^{1}H NMR. An analytically pure sample could be obtained in a 69% overall yield by flash chromatography of the precipitate on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/hexanes: ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.6–7.15 (m, 30 H), 3.13 (m, 1 H), 2.77 (dd, J_1 = 12 Hz, J_2 = 5 Hz, 1 H), 2.25 (br, 1 H), 1.97 (m, 1 H), 1.17 (br t, J = 15 Hz, 1 H), 0.83 (t, J = 7.5 Hz, J_{Pt-H} = 40 Hz, 3 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.06 (dt, J_{P-P} = 12 Hz, J_{Pt-P} = 1796 Hz), 18.21 (dt, J_{P-P} = 12 Hz, J_{Pt-P} = 2927 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.8–127.5 (m), 68.50 (dt, J_{P-C} = 9 Hz, J_{Pt-C} = 235 Hz), 44.70 (dd, J_1 = 73 Hz, J_2 = 4 Hz, J_{Pt-C} = 570 Hz), 33.30, 21.35 (br); IR ($CDCl_3$) 1180, 1045 cm^{-1}. Anal. Calcd for $C_{40}H_{38}O_2P_2PtS$: C, 57.20; H, 4.56; P, 7.38; S, 3.82. Found: C, 57.09; H, 5.05; P, 7.02; S, 3.81.

$(Ph_3P)_2PtSO_2CH_2CH_2CH_2CH(CH_3)$ (15). To a stirred suspension of freshly prepared pentene-5-sulfinic acid (**10**; 157 mg, 1.17 mmol) in diethyl ether/benzene (1:1, 50 mL) at 25 °C was added $(Ph_3P)_4Pt$ (746 mg, 0.60 mmol). The resulting clear yellow solution was stirred under an argon atmosphere. After 1 h a fine colorless precipitate began forming. After 12 h the reaction mixture was filtered and the precipitate washed with diethyl ether and dried under high vacuum to yield 270 mg of **15** (53% yield) that was greater than 95% pure by ^{1}H NMR. An analytically pure sample could be obtained in a 37% overall yield by flash chromatography of the precipitate on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/hexanes: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6–7.1 (m, 30 H), 2.70 (br m, 2 H), 2.16 (br m, 2 H), 1.76 (br, 1 H), 1.30 (t, J = 7.5 Hz, J_{Pt-H} = 33 Hz, 3 H), 1.07 (br, 1 H), 0.72 (br, 1 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 23.59 (d, J = 12 Hz, J_{Pt-P} = 1762 Hz), 16.66 (d, J = 12 Hz, J_{Pt-P} = 2886 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.48–127.42 (m), 60.50 (d, J_{P-C} = 16 Hz, J_{Pt-C} = 160 Hz), 31.98, 21.07, 21.02. IR ($CDCl_3$) 1170, 1150, 1040 cm^{-1}. Anal. Calcd for $C_{41}H_{40}O_2P_2PtS$: C, 57.67; H, 4.72; P, 7.25; S, 3.75. Found: C, 57.52; H, 4.89; P, 7.06; S, 3.70.

$(Ph_3P)_2PtSO_2CH_2CH_2CH(CH_2CH_3)$ (16). To a stirred suspension of freshly prepared pentene-5-sulfinic acid (**10**; 174 mg, 1.30 mmol) in toluene/tetrahydrofuran (1:1, 100 mL) at 25 °C was added $(Ph_3P)_4Pt$ (1243 mg, 1.0 mmol). The resulting clear yellow solution was heated at 70 °C under an argon atmosphere for 36 h. After the solvent was removed under high vacuum, the yellow residue was flash chromatographed on silica gel (4% methanol in dichloromethane). Recrystallization from dichloromethane/hexanes produced 230 mg of **16** (27% yield) as a fine colorless powder: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.5–7.1 (m, 30 H), 3.12 (m, 1 H), 2.85 (dd, J_1 = 12 Hz, J_2 = 5 Hz, 1 H), 2.12 (m, 1 H), 1.75 (m, 1 H), 1.50 (m, 2 H), 1.08 (br, 1 H), 0.22

(t, J = 7 Hz, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.00 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 1769 Hz), 18.65 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 2979 Hz); $^{13}C\{^1H\}$ NMR (22.49 MHz, $CDCl_3$) δ 134.8–127.1 (m), 68.0 (dt, J_{P-C} = 8 Hz, J_{Pt-C} = 235 Hz), 50.3 (dt, J_{P-C} = 81 Hz, J_{Pt-C} = 570 Hz), 26.8, 25.7, 13.0 (dt, J_{P-C} = 8 Hz, J_{Pt-C} = 64 Hz); IR ($CDCl_3$) 1180, 1050 cm^{-1}. Anal. Calcd for $C_{41}H_{40}O_2P_2PtS$: C, 57.67; H, 4.72; P, 7.25; S, 3.75. Found: C, 57.49; H, 4.81; P, 7.43; S, 3.80.

$(Ph_3P)_2PtSO_2CH(CH_3)CH_2CH_2CH(CH_3)$ (18a/18b). To a stirred suspension of freshly prepared hexene-5-sulfinic acid (**17**; 125 mg, 0.84 mmol) in diethyl ether (50 mL) at 25 °C was added $(Ph_3P)_4Pt$ (800 mg, 0.64 mmol). The resulting suspension was stirred under an argon atmosphere for 6 h and then filtered. Flash chromatography of the precipitate on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/pentanes afforded 265 mg of **18a** and **18b** (47% yield) as an inseparable mixture: ^1H NMR (300 MHz, $CDCl_3$) δ 7.8–7.0 (m), 2.45 (m), 2.28 (m), 2.00 (m), 1.57 (m), 1.41 (d, J = 7.0 Hz), 1.30 (d, J = 7.0 Hz), 1.20 (t, J = 7.0 Hz), 1.01 (d, J = 7.0 Hz), 0.84 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 23.83 (m, J_{Pt-P} = 1731 Hz), 18.85 (m, J_{Pt-P} = 2871 Hz); IR ($CDCl_3$) 1155, 1030 cm^{-1}.

$(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ (*trans*-19). To a stirred suspension of freshly prepared hexene-5-sulfinic acid (71 mg, 0.48 mmol) in toluene (25 mL) at 25 °C was added $(Ph_3P)_4Pt$ (460 mg, 0.37 mmol). The resulting clear yellow solution was heated to 50 °C under an argon atmosphere, at which time a flocculent colorless precipitate formed. When this reaction mixture was heated to 82 °C, the precipitate dissolved after a few hours to again form a clear yellow solution. After 12 h the solvent was removed under high vacuum. Flash chromatography of the residue on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/pentanes produced 115 mg of *trans*-**19** (36% yield) as a fine colorless powder: ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.0 (m, 30 H), 3.13 (m, 1 H), 1.91 (br, 1 H), 1.60 (m, 1 H), 1.46 (m, 2 H), 1.32 (br, 1 H), 1.18 (d, J = 6.5 Hz, 3 H), 0.26 (t, J = 7.0 Hz, 3 H); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 20.26 (dt, J_{P-P} = 13 Hz, J_{Pt-P} = 1731 Hz), 19.49 (dt, J_{P-P} = 13 Hz, J_{Pt-P} = 3013 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 134.8–127.4 (m), 70.12 (dd, J_1 = 7 Hz, J_2 = 5 Hz, J_{Pt-C} = 223 Hz), 48.37 (dd, J_1 = 71 Hz, J_2 = 4 Hz, J_{Pt-C} = 564 Hz), 35.20 (J_{Pt} = 372 Hz), 27.19 (J_{Pt-C} = 899 Hz), 13.70 (J_{Pt-C} = 64 Hz), 8.64 (J_{Pt-C} = 108 Hz); IR ($CDCl_3$) 1180, 1045 cm^{-1}. Anal. Calcd for $C_{42}H_{42}O_2P_2PtS$: C, 58.13; H, 4.88; P, 7.14; S, 3.69. Found: C, 58.03; H, 4.86; P, 7.30; S, 3.71.

$(Ph_3P)_2Pt[cis\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ (*cis*-20). To a stirred suspension of freshly prepared pentene-4-sulfinic acid (**6**; 97 mg, 0.72 mmol) in diethyl ether/benzene (4:1, 50 mL) at 25 °C was added $(Ph_3P)_4Pt$ (746 mg, 0.60 mmol). The resulting clear yellow solution was stirred under an argon atmosphere. After 10 min a fine colorless precipitate began to form. After 12 h the supernatant had become a dark yellow color. The reaction mixture was filtered and the precipitate dried under high vacuum to yield 316 mg of *cis*-**20** (62% yield) that was greater than 95% pure by ^1H NMR. An analytically pure sample could be obtained in a 47% overall yield by flash chromatography of the precipitate on silica gel (4% methanol in dichloromethane) followed by recrystallization from dichloromethane/pentanes: ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.1 (m, 30 H), 3.14 (m, 1 H), 2.08 (br m, 1 H), 1.60 (m, 1 H), 1.32 (m, 1 H), 1.20 (d, J = 6.5 Hz, 3 H), 1.05 (td, J_1 = 7.5 Hz, J_2 = 2.5 Hz, J_{Pt-H} = 50 Hz, 3 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.36 (d, J_{P-P} = 12 Hz, J_{Pt-P} = 1728 Hz), 19.42 (dt, J_{P-P} = 12 Hz, J_{Pt-P} = 2957 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 135.1–127.7 (m), 77.55 (dd, J_1 = 10 Hz, J_2 = 4 Hz, J_{Pt-C} = 270 Hz), 42.63 (dt, J_{P-C} = 73 Hz, J_{Pt-C} = 591 Hz), 41.41 (J_{Pt-C} = 97 Hz), 26.80 (J_{Pt-C} = 109 Hz), 9.08 (J_{Pt-C} = 111 Hz); IR ($CDCl_3$) 1170, 1045 cm^{-1}. Anal. Calcd for $C_{41}H_{40}O_2P_2PtS$: C, 57.67; H, 4.72; P, 7.25; S, 3.75. Found: C, 57.57; H, 4.83; P, 7.34; S, 3.67.

$(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_3)]$ (*trans*-20). To a stirred suspension of freshly prepared pentene-4-sulfinic acid (112 mg, 0.84 mmol) in toluene (50 mL) at 25 °C was added $(Ph_3P)_4Pt$ (864 mg, 0.70 mmol). The resulting clear yellow solution was heated at 80 °C under an argon atmosphere for 12 h. After the solvent was removed under high vacuum, the yellow brown residue was flash chromatographed on silica gel (4% methanol in dichloromethane). Recrystallization from dichloromethane/pentanes produced 335 mg of *trans*-**20** (56% yield) as colorless microcrystals: ^1H NMR (300 MHz, $CDCl_3$) δ 7.6–7.1 (m, 30 H), 3.23 (m, 1 H), 2.02 (br m, 1 H), 1.73 (td, J_1 = 14 Hz, J_2 = 5 Hz, 1 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.15 (br t, J = 15 Hz, 1 H), 0.97 (t, J = 7 Hz, J_{Pt-H} = 40 Hz, 3 H); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ 20.13 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 1758 Hz), 19.19 (dt, J_{P-P} = 15 Hz, J_{Pt-P} = 2944 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 135.4–127.8 (m), 70.94 (dt, J_{P-C} = 6 Hz, J_{Pt-C} = 223 Hz), 42.32 (J_{Pt-C} = 110 Hz), 41.59 (dt, J_{P-C} = 71 Hz, J_{Pt-C} = 563 Hz), 23.32 (br), 8.89 (J_{Pt-C} = 108 Hz); IR ($CDCl_3$) 1170, 1045 cm^{-1}. Anal. Calcd for $C_{41}H_{40}O_2P_2PtS$: C, 57.67; H, 4.72; P, 7.25; S, 3.75. Found: C, 57.51; H, 4.68; P, 7.42; S, 3.65.

Single-Crystal X-ray Structure Determination of *trans*-19. Crystals of *trans*-**19** were grown by slow evaporation from methanol. A crystal of approximate dimensions 0.3 × 0.3 × 0.3 mm was chosen and mounted on a glass fiber by using epoxy. Preliminary X-ray photographs displayed monoclinic symmetry, and accurate lattice constants of a = 10.563 (1) Å, b = 9.733 (17) Å, and c = 36.362 (42) Å were determined from a least-squares fit of 15 diffractometer-measured 2θ values. An estimated crystal density of 1.3 g/cm^3 indicated the presence of four molecules of *trans*-**19** per unit cell (calculated crystal density = 1.76 g/cm^3). Systematic extinctions were consistent with space group $P2_1/c$. All unique diffraction maxima with $2\theta \leq 100°$ were collected on a computer-controlled four-circle diffractometer using variable speed 1° ω-scans and graphite-monochromated Cu Kα radiation (1.541 78 Å). Of the 4299 reflections measured in this fashion, 2364 (55%) were judged observed ($F_o \geq 3\sigma(F_o)$) after correction for Lorentz, polarization, and background effects. A phasing model was found by employing the heavy-atom technique. All non-hydrogen atoms were located by successive ΔF syntheses. Block-diagonal least-squares refinements with anisotropic non-hydrogen atoms converged to a crystallographic residual of 0.0981 (R_w = 0.0989) for the observed data. The high R_w arose from the use of Cu Kα radiation source without corrections made for large absorption effects. Further results of the crystallographic experiment are given in Tables V–X (supplementary material).

All crystallographic calculations were done on a PRIME 9950 computer operated by the Cornell Chemistry Computing Facility. Principal programs employed were the following: REDUCE and UNIQUE, data reduction programs by M. E. Leonowicz, Cornell University, 1978; MULTAN 80 and RANTAN 80, systems of computer programs for the automatic solution of crystal structures from X-ray diffraction data (locally modified to perform all Fourier calculations including Patterson syntheses) written by P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, University of York, England, 1980; BLS78A, an anisotropic block-diagonal least-squares refinement written by K. Hirotsu and E. Arnold, Cornell University, 1980; PLUTO78, a locally modified crystallographic Data Centre, 1978; and BOND, a program to calculate molecular parameters and prepare tables written by K. Hirotsu and G. Van Duyne, Cornell Univesity, 1985.

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Supplementary Material Available: Tables of fractional coordinates, bond distances, bond angles, and torsional angles for $(Ph_3P)_2Pt[trans\text{-}SO_2CH(CH_3)CH_2CH(CH_2CH_3)]$ (*trans*-**19**) (7 pages); a listing of observed and calculated structure factors for *trans*-**19** (12 pages).