Reactions of Coordinatively Unsaturated Platinum(II)–η^1-Allyl Complexes with the Electrophilic Reagents Sulfur Dioxide, Chlorosulfonyl Isocyanate, and Hexafluorophosphoric Acid Etherate

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New platinum(II)–η^1-allyl complexes of the type *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl (PR_3 = PMe_2Ph, P(*i*-Pr)$_3$, P(*t*-Bu)$_3$) have been synthesized by reaction of $[(C_3H_5)PtCl]_4$ with 8 equiv of PR_3. These and known complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl (PR_3 = PEt_3, PCy_3) and *trans*-(η^1-$CH_2CH{=}CHMe$)Pt(PEt_3)$_2$Cl have been investigated with respect to their behavior toward the electrophiles SO_2, $ClSO_2NCO$, and $HPF_6{\cdot}Et_2O$. The complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl react with SO_2 in benzene solution at 25 °C to afford *trans*-($CH_2{=}CHCH_2S(O)_2$)Pt(PR_3)$_2$Cl, the order of reactivity as a function of PR_3 being PEt_3, PMe_2Ph > P(*i*-Pr)$_3$ > P(*t*-Bu)$_3$ (no reaction). The crotyl isotopomers *trans*-($CH_2CH{=}C{*}HMe$)Pt(PEt_3)$_2$Cl (*H = H, D) insert SO_2 with rearrangement of the η^1-allyl fragment to give *trans*-($CH_2{=}CHC{*}H(Me)S(O)_2$)Pt(PEt_3)$_2$Cl. These sulfinato-*S* products were characterized by chemical analysis and IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and the structure of *trans*-($CH_2{=}CHCH_2S(O)_2$)Pt(PMe_2Ph)$_2$Cl was determined by X-ray crystallography. Treatment of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl (PR_3 = PEt_3, PCy_3) and *trans*-(η^1-$CH_2CH{=}CHMe$)Pt(PEt_3)$_2$Cl with $HPF_6{\cdot}Et_2O$ in diethyl ether or toluene affords the η^2-propene and η^2-1-butene complexes [*trans*-(η^2-$CH_2{=}CHMe$)Pt(PR_3)$_2$Cl]PF_6 and [*trans*-(η^2-$CH_2{=}CHEt$)Pt(PEt_3)$_2$Cl]PF_6, respectively. The reactions with SO_2 and $HPF_6{\cdot}Et_2O$ have been rationalized to proceed by attack of the electrophile at the allyl C=C; they appear to be analogous to the corresponding reactions of the 18-electron transition-metal–η^1-allyl carbonyls and of related complexes. Treatment of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl (PR_3 = PEt_3, P(*i*-Pr)$_3$, PCy_3) with $ClSO_2NCO$ in toluene at 25 °C affords *trans*-Pt(PR_3)$_2$Cl$_2$; in contrast, when these reactions are conducted at −78 °C with gradual warming, *trans*-Pt(PR_3)$_2$Cl$_2$ and/or another product, tentatively formulated as the cycloadduct *trans*-$CH_2N(SO_2Cl)C(O)CH_2CHPt(PR_3)_2Cl$, are obtained. The presumed cycloadduct could not be separated from *trans*-Pt(PR_3)$_2$Cl$_2$ and was only characterized by $^{31}P\{^1H\}$ NMR spectroscopy and FAB mass spectrometry in the mixture. When L = PEt_3, a precursor of *trans*-Pt(PEt_3)$_2$Cl$_2$, possibly (η^1-C_3H_5)Pt(PEt_3)$_2$Cl$_2$(SO_2NCO), is observed. The reactions with $ClSO_2NCO$ are provisionally explained by competing [3 + 2] cycloaddition and oxidative addition–reductive elimination pathways. Crystallographic data: monoclinic, space group $P2_1/n$, a = 10.633 (2) Å, b = 16.830 (4) Å, c = 13.745 (3) Å, β = 112.77 (2)°, Z = 4, R = 0.032, and R_w = 0.038.

Introduction

In a recent paper we reported[1] on reactions of 16-electron platinum(II)–η^1-allyl complexes of the type (η^1-C_3H_5)PtL_2Cl (L = tertiary phosphine or $^1/_2$diphosphine) with tetracyanoethylene (TCNE). These reactions afford products of [3 + 2] cycloaddition of TCNE to the allyl fragment, $CH_2C(CN)_2C(CN)_2CH_2CHPtL_2Cl$. Thus, they are analogous to the cycloadditions involving 18-electron transition-metal–η^1-allyl complexes, e.g., (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_3H_5), and a variety of electrophilic reagents, including TCNE.[2-4]

To explore the scope of interaction of 16-electron platinum(II)–η^1-allyl complexes with electrophiles, we have now extended these studies to SO_2, $ClSO_2NCO$, and $HPF_6{\cdot}Et_2O$. An important goal of this investigation was to ascertain what reactions are operative for coordinatively unsaturated metal–η^1-allyl complexes and to develop a comparison with corresponding reactions of 18-electron η^1-allyl compounds. Reported here are results of our study.

Experimental Section

General Procedures and Measurements. Unless otherwise stated, all reactions and manipulations of air-sensitive compounds were carried out at ambient temperatures under an atmosphere of purified N_2 by using standard procedures.[5] Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, TN. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 337 or 283B spectrophotometer and were calibrated with polystyrene. ^1H NMR spectra were obtained on a Varian Associates EM-390, an IBM NR-80, or a Bruker AM-500 spectrometer. ^2H NMR spectra were recorded on a General Electric NT-300 spectrometer at 46.06 MHz and were standardized against the absolute frequency of the instrument. ^{13}C NMR spectra were collected on the Bruker AM-500 at 125.70 MHz. All chemical shifts are given in parts per million downfield from Me_4Si. ^{31}P NMR spectra were recorded on a Bruker HX-90 (at 36.43 MHz) or AM-500 (at 202.42 MHz) spectrometer. Chemical shifts are given with reference to 85% H_3PO_4. All high-field NMR spectra were obtained with the assistance of Dr. C. Cottrell. Mass spectral measurements were made by use of the fast atom bombardment (FAB) technique on a Kratos MS-30 spectrometer by Mr. C. R. Weisenberger.

Materials. Solvents were purified by distillation under an atmosphere of N_2 immediately before use as described previously.[6]

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Tertiary phosphines were purchased from Strem. Chlorosulfonyl isocyanate and *p*-toluenesulfonyl isocyanate were obtained from Alfa and Aldrich, respectively. Hexafluorophosphoric acid etherate ($HPF_6{\cdot}Et_2O$) was purchased from Columbia Organic Chemical Co. All were used without further purification. Sulfur dioxide, from Matheson, was dried over P_4O_{10} and concentrated H_2SO_4 before use. Other reagents were obtained from various commercial sources and used as received. The deuteriated crotyl chloride (*Z*)-$ClCH_2CH{=}CDMe$ was prepared as described in the literature.[7] The complexes $[(C_3H_5)PtCl]_4$,[8] $Pt(PEt_3)_4$,[9] *trans*-$(\eta^1\text{-}C_3H_5)Pt(PCy_3)_2Cl$,[1] and *trans*-$(\eta^1\text{-}CH_2CH{=}CHMe)Pt(PEt_3)_2Cl$[10] were synthesized by published procedures.

Preparation of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl$. All complexes containing an $\eta^1\text{-}CH_2CH{=}CH_2$ ligand were prepared by reaction of $[(C_3H_5)PtCl]_4$ with appropriate tertiary phosphines.[1] General procedures employed and variations therein are described below.

(i) *trans*-$(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl$. To a yellow suspension of 1.085 g (1.000 mmol) of $[(C_3H_5)PtCl]_4$ in 30 mL of diethyl ether at 0 °C was added a solution of 1.08 g (9.19 mmol) of PEt_3 in 20 mL of diethyl ether, also at 0 °C, over 20 min. The reaction mixture turned into a colorless suspension, which was stirred at room temperature for 18 h and then was filtered. Solvent was removed from the filtrate to afford a white oily residue. This residue was crystallized from 4 mL of *n*-hexane at −78 °C to yield 1.41 g (69%) of white crystals. The product was identified by comparison of its IR and ^1H NMR spectra with those reported in the literature:[10] IR (Nujol) ν(C=C) 1607 (ms), ν(PtCl) 258 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 6.17 (m, =CH), 5.23–4.62 (m, $=CH_2$), 2.31 (quartet + unresolved ^{195}Pt satellites, $J(CH_2,{=}CH) \approx J(CH_2,P)$ = 8 Hz, $PtCH_2$), 1.81 (m, 6 PCH_2), 0.97 (quintet (overlapping tt), $J(Me,CH_2) \approx J(Me,P)$ = 8 Hz, 6 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 13.32 ($J(P,^{195}Pt)$ = 2902 Hz).

(ii) *trans*-$(\eta^1\text{-}C_3H_5)Pt(P(i\text{-}Pr)_3)_2Cl$. Reaction of $[(C_3H_5)PtCl]_4$ with 8 equiv of $P(i\text{-}Pr)_3$ was carried out similarly, except that the addition was made at 25 °C and the stirring continued for 24 h. The yield of a white solid was 87%: IR (Nujol) ν(C=C) 1609 (m), ν(PtCl) 260 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 6.38–6.05 (m, =CH), 5.28–4.68 (m, $=CH_2$), 3.25–2.40 (m, 6 PCH), 2.38 (quartet + unresolved ^{195}Pt satellites, $J(CH_2,{=}CH) \approx J(CH_2,P)$ = 7 Hz, $PPtCH_2$), 1.26 (quartet (overlapping dt), $J(Me,CH) \approx J(Me,P)$ = 7 Hz, 12 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 28.06 ($J(P,^{195}Pt)$ = 2904 Hz); mass spectrum, *m/e* 558, $(M + H - Cl)^+$. Anal. Calcd for $C_{21}H_{47}ClP_2Pt$: C, 42.61; H, 8.00. Found: C, 42.44; H, 8.14.

(iii) *trans*-$(\eta^1\text{-}C_3H_5)Pt(PMe_2Ph)_2Cl$. A yellow suspension of 0.826 g (0.760 mmol) of $[(C_3H_5)PtCl]_4$ in 30 mL of CH_2Cl_2 at −78 °C was treated dropwise with a solution of 4 equiv (0.420 g, 3.05 mmol) of PMe_2Ph in 25 mL of CH_2Cl_2 at −30 °C over 30 min. The resulting mixture was stirred at room temperature for ca. 24 h and filtered to remove a small amount of an uncharacterized white solid. To the yellow filtrate was added 4 more equiv (0.420 g, 3.05 mmol) of PMe_2Ph in 25 mL of CH_2Cl_2. The mixture was again stirred at room temperature for 24 h, concentrated to 10 mL, and treated with *n*-pentane to induce the precipitation of a pale yellow solid. The precipitate was dried in vacuo at 55 °C for 24 h to yield 0.535 g (32%) of product: IR (Nujol) ν(C=C) 1614 (m), ν(PtCl) 265 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 7.84–6.56 (m, 2 Ph), 5.79 (m br, =CH), 4.83–4.27 (m, $=CH_2$), 2.06 (m, $PtCH_2$), 1.49 (t br + unresolved ^{195}Pt satellites, 4 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −4.57 ($J(P,^{195}Pt)$ = 2991 Hz).

(iv) *trans*-$(\eta^1\text{-}C_3H_5)Pt(P(t\text{-}bu)_3)_2Cl$. To a suspension of 0.450 g (0.415 mmol) of $[(C_3H_5)PtCl]_4$ in 30 mL of CH_2Cl_2 at −15 °C was slowly added a solution of 4 equiv (0.335 g, 1.66 mol) of $P(t\text{-}Bu)_3$ in 20 mL of CH_2Cl_2 with vigorous stirring over 30 min. The resulting mixture was set aside at −10 °C for ca. 24 h until most of the yellow solid dissolved. It was then filtered, and the filtrate was cooled to −78 °C and treated with 4 more equiv (0.335 g, 1.66 mmol) of $P(t\text{-}Bu)_3$ in 20 mL of CH_2Cl_2, also at −78 °C, over 30 min. The mixture was kept at −78 °C for 12 h and then was stirred at −10 °C for an additional 5 h. The solvent was removed, and the residue was extracted with 1:3 CH_2Cl_2–*n*-pentane and filtered. The filtrate was evaporated to dryness, and the residue was washed with 1 mL of diethyl ether to yield 0.250 g (22%) of product as a white solid: IR (Nujol) ν(C=C) 1631 (w), ν(PtCl) 253 (m) cm^{-1}; ^1H NMR (C_6D_6) δ 6.15 (m, =CH), 5.40–4.90 (m br, $=CH_2$), 2.29 (m, $PtCH_2$), 1.55 (t, J(Me,P) = 6 Hz, 18 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 75.21 ($J(P,^{195}Pt)$ = 2948 Hz). Anal. Calcd for $C_{27}H_{59}ClP_2Pt{\cdot}CH_2Cl_2$: C, 44.18; H, 8.58. Found: C, 44.55; H, 8.44 (sample crystallized from CH_2Cl_2–*n*-pentane).

Preparation of *trans*-$(\eta^1\text{-}CH_2CH{=}CDMe)Pt(PEt_3)_2Cl$. To an orange solution of 1.5 g (2.3 mmol) of $Pt(PEt_3)_4$ in 15 mL of *n*-hexane was added dropwise a solution of 0.23 g (2.5 mmol) of (*Z*)-$ClCH_2CH{=}CDMe$ also in 15 mL of *n*-hexane. After being stirred at 25 °C for ca. 10 min, the resulting solution turned colorless. Stirring was continued for 20 min (30 min total), solvent was removed, and the residue was crystallized from 5 mL of *n*-hexane at −78 °C to yield 0.785 g (65%) of white product: IR (Nujol) ν(C=C) 1645 (w br), ν(PtCl) 263 (w) cm^{-1}; ^1H NMR (C_6D_6) δ 5.76 (m, =CH), 2.20 (quartet + unresolved ^{195}Pt satellites, $J(CH_2,{=}CH) \approx J(CH_2,P)$ = 6.6 Hz, $PtCH_2$), 1.80 (m, 6 PCH_2), 1.73 (s, =CDMe), 0.96 (quintet (overlapping tt), $J(Me,CH_2) \approx J(Me,P)$ = 8 Hz, 6 $CH_2\mathit{Me}$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 13.65 ($J(P,^{195}Pt)$ = 2944 Hz, relative intensity 7, *E* isomer), 13.48 ($J(P,^{195}Pt)$ = 2925 Hz, relative intensity 1, *Z* isomer); ^2H NMR (C_6H_6) δ 5.42 (s).

Preparation of *trans*-$(C_3H_4R'S(O)_2)Pt(PR_3)_2Cl$ (R′ = H, Me).

(i) *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PEt_3)_2Cl$. Dry SO_2 was passed into a solution of 0.124 g (0.244 mmol) of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl$ in 30 mL of benzene at room temperature for 5 min. The solution first turned deep yellow and then pale yellow. Volatile matter was removed under reduced pressure, and the oily residue was washed with 5 mL of *n*-hexane and dried in vacuo for 6 h to give 0.135 g (97% yield) of a solid product: IR (Nujol) ν(C=C) 1639 (m), $\nu(SO_2)$ 1212 (s), 1076 (s), ν(PtCl) 289 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.22 (m, =CH), 5.56–5.21 (m, $=CH_2$), 3.84 (d, $J(CH_2,{=}CH)$ = 7.7 Hz, SCH_2), 2.15 (m, 6 PCH_2), 1.00 (quintet (overlapping tt), $J(Me,CH_2) \approx J(Me,P)$ = 8 Hz, 6 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 20.2 ($J(P,^{195}Pt)$ = 2705 Hz). Anal. Calcd for $C_{15}H_{35}ClO_2P_2PtS$: S, 5.60. Found: S, 5.37.

(ii) *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PMe_2Ph)_2Cl$. The procedure was similar to that described above, except that *trans*-$(\eta^1\text{-}C_3H_5)Pt(PMe_2Ph)_2Cl$ and SO_2 were allowed to react for 30 min. The yield of a pale yellow solid was essentially quantitative. The product was crystallized from 1:6 benzene–*n*-hexane: IR (Nujol) ν(C=C) 1634 (m), $\nu(SO_2)$ 1223 (s), 1065 (s), ν(PtCl) 299 (ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.84–6.80 (m, 2 Ph), 5.68 (m, =CH), 5.15–4.70 (m, $=CH_2$), 3.11 (d, $J(CH_2,{=}CH)$ = 6.8 Hz, SCH_2), 1.66 (t + ^{195}Pt satellites, J(Me,P) = 4 Hz, $J(Me,^{195}Pt)$ = 26 Hz, 4 Me); $^{31}P\{^1H\}$ NMR (C_6H_6) δ −3.86 ($J(P,^{195}Pt)$ = 2780 Hz); mass spectrum, *m/e* 613, $(M + H)^+$. Anal. Calcd for $C_{19}H_{27}ClO_2P_2PtS$: C, 37.36; H, 4.29. Found: C, 37.34; H, 4.36.

(iii) *trans*-$(CH_2{=}CHC^*H(Me)S(O)_2)Pt(PEt_3)_2Cl$ (*H = H, D). Reactions between *trans*-$(\eta^1\text{-}CH_2CH{=}C^*HMe)Pt(PEt_3)_2Cl$ and SO_2 in benzene were carried out for 15 min. Removal of the volatiles afforded a colorless oil in ca. 95% yield: IR (Nujol) ν(C=C) 1634 (m), $\nu(SO_2)$ 1213 (s), 1065 (s), ν(PtCl) 291 (ms) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.18 (m, =CH), 5.27 (m, $=CH_2$), 3.50 (for *H = H only, m, C*H*Me), 1.95 (m, 6 PCH_2), 1.48 (for *H = H, d, J(Me,CH) = 6.9 Hz; for *H = D, s, C*H*Me*), 0.96 (quintet (overlapping tt), $J(Me,CH_2) \approx J(Me,P)$ = 8 Hz, 6 $CH_2\mathit{Me}$); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 19.37 ($J(P,^{195}Pt)$ = 2726 Hz); ^2H NMR (C_6H_6) δ 3.43 (for *H = D only, s). Anal. Calcd for $C_{16}H_{37}ClO_2P_2PtS$: C, 32.79; H, 6.36. Found: C, 32.68; H, 6.15.

(iv) *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(P(i\text{-}Pr)_3)_2Cl$. Dry SO_2 was passed into a solution of 0.105 g (0.177 mmol) of *trans*-$(\eta^1\text{-}C_3H_5)Pt(P(i\text{-}Pr)_3)_2Cl$ in 30 mL of diethyl ether at room temperature. After 1 h, a $^{31}P\{^1H\}$ NMR spectrum of the solution revealed that ca. 50% of the starting material remained unreacted. The reaction was continued for an additional 3 h, the volatiles were removed, and the residue was dissolved in 3 mL of CH_2Cl_2. Addition of 10 mL of *n*-pentane precipitated an impurity, which was filtered off. The filtrate was evaporated to dryness to leave impure title complex as a pale yellow solid: IR (Nujol) ν(C=C) 1635 (w), ν(PtCl) 291 (ms) cm^{-1}; $^{31}P\{^1H\}$ NMR (CH_2Cl_2) δ 30.34 ($J(P,^{195}Pt)$ = 2766 Hz). Further crystallization did not remove the impurities.

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Attempted Reaction of *trans*-(η^1-C_3H_5)Pt(P(t-Bu)$_3$)$_2$Cl with SO_2. Dry SO_2 was passed into a solution of 0.04 g (0.06 mmol) of the title complex in 15 mL of benzene at room temperature for 2 h, and then the reaction mixture was kept under a slightly positive pressure of SO_2 for 16 h. The volatiles were removed, and the pale yellow residue was shown by $^{31}P\{^1H\}$ NMR spectroscopy to be unreacted η^1-allyl complex.

Preparation of [*trans*-(η^2-CH_2=CHMe)Pt(PEt$_3$)$_2$Cl]PF_6. To a solution of 0.230 g (0.453 mmol) of *trans*-(η^1-C_3H_5)Pt(PEt$_3$)$_2$Cl in 15 mL of diethyl ether at −78 °C was added 0.10 g (0.45 mmol) of HPF_6·Et_2O. The resulting mixture was stirred at −78 °C for 30 min resulting in the formation of a white precipitate. Warming to room temperature over 1.5 h, filtration, and washing with diethyl ether (2 × 10 mL) afforded 0.170 g (72%) of product as a white solid: IR (Nujol) ν(C=C) 1509 (w), $\nu(PF_6)$ 842 (s br), $\delta(PF_6)$ 557 (m), ν(PtCl) 326 (m) cm^{-1}; 500-MHz ^1H NMR[11] ($CDCl_3$) δ 5.42 (m, H_c), 4.08 (d + ^{195}Pt satellites, $J(H_a,H_c)$ = 13.8 Hz, $J(H_a,^{195}Pt)$ = 75 Hz, H_a), 3.90 (d + ^{195}Pt satellites, $J(H_b,H_c)$ = 7.3 Hz, $J(H_b,^{195}Pt)$ = 76 Hz, H_b), 2.12 (m, 3 PCH_2), 2.00 (m, 3 PCH_2), 1.89 (d + ^{195}Pt satellites, J(Me,H_c) = 5.9 Hz, J(Me,^{195}Pt) = 28 Hz, CH*Me*), 1.21 (m, 3 CH_2*Me*), 1.18 (m, 3 CH_2*Me*); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 93.00 (t, J(C,^{195}Pt) = 73.8 Hz, =CH_2), 63.43 (t, J(C,^{195}Pt) = 79.6 Hz, =CH), 22.35 (s, CH*Me*), 14.40 (m, 3 PCH_2), 12.20 (m, 3 PCH_2), 7.99 (s, 3 CH_2*Me*), 7.70 (s, 3 CH_2*Me*); $^{31}P\{^1H\}$ NMR (C_6H_6) δ 18.80 (J(P,^{195}Pt) = 2056 Hz), 18.66 (J(P,^{195}Pt) = 2086 Hz), −145 (J(P,F) = 712 Hz); mass spectrum, *m/e* 655, (M + H)$^+$. Anal. Calcd for $C_{15}H_{36}ClF_6P_3Pt$: C, 41.65; H, 6.74. Found: C, 41.33; H, 6.50.

This reaction was also conducted in THF at −78 °C with warming to −15 °C. A $^{31}P\{^1H\}$ NMR spectrum showed the formation of mainly [*trans*-(η^2-CH_2=CHMe)Pt(PEt$_3$)$_2$Cl]$^+$ and some [(η^3-C_3H_5)Pt(PEt$_3$)$_2$]$^+$ (δ 10.37 (J(P,^{195}Pt) = 3713 Hz)). The products were not separated.

Preparation of [*trans*-(η^2-CH_2=CHMe)Pt(PCy$_3$)$_2$Cl]PF_6. A solution of 0.210 g (0.252 mmol) of *trans*-(η^1-C_3H_5)Pt(PCy$_3$)$_2$Cl in 20 mL of toluene was treated with 0.070 g (0.32 mmol) of HPF_6·Et_2O. The resulting mixture was warmed to room temperature over 2 h, as a white precipitate formed at ca. −30 °C. The precipitate was filtered off at room temperature and washed with *n*-pentane (2 × 5 mL) to give 0.235 g (95%) yield) of product: IR (Nujol) ν(C=C) 1510 (w), ν(PtCl) 325 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (C_6H_6) δ 20.92 (J(P,^{195}Pt) = 2017 Hz), 20.69 (J(P,^{195}Pt) = 1998 Hz), −145 (J(P,F) = 712 Hz). Anal. Calcd for $C_{39}H_{72}ClF_6P_3Pt$: P, 9.50. Found: P, 9.07.

Preparation of [*trans*-(η^2-CH_2=CHEt)Pt(PEt$_3$)$_2$Cl]PF_6. To a solution of 0.105 g (0.201 mmol) of *trans*-(η^1-CH_2CH=CHMe)Pt(PEt$_3$)$_2$Cl in 5 mL of diethyl ether at −78 °C was added 0.045 g (0.20 mmol) of HPF_6·Et_2O. While the mixture was allowed to warm to ca. 25 °C with stirring, a white solid precipitated from solution. Stirring was continued at room temperature (total reaction time 18 h), and the precipitate was filtered off, washed with diethyl ether (2 × 4 mL), and dried in vacuo to yield 0.089 g (66%) of product: ^1H NMR (C_6D_6, lettering scheme as in ref 11) δ 5.45 (m, H_c), 4.21 (d, $J(H_a,H_c)$ = 14.6 Hz, H_a), 3.98 (d + ^{195}Pt satellites, $J(H_b,H_c)$ = 7.2 Hz, $J(H_b,^{195}Pt)$ = 73 Hz, H_b), 2.12 (m, CHCH_2), 1.79 (m, 3 PCH_2), 1.61 (m, 3 PCH_2), 1.33 (t, J(Me,CH_2) = 7.3 Hz, CCH_2*Me*), 0.87 (m, 3 PCH_2*Me*), 0.84 (m, 3 PCH_2*Me*); $^{31}P\{^1H\}$ NMR (C_6H_6, upfield to δ −50) δ 17.67 (J(P,^{195}Pt) = 2076 Hz), 17.43 (J(P,^{195}Pt) = 2096 Hz) (also signals at δ 9.17 (J(P,^{195}Pt) = 3760 Hz), 9.07 (J(P,^{195}Pt) = 3763 Hz), 8.81 (J(P,^{195}Pt) = 3753 Hz), and 8.71 (J(P,^{195}Pt) = 3750 Hz) of the syn and anti isomers of [(η^3-C_3H_4Me)Pt(PEt$_3$)$_2$]$^+$ with ≤10% intensity of the signals of [*trans*-(η^2-CH_2=CHEt)Pt(PEt$_3$)$_2$Cl]$^+$); mass spectrum, *m/e* (M + H)$^+$, (M − PF_6)$^+$, (M − PF_6 − Cl)$^+$.

Reactions of *trans*-(η^1-C_3H_5)Pt(PR$_3$)$_2$Cl with $ClSO_2NCO$. To a solution of 0.074 g (0.13 mmol) of *trans*-(η^1-C_3H_5)Pt(P(*i*-Pr)$_3$)$_2$Cl in 2 mL of toluene at −78 °C was added 0.018 g (0.13 mmol) of $ClSO_2NCO$. The mixture was allowed to warm to room temperature over 2 h, and a $^{31}P\{^1H\}$ NMR spectrum was recorded: δ 27.16 (J(P,^{195}Pt) = 2782 Hz, more intense signal), 26.96 (J(P,^{195}Pt) = 2441 Hz, less intense signal). The solvent was removed under reduced pressure to leave a yellow solid: mass spectrum, *m/e* 664, 587, among other peaks. All attempts at separation of this mixture by column chromatography on alumina or Florisil resulted in decomposition of the major component.

When this reaction was carried out similarly at room temperature, only the product with the $^{31}P\{^1H\}$ NMR at δ 26.96, *trans*-Pt(P(*i*-Pr)$_3$)$_2$Cl$_2$, was observed. Likewise, reaction of each of *trans*-(η^1-C_3H_5)Pt(PEt$_3$)$_2$Cl and *trans*-(η^1-C_3H_5)Pt(PCy$_3$)$_2$Cl with 1 equiv of $ClSO_2NCO$ in toluene at room temperature afforded only *trans*-Pt(PEt$_3$)$_2$Cl$_2$ (δ 11.64 (J(P,^{195}Pt) = 2434 Hz)) and *trans*-Pt(PCy$_3$)$_2$Cl$_2$ (δ 16.27 (J(P,^{195}Pt) = 2425 Hz)), respectively, as shown by $^{31}P\{^1H\}$ NMR spectroscopy. The complexes *trans*-Pt(PR$_3$)$_2$Cl$_2$ were characterized by comparison of their IR and $^{31}P\{^1H\}$ NMR spectra with those of authentic samples.[9,12,13]

Attempted Reactions of *trans*-(η^1-C_3H_5)Pt(PR$_3$)$_2$Cl with *p*-MeC$_6$H$_4$SO$_2$SO$_2$NCO. A solution of 0.162 g (0.329 mmol) of *trans*-(η^1-C_3H_5)Pt(PEt$_3$)$_2$Cl was treated with 0.063 g (0.32 mmol) of *p*-MeC$_6$H$_4$SO$_2$NCO in 5 mL of toluene, and the resulting mixture was stirred at room temperature for 3 days. Only unreacted *trans*-(η^1-C_3H_5)Pt(PEt$_3$)$_2$Cl was observed in a $^{31}P\{^1H\}$ NMR spectrum of the reaction solution.

Similarly, there was no observed reaction after a solution of 0.082 g (0.14 mmol) of *trans*-(η^1-C_3H_5)Pt(P(*i*-Pr)$_3$)$_2$Cl and 0.044 g (0.22 mmol) of *p*-MeC$_6$H$_4$SO$_2$NCO in 40 mL of benzene was stirred at 50 °C for 27 h.

Crystallographic Analysis of *trans*-(CH$_2$=CHCH$_2$S(O)$_2$)Pt(PMe$_2$Ph)$_2$Cl. Crystals of the title complex suitable for X-ray diffraction were grown from 1:2 benzene–*n*-pentane at room temperature.

Space group and cell parameters were obtained by using Weissenberg and precession photographs. Accurate unit cell parameters were obtained by a least-squares procedure applied to the setting angles of 20 reflections with 11.2 ≤ θ ≤ 15.6° on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. Intensity data were collected with the same diffractometer. Crystallographic data of interest are

Table I. Crystallographic Data

mol formula	$C_{19}H_{27}ClO_2P_2SPt$
mol wt	612
cryst system	monoclinic
space group	$P2_1/n$
a, Å	10.633 (2)
b, Å	16.830 (4)
c, Å	13.745 (3)
β, deg	112.77 (2)
V, Å^3	2268.0 (9)
Z	4
D(calcd), g cm^{-3}	1.792
λ(Mo Kα), Å	0.71069 (graphite-monochromated)
μ(Mo Kα), cm^{-1}	66.1
transmissn factors	0.737–0.999
cryst size, mm	0.12 × 0.28 × 0.42
scan type	$\omega/2\theta$
θ range, deg	2–28
orientatn monitors[a]	3
intensity monitors[b]	3
no. of collected data[c]	5857
unique data with $I > n\sigma(I)$; *n*	3792; 3
final no. of variables	235
R^d	0.032
R_w[e]	0.038
error in observn of unit wt	2.85
largest parameter shift	1.02

[a] Measured after each 800 reflections. New orientation matrix if angular change >0.1. [b] Measured after each hour. [c] $\pm h,k,l$. [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [e] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

(11) Proton lettering scheme:

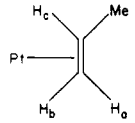

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B,[a] Å²
Pt	0.03550 (3)	0.10457 (2)	0.16214 (2)	2.646 (4)
Cl	−0.1820 (2)	0.0470 (1)	0.1077 (2)	5.67 (6)
S	0.2419 (2)	0.1607 (1)	0.2300 (1)	3.12 (4)
P(1)	0.1276 (2)	−0.0219 (1)	0.2141 (2)	3.30 (4)
P(2)	−0.0684 (2)	0.2270 (1)	0.1017 (1)	2.98 (4)
O(1)	0.3353 (6)	0.1141 (4)	0.3180 (4)	4.3 (1)
O(2)	0.2352 (6)	0.2447 (3)	0.2534 (4)	4.1 (1)
C(1)	0.3116 (8)	0.1580 (6)	0.1258 (6)	4.4 (2)
C(2)	0.450 (1)	0.198 (1)	0.1694 (9)	9.5 (4)
C(3)	0.557 (1)	0.170 (2)	0.181 (1)	17.2 (8)
C(4)	0.2888 (8)	−0.0473 (6)	0.2030 (7)	4.5 (2)
C(5)	0.0190 (9)	−0.1027 (5)	0.1368 (7)	4.5 (2)
C(6)	0.1509 (8)	−0.0442 (5)	0.3498 (6)	3.9 (2)
C(7)	0.279 (1)	−0.0393 (6)	0.4313 (7)	4.8 (2)
C(8)	0.295 (1)	−0.0609 (6)	0.5346 (8)	5.9 (3)
C(9)	0.185 (1)	−0.0843 (7)	0.5543 (8)	6.6 (3)
C(10)	0.055 (1)	−0.0866 (8)	0.4760 (8)	7.2 (3)
C(11)	0.036 (1)	−0.0668 (7)	0.3699 (8)	6.0 (3)
C(12)	0.0138 (8)	0.2910 (5)	0.0364 (6)	4.0 (2)
C(13)	−0.2431 (8)	0.2217 (5)	0.0031 (6)	4.1 (2)
C(14)	−0.0878 (7)	0.2861 (4)	0.2065 (6)	3.2 (2)
C(15)	−0.0669 (8)	0.2503 (6)	0.3024 (6)	4.0 (2)
C(16)	−0.0902 (9)	0.2952 (7)	0.3795 (7)	5.3 (2)
C(17)	−0.1301 (9)	0.3728 (7)	0.3626 (8)	5.6 (2)
C(18)	−0.150 (1)	0.4095 (6)	0.2665 (8)	5.8 (3)
C(19)	−0.1308 (9)	0.3655 (5)	0.1872 (7)	4.8 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

summarized in Table I. The intensities were corrected for Lorentz and polarization factors. Anomalous dispersion terms were also taken into account, and an empirical absorption correction was applied by using the ψ-scan data from close to axial (i.e., $\chi > 80\%$) reflections.

The structure was solved by the heavy-atom method; the position of the Pt atom was determined from the Patterson map and was then used to phase a Fourier map which revealed all other non-hydrogen atoms. No attempt was made to locate hydrogen atoms. Final anisotropic full-matrix least-squares refinement, with unit weights, converged to $R = 0.032$. Atomic scattering factors and anomalous dispersion terms were taken from the literature.[14] All calculations were carried out on a PDP 11/44 computer by using programs from the Enraf-Nonius SDP package.[15]

The final positional parameters are listed in Table II. Listings of temperature factors and structure factors are available as supplementary material.[16]

Results and Discussion

Preparation and Characterization of Platinum(II)–η^1-Allyl Complexes. All Pt–η^1-C_3H_5 complexes used in this study were prepared by reaction of $[(C_3H_5)PtCl]_4$ with at least 8 equiv of appropriate PR_3 in diethyl ether[1] or CH_2Cl_2 (eq 1). This method has an advantage over that

$$[(C_3H_5)PtCl]_4 + 8PR_3 \rightarrow 4\,trans\text{-}(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl \quad (1)$$

involving oxidative addition of allyl chloride to $Pt(PR_3)_4$ in that it requires only one platinum-containing starting material, which is air-stable and easy to make.[8] Nevertheless, some variations in procedure and special precautions are needed to ensure that at least a reasonable yield of *pure* product is obtained. Thus, the complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl with PR_3 = PEt_3 and $P(i\text{-}Pr)_3$ were prepared in good yield (69 and 87%, respectively) by slow addition of 8 equiv of PR_3 to a suspension of $[(C_3H_5)PtCl]_4$ in diethyl ether followed by prolonged stirring. In contrast, the synthesis of pure *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl with PR_3 = PMe_2Ph and $P(t\text{-}Bu)_3$ even in modest yield (32 and 22%, respectively) required that the addition be conducted in two stages in CH_2Cl_2 suspension/solution. First, 4 equiv of PR_3 were introduced slowly, and the mixture was allowed to react for about 24 h; then the remaining 4 equiv of PR_3 were added, also followed by about 24 h of reaction time. The rate of addition of PR_3 to $[(C_3H_5)PtCl]_4$ and the temperature control are very important in these preparations. Details are provided in Experimental Section.

By analogy to known reactions of $[(C_3H_5)PtCl]_4$ with organic isocyanides,[17] the formation of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl is thought to proceed as shown in eq 2–4. However, no attempts were made at isolation and/or characterization of proposed intermediates in this study.

$$[(C_3H_5)PtCl]_4 + 4PR_3 \rightarrow 2[(\eta^1\text{-}C_3H_5)Pt(PR_3)Cl]_2 \quad (2)$$

$$2[(\eta^1\text{-}C_3H_5)Pt(PR_3)Cl]_2 \xrightarrow{\text{dissolution}} 4(\eta^3\text{-}C_3H_5)Pt(PR_3)Cl \quad (3)$$

$$4(\eta^3\text{-}C_3H_5)Pt(PR_3)Cl + 4PR_3 \rightarrow 4\,trans\text{-}(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl \quad (4)$$

All complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl were characterized by a combination of elemental analysis and spectroscopic properties, reported in Experimental Section. Thus, their $^{31}P\{^1H\}$ NMR spectra in C_6H_6 solution show only one signal that is flanked by ^{195}Pt satellites. The position of this signal and the magnitude of $J(P,^{195}Pt)$ (2900–3000 Hz) accord with the corresponding values found for other complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl.[1] Moreover, the appearance of only one sharp set of $^{31}P\{^1H\}$ resonances (i.e. a singlet and ^{195}Pt satellites) shows that the equilibrium between η^1- and η^3-allyl complexes (eq 5), known to occur for several complexes (η^1-C_3H_5)PtL_2Cl in polar solvents,[18–23] lies far on the side of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl in C_6H_6 solution.

$$trans\text{-}(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl \rightleftharpoons [(\eta^3\text{-}C_3H_5)Pt(PR_3)_2]^+ + Cl^- \quad (5)$$

^1H NMR spectra of all Pt–η^1-C_3H_5 complexes show separate signals for the $=CH_2$, $=CH$, and $PtCH_2$ protons, the chemical shifts of which agree with the σ nature of the C_3H_5 fragment.[1,21,22,24] In addition, the observed splitting patterns of the resonances of the Me groups of the four different PR_3 ligands, viz. PEt_3, $P(i\text{-}Pr)_3$, PMe_2Ph, and $P(t\text{-}Bu)_3$, are those expected and, in some cases, reported for various *trans*-$Pt(PR_3)_2XY$ complexes with these same phosphine ligands.[25] The IR spectra of Nujol mulls show

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ν(C=C) and ν(PtCl) absorption bands at 1631–1607 and 265–253 cm^{-1}, respectively, as for related platinum(II)-η^1-allyl complexes.[1,17-22,24]

The crotyl complex *trans*-(η^1-C_4H_7)Pt(PEt_3)$_2$Cl was synthesized by reaction of Pt(PEt_3)$_4$ with $ClCH_2CH$=CHMe as described by Pearson.[10] The deuteriated analogue *trans*-(η^1-CH_2CH=CDMe)Pt(PEt_3)$_2$Cl, prepared for a study of reaction with SO_2 (vide infra), was obtained similarly by using $ClCH_2CH$=CDMe (eq 6). Both iso-

$$\text{Pt}(PEt_3)_4 + ClCH_2CH{=}CDMe \rightarrow \textit{trans}\text{-}(\eta^1\text{-}CH_2CH{=}CDMe)\text{Pt}(PEt_3)_2Cl + 2PEt_3 \quad (6)$$

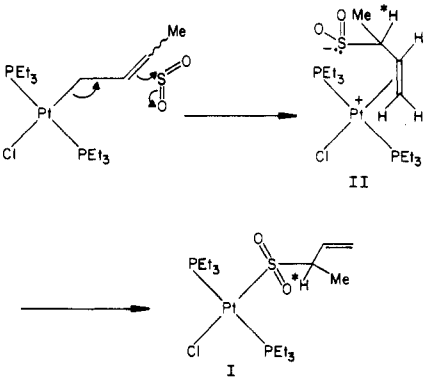
topomers exhibit only σ-bonded platinum(II)–allyl species in C_6H_6 (C_6D_6) solution, as evidenced by their $^{31}P\{^1H\}$ and ^1H NMR spectra. However, each shows two sets of $^{31}P\{^1H\}$ NMR signals at δ 13.65 (J(P,^{195}Pt) = 2944 Hz) and 13.48 (J(P,^{195}Pt) = 2925 Hz) in an approximate intensity ratio of 7:1 to indicate the presence of isomers. An examination of the ^1H NMR spectrum of the protio complex in C_6D_6 solution at 500 MHz in the δ 6.1–5.3 region corroborates this observation, which was not reported with the original preparation of *trans*-(η^1-C_4H_7)Pt(PEt_3)$_2$Cl.[10] The spectrum shows signals at δ 5.99, 5.82, 5.45, and 5.33 as multiplets with the relative intensities ca 1:7:7:1. These resonances are unequivocally assigned with the aid of homonuclear decoupling. Thus, irradiation at the frequency of the δ 1.73 (CH*Me*) signal collapses the δ 5.45 multiplet to a doublet (J = 14.7 Hz) and the δ 5.33 multiplet to an unsymmetrical doublet (J = 11.0 Hz) owing to off-resonance effects. On this basis, the multiplets at δ 5.45 and 5.33 are assigned to the C*H*Me protons of the *E* and *Z* isomers, respectively, from the magnitude of the two coupling constants, J(=CH,=CH).[26] The remaining multiplets at δ 5.99 and 5.82 are those of the C*H*CH_2 protons of the *Z* and *E* isomers, respectively. Isomer *E* is the major species in the mixture.

Reactions of Platinum(II)-η^1-Allyl Complexes with SO_2. Coordinatively saturated transition-metal-η^1-allyl complexes react with SO_2 to yield sulfinato-*S* insertion products.[27] These reactions have been reported for a variety of metal-η^1-allyl complexes; they occur in liquid SO_2 as well as in solution of SO_2 in organic solvents.

In the present study, platinum(II)-η^1-allyl complexes were allowed to react with SO_2 in nonpolar benzene to minimize the formation of the η^3-allyl complexes according to eq 5. The reactions of *trans*-(η^1-C_3H_5)Pt(PEt_3)$_2$Cl, *trans*-(η^1-C_3H_5)Pt(PMe_2Ph)$_2$Cl, and *trans*-(η^1-CH_2CH=C*HMe)Pt(PEt_3)$_2$Cl (*H = H, D) with SO_2 in C_6H_6 at room temperature all went to completion in less than 30 min and led to the isolation of sulfinato-*S* products in almost quantitative yields. With *trans*-(η^1-C_3H_5)Pt(P(*i*-Pr)$_3$)$_2$Cl, the insertion of SO_2 was about 50% complete in 1 h under similar conditions, and the product isolated after 4 h was impure and could be only partially characterized. No reaction was observed between *trans*-(η^1-C_3H_5)Pt(P(*t*-Bu)$_3$)$_2$Cl and SO_2 in 18 h under comparable conditions. Thus, the rates of SO_2 insertion of these *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl complexes decrease with increasing steric demands of the phosphine ligands as measured by the Tolman cone angle, θ[28] (given in parentheses), viz., PR_3 = PMe_2Ph (122°), PEt_3 (132°) > P(*i*-Pr)$_3$ (160°) > P(*t*-Bu)$_3$ (182°).

The sulfinato-*S* products have been characterized by a combination of elemental analysis and spectroscopic data

Scheme I



(Experimental Section), and the structure of *trans*-(CH_2=$CHCH_2S(O)_2$)Pt(PMe_2Ph)$_2$Cl was elucidated by X-ray crystallography (vide infra). The complexes show IR $\nu(SO_2)$ bands at 1223–1212 and 1078–1068 cm^{-1}, which compare well with those reported[27,29] for various $MS(O)_2R$ metal sulfinates. The ν(C=C) absorptions at 1639–1634 cm^{-1} indicate that the allyl fragment remains intact and rules out possible cycloaddition reactions.[30] All ^1H and $^{31}P\{^1H\}$ NMR data are also in complete accord with the assigned structures.

Of particular interest is the structure of the complexes derived from the reactions of *trans*-(η^1-CH_2CH=C*HMe)Pt(PEt_3)$_2$Cl (*H = H, D) with SO_2, because of the possibility of rearrangement of the crotyl group during the insertion.[31] ^1H NMR spectra of the reaction products show the resonance of the C*H*Me* protons as a doublet (when *H = H, J = 6.9 Hz) or a singlet (when *H = D) at δ 1.48. The signal of the C*H proton occurs at δ 3.50 (multiplet), essentially in the same position as the signal of the C*H deuterium (singlet) in the ^2H NMR spectrum. These and other NMR data given in Experimental Section indicate that the crotyl group underwent rearrangement and that the structure of the sulfinato-*S* products is as represented in I (see Scheme I).

The foregoing structure strongly suggests that the reactions of *trans*-(η^1-CH_2CH=C*HMe)Pt(PEt_3)$_2$Cl, and most likely also of various *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl, with SO_2 proceed by electrophilic attack of SO_2 at the allyl C=C to generate zwitterion II.[32] This zwitterion then reacts by displacement of coordinated C=C by the sulfinate sulfur to yield the sulfinato-*S* product I. The proposed pathway is depicted in Scheme I. It is very similar to that presented earlier[27,30] for reactions of SO_2 with various complexes (η^5-C_5H_5)Fe(CO)$_2$(η^1-allyl), except that dissociation of ligated C=C and formation of a sulfinato-*O* intermediate need not be invoked, since the platinum(II) center is coordinatively unsaturated (16-electron). One should note that this mechanism differs from that suggested by Faraone et al.[33] for the reactions of *trans*-PtL_2RCl (R = alkyl, aryl) with SO_2, where the formation

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(32) We cannot unequivocally rule out the possibility that *trans*-(η^1-CH_2CH=C*HMe)Pt(PEt_3)$_2$Cl exists in rapid equilibrium with unknown isomeric *trans*-(η^1-C*H(Me)CH=CH_2)Pt(PEt_3)$_2$Cl which is present in a small, spectroscopically (^1H and $^{31}P\{^1H\}$ NMR) undetectable amount. The latter then rapidly "inserts" SO_2 into the Pt–C*H bond. However, we consider such a mechanistic scenario rather unlikely, since SO_2 insertion reactions of platinum(II)–alkyl and –aryl complexes of the type *trans*-PtL_2RCl are appreciably slower[33] than those of the allyl complexes under present study.
(33) Faraone, F.; Silvestro, L.; Sergi, S.; Pietropaolo, R. *J. Organomet. Chem.* **1972**, *46*, 379.

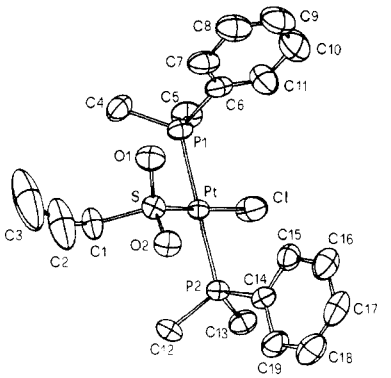

Figure 1. ORTEP plot of *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PMe_2Ph)_2Cl$ showing atom numbering scheme. Atoms are drawn at the 50% probability level. Hydrogen atoms are omitted.

of *trans*-$PtL_2(S(O)_2R)Cl$ is thought to involve coordination of SO_2 to platinum followed by migration of R onto sulfur.

Description of the Molecular Structure of *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PMe_2Ph)_2Cl$. The crystal structure of the title complex consists of discrete molecules which exhibit the expected trans-square-planar coordination at the platinum center, with a slight tetrahedral distortion. The deviations (Å) from the best weighted least-squares plane, calculated through Pt, P(1), P(2), Cl, and S, are as follows: Pt, 0.002 (0); P(1), 0.039 (2); P(2), 0.034 (2); Cl, −0.147 (3); S, −0.080 (2).

An ORTEP drawing of the molecule is shown in Figure 1. Selected bond lengths and angles are given in Table III.

The two phosphine ligands are slightly bent back away from the sulfinate ligand (mean P–Pt–S angle = 91.67 (8)°, and mean P–Pt–Cl angle = 88.4 (5)°). This is indicative of steric interactions among the ligands, confirmed by some close intramolecular contacts (e.g., S···C(4) = 3.576 (6), S···C(12) = 3.575 (5), O(1)···C(4) = 3.084 (7), O(2)···C(12) = 3.101 (6), C(1)···C(4) = 3.649 (8), C(1)···C(5) = 3.228 (6), C(1)···C(12) = 3.680 (8), C(1)···C(13) = 3.226 (5) Å).

The Pt–P distances of 2.334 (1) and 2.337 (1) Å are, to our knowledge, the longest Pt–P distances so far observed in *trans*-$(PMe_2Ph)_2Pt^{II}$ complexes, which range from 2.282 (4) to 2.312 (4) Å.[34] As expected, they are much longer than those found in related cis compounds, such as *cis*-$Pt(PMe_2Ph)_2Cl_2$, where they are 2.245 (1) and 2.248 (1) Å.[35] The Pt–P mean value of 2.336 (2) Å is close to the Pt–P distance found in *trans*-bis(trialkylphosphine)platinum(II) complexes such as *trans*-$Pt(P(n\text{-}Bu)_3)_2(SPh)_2$ (2.329 (8) Å)[36a] or *trans*-$Pt(PCy_3)_2Cl_2$ (2.340 (2) Å).[36b]

The Pt–S distance of 2.235 (1) Å is significantly longer than that in square-planar Pt complexes containing chelating disulfoxide ligands (2.192 (4)–2.217 (2) Å).[37] It is closer to the values found in dialkyl sulfoxide complexes of platinum(II), which range from 2.220 (2) to 2.244 (2) Å.[38,39]

The Pt–Cl bond length of 2.347 (1) Å appears longer than the mean value of 2.309 (4) Å found in *cis*-$Pt(S(O)Me_2)_2Cl_2$.[39] Thus, the Pt–Cl distance suggests that the $S(O)_2C_3H_5$ ligand has a greater trans influence than $S(O)Me_2$.

Table III. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations

Bond Distances			
Pt–Cl	2.347 (1)	P(1)–C(5)	1.834 (5)
Pt–S	2.235 (1)	P(1)–C(6)	1.823 (5)
Pt–P(1)	2.337 (1)	P(2)–C(12)	1.827 (5)
Pt–P(2)	2.334 (1)	P(2)–C(13)	1.830 (5)
S–O(1)	1.461 (3)	P(2)–C(14)	1.826 (5)
S–O(2)	1.456 (3)	C(1)–C(2)	1.519 (9)
S–C(1)	1.850 (5)	C(2)–C(3)	1.179 (14)[a]
P(1)–C(4)	1.829 (5)		

Bond Angles			
Cl–Pt–S	174.24 (6)	Pt–P(1)–C(5)	113.8 (2)
Cl–Pt–P(1)	88.07 (5)	Pt–P(1)–C(6)	112.0 (2)
Cl–Pt–P(2)	88.78 (5)	C(4)–P(1)–C(5)	100.3 (3)
S–Pt–P(1)	91.72 (4)	C(4)–P(1)–C(6)	106.1 (3)
S–Pt–P(2)	91.61 (4)	C(5)–P(1)–C(6)	104.3 (3)
P(1)–Pt–P(2)	176.33 (4)	Pt–P(2)–C(12)	116.4 (2)
Pt–S–O(1)	111.2 (2)	Pt–P(2)–C(13)	115.2 (2)
Pt–S–O(2)	112.2 (2)	Pt–P(2)–C(14)	112.5 (2)
Pt–S–C(1)	106.8 (2)	C(12)–P(2)–C(13)	101.9 (3)
O(1)–S–O(2)	114.5 (2)	C(12)–P(2)–C(14)	106.8 (2)
O(1)–S–C(1)	106.2 (2)	C(13)–P(2)–C(14)	102.6 (2)
O(2)–S–C(1)	105.3 (2)	S–C(1)–C(2)	107.5 (4)
Pt–P(1)–C(4)	118.8 (2)	C(1)–C(2)–C(3)	128 (1)

[a] See text.

The sulfur atom adopts a distorted tetrahedral geometry, similar to that found in $(\eta^5\text{-}C_5Me_5)Fe(CO)_2(S(O)_2CH_2CH{=}CHPh)$.[40] The average S–O and S–C distances of 1.459 (4) and 1.850 (5) Å, respectively, are comparable, within experimental error, with those found in the above iron compound.[40]

The C(2)–C(3) distance of 1.179 (14) Å appears to be severely affected by thermal motion. Correction for this effect, assuming a "riding" motion,[41] yields a value of 1.30 Å, consistent with a C=C bond. The S–C(1)–C(2) and C(1)–C(2)–C(3) bond angles are 107.5 (4) and 128 (1)°, respectively.

Reactions of Platinum(II)–η^1-Allyl Complexes with $HPF_6{\cdot}Et_2O$. Addition of 1 equiv of $HPF_6{\cdot}Et_2O$ to a solution of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl$ in diethyl ether at −78 °C results in the formation of a white precipitate of [*trans*-$(\eta^2\text{-}CH_2{=}CHMe)Pt(PEt_3)_2Cl]PF_6$. When this reaction was carried out in THF at −78 °C with warming to −15 °C, the same product together with a smaller amount of $[(\eta^3\text{-}C_3H_5)Pt(PEt_3)_2]^+$ were obtained in solution. The latter species was prepared independently as the PF_6^- salt by treatment of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl$ with $AgPF_6$ to aid its identification in the above reaction mixture. Similar protonation of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PCy_3)_2Cl$ with $HPF_6{\cdot}Et_2O$ in toluene afforded [*trans*-$(\eta^2\text{-}CH_2{=}CHMe)Pt(PCy_3)_2Cl]PF_6$, also as a white precipitate, at ca. −30 °C.

The product [*trans*-$(\eta^2\text{-}CH_2{=}CHMe)Pt(PEt_3)_2Cl]PF_6$ (III) was thoroughly characterized by elemental analysis, mass spectrometry, and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Its mass spectrum shows a peak corresponding to $(M + H)^+$ at m/e 655; such $(M + H)^+$ peaks are common to spectra obtained by fast atom bombardment.[42] In the 500-MHz ^1H NMR spectrum, separate signals are observed for the three olefinic protons and the Me group of the propene ligand; they are listed in Experimental Section. Assignment of these resonances and

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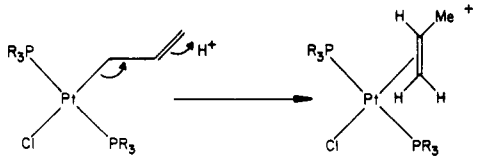
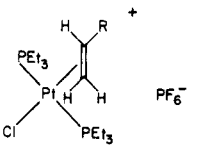
(41) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1964**, *17*, 142.
(42) Rinehart, K. L., Jr. *Science (Washington, DC)* **1982**, *218*, 254.

Scheme II



determination of the coupling constants were aided by homonuclear decoupling experiments. For the PEt_3 ligands, two proton signals are observed for each of the CH_2 and Me fragments to demonstrate that the phosphines are not equivalent. This observation is corroborated by the $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra. The former spectrum also shows two signals for each of the CH_2 and Me fragments of the Et group, among the resonances that fully support the assigned structure. The latter spectrum exhibits two closely spaced resonance sets at δ 18.80 and 18.66, with similar $J(P,^{195}Pt)$ values of 2056 and 2086 Hz, respectively. The magnitude of $J(P,^{195}Pt)$ as well as the absence of detectable phosphorus–phosphorus coupling militate against a cis structure of the cation. The nonequivalence of the PEt_3 ligands is best rationalized by a trans-square-planar geometry in which the phosphines are on the same and opposite sides with reference to the Me group of the propene (see III).



III

R = Me, Et

The proposed structure of [*trans*-(η^2-CH_2=CHMe)Pt-(PCy_3)$_2$Cl]PF_6, similar to that of its PEt_3 analogue, receives support from spectroscopic data and chemical analysis. Again, particularly revealing is the $^{31}P\{^1H\}$ NMR spectrum which shows two sets of PCy_3 resonances at δ 20.92 and 20.69, with $J(P,^{195}Pt)$ = 2017 and 1998 Hz, respectively. The complex is thermally less stable than that containing PEt_3 and requires storage at ca. 0 °C.

Two pathways for protonation reactions of platinum(II)–η^1-allyl complexes merit special consideration. First, addition of H^+ may occur to the allyl C=C with rearrangement to an η^2-alkene structure as reported[43-46] for a number of 18-electron transition-metal–η^1-allyl complexes, including (η^5-C_5H_5)Fe(CO)$_2$(η^1-C_3H_5). Alternatively, HPF_6 may undergo oxidative addition to the platinum center in *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl to furnish (η^1-C_3H_5)Pt-(PR_3)$_2$ClH(FPF_5) (or [(η^1-C_3H_5)Pt(PR_3)$_2$ClH(solvent)]$^+$), which then reductively eliminates propene to leave Pt-(PR_3)$_2$Cl(FPF_5) (or [Pt(PR_3)$_2$Cl(solvent)]$^+$). The latter process is precedented by the reactions of *trans*-Pt-(PR_3)$_2$(Me)X (X = Cl, I) with HCl to give *trans*-Pt-(PEt_3)$_2$ClX and methane.[47] Those reactions are thought to proceed by the sequence oxidative addition of HCl and reductive elimination of CH_4.

The formation of [*trans*-(η^2-CH_2=CHMe)Pt(PR_3)$_2$Cl]-PF_6 upon treatment of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl with HPF_6·Et_2O is entirely consistent with the former pathway, shown in Scheme II. The possibility that the latter pathway is operative and that the released propene replaces PF_6^- (or solvent) in Pt(PR_3)$_2$Cl(FPF_5) (or [Pt-(PR_3)$_2$Cl(solvent)]$^+$) to afford the η^2-alkene product must be considered unlikely. The protonation was conducted under a stream of N_2, which would have removed at least a substantial amount of propene from the reacting mixture before its coordination to platinum. The high yield of isolated products indicates that the propene was very effectively retained in this system. Furthermore, the reactions in question proceed considerably faster than the protonation reactions of platinum(II)–alkyl complexes that are initiated by oxidative addition of acid.[47]

The most definitive evidence for the protonation of the allyl C=C is derived from a study of the reaction of *trans*-(η^1-CH_2CH=CHMe)Pt(PEt_3)$_2$Cl with HPF_6·Et_2O in diethyl ether. The product of this reaction has been characterized as the 1-butene complex [*trans*-(η^2-CH_2=CHEt)Pt(PEt_3)$_2$Cl]PF_6. Accordingly, its ^1H NMR spectrum is very similar to that of [*trans*-(η^2-CH_2=CHMe)-Pt(PEt_3)$_2$Cl]PF_6 but shows the presence of an Et rather than a Me group in the η^2-alkene ligand. The $^{31}P\{^1H\}$ NMR spectrum bears a strong resemblance to that of [*trans*-(η^2-CH_2=CHMe)Pt(PEt_3)$_2$Cl]PF_6 and shows nonequivalence of the PEt_3 ligands; this nonequivalence arises as illustrated in III. Oxidative addition of H^+ to the platinum center and reductive elimination of H and η^1-CH_2CH=CHMe would have afforded a mixture of (*E*)- and (*Z*)-2-butene in ca. 7:1 ratio provided that no isomerization occurred. The ^1H and $^{31}P\{^1H\}$ NMR spectra of the isolated product are clearly inconsistent with the presence of coordinated 2-butene.

Reactions of Platinum(II)–η^1-Allyl Complexes with $ClSO_2NCO$. The complexes *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl with PR_3 = PEt_3, P(*i*-Pr)$_3$, and PCy_3 react with $ClSO_2NCO$ in toluene at room temperature to afford *trans*-Pt-(PR_3)$_2$Cl$_2$. In contrast, no reaction was observed between *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl (PR_3 = PEt_3 or P(*i*-Pr)$_3$) and *p*-$MeC_6H_4SO_2NCO$ at 25–50 °C after at least 27 h.

The reactions of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl with $ClSO_2NCO$ were monitored at low temperature by $^{31}P\{^1H\}$ NMR spectroscopy to shed some light on their mechanism. Thus, when a toluene solution of equimolar amounts of *trans*-(η^1-C_3H_5)Pt(P(*i*-Pr)$_3$)$_2$Cl and $ClSO_2NCO$ at −78 °C was gradually warmed to −25 °C, a new set of signals appeared at δ 27.16 with $J(P,^{195}Pt)$ = 2782 Hz. Further warming to −15 °C resulted in a growth of these resonances and the appearance of another set of signals at δ 26.96 with $J(P,^{195}Pt)$ = 2441 Hz, which rapidly gained intensity with increasing temperature. This latter species was shown to be *trans*-Pt(P(*i*-Pr)$_3$)$_2$Cl$_2$ by comparison of its $^{31}P\{^1H\}$ NMR data with those of an authentic sample. The initially appearing compound may be the cycloadduct *trans*-$\overline{CH_2N(SO_2Cl)C(O)CH_2CHPt(P(i\text{-}Pr)_3)_2Cl}$ as suggested by a similarity of its $J(P,^{195}Pt)$ value to that of previously reported[1] [3 + 2] cycloaddition products of *trans*-(η^1-C_3H_5)Pt(PR_3)$_2$Cl and TCNE. At ca. 25 °C, the signals of the starting material disappeared, and the signals of the presumed cycloadduct were somewhat more intense than those of *trans*-Pt(P(*i*-Pr)$_3$)$_2$Cl$_2$. Attempts at separation of the two products by column chromatography proved unsuccessful owing to decomposition of the former species. A FAB mass spectrum of the reaction mixture showed (M + H)$^+$ peaks of both products.

A similar study of the reaction of *trans*-(η^1-C_3H_5)Pt-(PEt_3)$_2$Cl with $ClSO_2NCO$ in toluene showed that three sets of resonances were present at −75 °C: δ 19.9 ($J(P,^{195}Pt)$ = 2680 Hz), 11.9 ($J(P,^{195}Pt)$ = 2430 Hz), and −3.9 (J-$(P,^{195}Pt)$ = 1700 Hz). When the solution was warmed to

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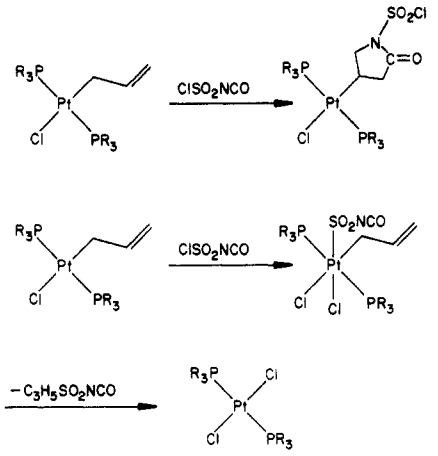
Scheme III



room temperature, the spectrum underwent the following changes. The signals (i.e. a singlet and ^{195}Pt satellites) at δ 19.9 remained essentially intact, whereas the intensity of the signals at δ 11.9 gradually increased and that of the signals at δ −3.9 gradually decreased. When the temperature reached 25 °C, only two resonance sets at δ 19.9 and 11.9 in a 1:3 intensity ratio were observed.

The species resonating at δ 11.9 was characterized as *trans*-$Pt(PEt_3)_2Cl_2$ by comparison of its $^{31}P\{^1H\}$ NMR data with those of an independently prepared sample. The product with the signals at δ 19.9 may be a cycloadduct analogous to that with the P(*i*-Pr)$_3$ ligands (vide supra). The identity of the intermediate resonating at δ −3.9 appears less obvious; however, the low value of its $J(P,^{195}Pt)$ (1700 Hz) suggests that it may be a platinum(IV) complex, possibly $(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl_2(SO_2NCO)$. In general, platinum(IV) complexes of the type $PtL_2R_2X_2$ show $J(P,^{195}Pt)$ in the range 1500–1900 Hz.[48]

A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PCy_3)_2Cl$ and $ClSO_2NCO$ in toluene at −75 °C showed a set of signals of the starting material at δ 16.20 ($J(P,^{195}Pt)$ = 2822 Hz) and another, weak, set at δ 15.53 ($J(P,^{195}Pt)$ = 2696 Hz). When the solution was warmed, the former resonances decreased and the latter increased in intensity. At −30 °C, all of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PCy_3)_2Cl$ was converted to the δ 15.53 product, which again may be a [3 + 2] cycloadduct of $ClSO_2NCO$ and the η^1-allyl complex.

Results of these low-temperature studies are best generalized in terms of two parallel and independent processes. The lower energy process could entail cycloaddition between *trans*-$(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl$ and $ClSO_2NCO$, similar to that of 18-electron transition-metal–η^1-allyl complexes, including $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}C_3H_5)$.[49] The higher energy process may involve oxidative addition of $ClSO_2NCO$ to the platinum center in *trans*-$(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl$, followed by reductive elimination of $C_3H_5SO_2NCO$. This would generate *trans*-$Pt(PR_3)_2Cl_2$, which was indeed either observed or isolated as a final product. Scheme III summarizes our tentative proposal of these reactions. Unfortunately, instability of the presumed cycloadducts and of what is thought to be a platinum(IV) intermediate prevented their complete characterization which would have rendered this proposal more definitive. It is further noteworthy that the η^1-allyl complexes with bulky PR_3 ligands, e.g., PCy_3, exhibit a preference for the presumed cycloaddition over the proposed oxidative addition as would be expected.

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Conclusions

The 16-electron platinum(II)–η^1-allyl complexes of the type *trans*-$(\eta^1\text{-}CH_2CH{=}CHR')Pt(PR_3)_2Cl$ (R′ = H, Me) react with the electrophilic reagents SO_2 and $HPF_6{\cdot}Et_2O$ to afford *trans*-$(CH_2{=}CHCH(R')S(O)_2)Pt(PR_3)_2Cl$ and [*trans*-$(\eta^2\text{-}CH_2{=}CHR'')Pt(PR_3)_2Cl]PF_6$ (R″ = Me, Et), respectively. These products are analogous to those of the corresponding reactions of 18-electron transition-metal–η^1-allyl carbonyls and related complexes. The two reactions of platinum(II) are best rationalized to proceed by addition of the electrophile to the allyl C=C, as are those of the 18-electron compounds. Thus, the coordinative unsaturation of platinum(II) apparently has little effect on the mechanism. Reactions of *trans*-$(\eta^1\text{-}C_3H_5)Pt(PR_3)_2Cl$ with $ClSO_2NCO$ are more complex than the foregoing, probably owing to the presence of a reactive Cl–S bond and the coordinative unsaturation of the metal. They are tentatively formulated to occur by two parallel pathways: (1) [3 + 2] cycloaddition of $ClSO_2NCO$ to the $\eta^1\text{-}C_3H_5$ ligand and (ii) oxidative addition of $ClSO_2NCO$ and reductive elimination of $C_3H_5SO_2NCO$ to yield *trans*-$Pt(PR_3)_2Cl_2$.

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Registry No. I, 108103-21-5; III (R = Me), 108082-84-4; III (R = Et), 108082-86-6; *trans*-$(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl$, 65555-45-5; $[(C_3H_5)PtCl]_4$, 32216-28-7; *trans*-$(\eta^1\text{-}C_3H_5)Pt(P(i\text{-}Pr)_3)_2Cl$, 108103-19-1; *trans*-$(\eta^1\text{-}C_3H_5)Pt(PMe_2Ph)_2Cl$, 108082-78-6; *trans*-$(\eta^1\text{-}C_6H_5)Pt(P(t\text{-}Bu)_3)_2Cl$, 108082-79-7; *trans*-$(\eta^1\text{-}CH_2CH{=}CDMe)Pt(PEt_3)_2Cl$, 108082-80-0; $Pt(PEt_3)_4$, 33937-26-7; (*Z*)-$ClCH_2CH{=}CDMe$, 108082-81-1; *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PEt_3)_2Cl$, 108082-82-2; *trans*-$(CH_2{=}CHCH_2S(O)_2Pt(PMe_2Ph)_2Cl$, 108103-20-4; *trans*-$(\eta^1\text{-}CH_2CH{=}CHMe)Pt(PEt_3)_2Cl$, 65555-46-6; *trans*-$(CH_2{=}CHCD(Me)S(O)_2Pt(PEt_3)_2Cl$, 108103-22-6; *trans*-$(CH_2{=}CHCH_2S(O)_2]Pt(P(i\text{-}Pr)_3)_2Cl$, 108103-23-7; $[(\eta^3\text{-}C_3H_5)Pt(PEt_3)_2]^+$, 31833-26-8; *trans*-$(\eta^1\text{-}C_3H_5)Pt(PCy_3)_2Cl$, 81111-59-3; [*trans*-$(\eta^2\text{-}CH_2{=}CHMe)Pt(PCy_3)_2Cl]PF_6$, 108103-25-9; *syn*-$[(\eta^3\text{-}C_3H_4Me)Pt(PEt_3)_2]^+$, 108146-99-2; *anti*-$[(\eta^3\text{-}C_3H_4Me)Pt(PEt_3)_2]^+$, 108147-00-8; $ClSO_2NCO$, 1189-71-5; *trans*-$Pt(P(i\text{-}Pr)_3)_2Cl_2$, 59967-54-3; *trans*-$Pt(PEt_3)_2Cl_2$, 13965-02-1; *trans*-$Pt(PCy_3)_2Cl_2$, 60158-99-8; *trans*-$\overline{CH_2N(SO_2Cl)C(O)CH_2CH}Pt((i\text{-}Pr)_3P)_2Cl$, 108103-26-0; $(\eta^1\text{-}C_3H_5)Pt(PEt_3)_2Cl_2(SO_2NCO)$, 108103-27-1; *trans*-$\overline{CH_2N(SO_2Cl)C(O)CH_2CH}Pt(Et_3P)_2Cl$, 108082-87-7; *trans*-$\overline{CH_2N(SO_2Cl)C(O)CH_2CH}Pt(Cy_3P)_2Cl$, 108082-88-8.

Supplementary Material Available: A listing of temperature factors for *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PMe_2Ph)_2Cl$ (2 pages); a listing of structure factors for *trans*-$(CH_2{=}CHCH_2S(O)_2)Pt(PMe_2Ph)_2Cl$ (16 pages). Ordering information is given on any current masthead page.