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Hydride to Carbene Migration at Platinum(II). Synthesis and X-ray Structure of *cis*-$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}BF_4$

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Summary: The hydrido–dithiocarbene complex trans-$[(PPh_3)_2PtH(CSCH_2CH_2S)]BF_4$ *(1) undergoes thermal rearrangement in* CH_3CN *by hydride to carbene migration to form the complex cis-*$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}BF_4$ *(2), whose molecular structure has been determined by a single-crystal X-ray analysis (monoclinic,* $P2_1/n$*;* $a = 16.255$ *(3) Å,* $b = 20.423$ *(3) Å,* $c = 11.406$ *(2) Å,* $\beta = 94.42$ *(4)°,* $V = 3773(1)$ *Å*^{3}*,* $Z = 4$*,* $R = 0.047$*,* $R_w = 0.054$ *for 4447 measured reflections with* $I > 3\sigma(I)$*). The rearrangement of 1 to 2 proceeds also with* Cl^- *ions. In this latter reaction the neutral complex trans-*$[(PPh_3)_2PtCl[C(H)SCH_2CH_2S]$ *(3) could be isolated in the solid state, but it isomerizes in solution by intramolecular displacement of* Cl^- *by one sulfur atom of the dithiolane ring to give cis-*$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}Cl$ *(2′), which is structurally similar to 2.*

Hydride to carbene migration is an important process in transition metal carbene chemistry since it has catalytic implications, it constitutes C–H bond formation and it represents the reverse process of α-elimination of an alkyl group.[1] To our knowledge, there are only a few unambiguous examples on the occurrence of this process, which is known at least for zirconium,[2] iron,[3] molybdenum,[4] and rhodium.[5]

Our interest in the synthesis, chemical reactivity[6] and electrochemical behavior[7] of α-heteroatom carbene complexes of the late transition metal ions Pd(II) and Pt(II) led to the observation that carbenes having hydride as the trans ligand may undergo under mild conditions carbene–carbon cleavage[8] or carbene fragmentation[7b] processes, which are not observed with the parent derivatives having a halide as the trans ligand. Herein we report a facile and unprecedented 1,2 hydrogen shift occurring at the Pt(II) metal center of the hydrido–dithiocarbene complex *trans*-$[(PPh_3)_2PtH(CSCH_2CH_2S)]BF_4$ and the spectroscopic and structural characterization of the resulting migratory insertion product *cis*-$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}BF_4$.

Experimental Section

General Procedures and Materials. All reactions were carried out under a nitrogen atmosphere, but workup of the reaction products was performed in air. Diethyl ether and dichloromethane were distilled from sodium benzophenone ketyl. Acetone was dried over $CaSO_4$ and degassed before use. All other solvents were of reagent grade and used without further purification. HBF_4 (54% solution in Et_2O) and PPNCl (bis(triphenylphosphine)iminium chloride) were commercially available products and used as received. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer (abbreviation used: m = medium). ^1H, ^{31}P, and ^{13}C NMR spectra were recorded either on a Varian Unity 300 or Bruker AC-200 spectrometers in CD_2Cl_2 or CD_3CN solution; proton chemical shifts are reported from Me_4Si by taking the chemical shift of dichloromethane-d_2 as +5.32 ppm; phosphorus chemical shifts are from external H_3PO_4 85%; positive chemical shifts are downfield from the reference (abbreviations used: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; J are given in hertz). The fast atom bombardment (FAB) mass spectra were obtained using ni-

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trobenzyl alcohol as a matrix on a VG ZAB 2F instrument operating with a Xe-atom beam energy of 8 keV. The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected. The complex *trans*-$(PPh_3)_2PtH(CF_3)$ was prepared according to ref 9.

Synthesis of *trans*-$[(PPh_3)_2PtH(\overline{CSCH_2CH_2S})]BF_4$ (1). To a suspension of *trans*-$(PPh_3)_2PtH(CF_3)$ (1.6 g, 2.026 mmol) in anhydrous Et_2O (30 mL) was added $HSCH_2CH_2SH$ (2 mL) at 0 °C and immediately treated with HBF_4 (20 drops). The reaction mixture was stirred for 40 min at 0 °C and then for an additional 20 min at room temperature. The white precipitate was filtered off, washed with Et_20 (10 mL), and then recrystallized from CH_2Cl_2/Et_2O; yield 1.48 g (80%); mp 180–181 °C; IR (Nujol mull; cm^{-1}) ν (PtH) 2084 (m); ^1H NMR (CD_2Cl_2) δ (H) −6.16 (t), $^2J_{HP}$ 12.56, $^1J_{HPt}$ 700.68; δ (CH_2) 2.97 (s), $^4J_{HPt}$ 5.80; ^{13}C(^1H-coupled) NMR (CD_2Cl_2) δ $(C)_{carbene}$ 291.74 (d), $^2J_{CH}$ 40.9, $^1J_{CPt}$ 647.9; δ (CH_2) 43.73 (t), $^1J_{CH}$ 148.87, $^3J_{CPt}$ 43.42; $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ (P) 28.15 (s), $^1J_{PPt}$ 2800.6; FAB mass spectrum *m/e* 823 (16%, M^+), 718 (11.0%, $[M - {}^\bullet\overline{CHSCH_2CH_2S}]^{+\bullet}$), 561 (5.3%, $[M - PPh_3]^+$). Anal. Calcd for $C_{39}H_{35}P_2PtS_2BF_4$: C, 51.38; H, 3.87. Found: C, 51.47; H, 3.79.

Synthesis of *cis*-$\{(PPh_3)_2Pt[\overline{C(H)SCH_2CH_2S}]\}BF_4$ (2). The hydrido–dithiocarbene complex 1 (0.718 g, 0.788 mmol) was stirred in CH_3CN (30 mL) at 40 °C and the reaction was monitored by IR following the decrease of the Pt–H absorption at 2069 cm^{-1}. After 6 days, no residual Pt–H stretching of the starting hydrido complex was present. The yellow-orange solution was taken to dryness and the solid residue was treated with CH_2Cl_2 (5 mL). On addition of *n*-hexane (20 mL) a pale yellow solid precipitated, which was filtered off, washed with *n*-hexane (2 × 5 mL) and dried under vacuum: yield 0.650 g (91%); mp 119–120 °C dec; ^1H NMR (CD_2Cl_2) δ (CH) 4.67 (dd), $^2J_{HPt}$ 31.70, $^3J_{HP}$ 5.28 and 2.60; δ (CH_2) 2.88 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ (P trans to S) 21.60, $^1J_{PPt}$ 4820; δ (P trans to C) 20.43, $^1J_{PPt}$ 2917. ^{13}C (^1H-coupled) NMR (CD_2Cl_2) δ (CH) 73.00 (dd), $^1J_{CPt}$ 475.75, $^1J_{CH}$ 177.4, $^2J_{PC}$ 73.8. The $-CH_2CH_2-$ methylene protons of the dithiolane ring reveal a fluxional behavior in solution at 30 °C showing a broad signal centered at ca. 40 ppm. Cooling a CD_3CN solution of 2 to −20 °C resulted in the sharpening of the CH_2 signals and the ^{13}C NMR data are as follows: $^{13}C\{^1H\}$ NMR δ (CH_2 bound to S(2)) 46.10 (s), δ (CH_2 bound to S(1)) 38.76 (s), $^2J_{CPt}$ 26.7. ^{13}C(^1H-coupled) NMR δ (CH_2 bound to S(2)) 46.10 (t), $^1J_{CH}$ 146.9; δ (CH_2 bound to S(1)) 38.76 (t), $^1J_{CH}$ 141.8; FAB mass spectrum *m/e* 823 (20.0%, M^+), 822 (22.0%, $[M - H]^{+\bullet}$), 561 (8.0%, $[M - {}^\bullet\overline{CHSCH_2CH_2S}]^{+\bullet}$), 561 (8.0%, $[M - PPh_3]^+$). Anal. Calcd for $C_{39}H_{35}P_2PtS_2BF_4\cdot 1/2CH_2Cl_2$: C, 49.73; H, 3.91. Found: C, 49.68; H, 3.68.

Reaction of 1 with Cl^- Ions. Synthesis of *trans*-$\{(PPh_3)_2Pt(Cl)[\overline{C(H)SCH_2CH_2S}]\}$ (3) and *cis*-$\{(PPh_3)_2Pt[\overline{C(H)SCH_2CH_2S}]\}Cl$ (2′). The hydrido–dithiocarbene complex 1 (0.646 g, 0.71 mmol) was dissolved in CH_2Cl_2 (10 mL) and PPN^+Cl^- (0.60 g, 1.04 mmol) was added at room temperature. The uncolored solution turned pale yellow. After 12 h an IR spectrum of the reaction mixture showed that the Pt–H absorption at 2079 cm^{-1} had disappeared. The solution was then taken to dryness, the solid residue was treated with acetone (30 mL), and the insoluble white portion (compound 3) was filtered off and washed with Et_2O (2 × 5 mL): yield 0.120 g (20%); mp 159–160 °C; IR (Nujol mull; cm^{-1}): ν (PtCl) 283 (m); FAB mass spectrum *m/e* 858 (0.5%, $[M]^{+\bullet}$), 823 (15.0%, $[M - Cl^\bullet]^+$), 596 (1.5%, $[M - PPh_3]^{+\bullet}$). Anal. Calcd for $C_{39}H_{35}P_2ClS_2Pt$: C, 54.43; H, 4.10. Found: C, 54.45; H, 4.16. The filtered acetone solution was concentrated to 5 mL and addition of Et_2O (15 mL) gave a pale yellow solid which contained a mixture of PPN^+Cl^- and the migratory insertion product *cis*-$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}^+$, as evidenced by IR and NMR (^1H and ^{31}P), which could not be separated upon several attempted crystallizations.

When dissolved in dichloromethane, compound 3 isomerizes to 2′ by intramolecular Cl^- displacement by the sulfur atom of the 1,3-dithiolane ring as indicated by the ^1H and ^{31}P NMR data which are similar to those of 2: ^1H NMR (CD_2Cl_2) δ (CH) 4.73 (dd), $^2J_{HPt}$ 31.5, $^3J_{HP}$ 2.69 and 5.38; δ (CH_2) 2.88 (m); $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ (P trans to S) 20.04, $^1J_{PPt}$ 4802; δ (P trans to C) 19.79, $^1J_{PPt}$ 2906. Complex 2′ in acetone converts into 2 upon treatment with $NaBF_4$.

Table I. Summary of Crystallographic Data for *cis*-$\{(PPh_3)_2Pt[\overline{C(H)SCH_2CH_2S}]\}BF_4$

chem formula	$C_{39}H_{35}P_2S_2BF_4Pt$
mol wt	911.67
cryst dimens, mm	0.48 × 0.44 × 0.29
cryst syst	monoclinic
a, Å	16.255(3)
b, Å	20.423(3)
c, Å	11.406(2)
β, deg	94.92(4)
V, $Å^3$	3773(1)
space group	$P2_1/n$
Z	4
d, calcd (g cm^{-3})	1.61
temp, °C	22
data collected	$\pm h,k,l$
F(000)	1800
λ(Mo Kα), Å	0.71069
μ(Mo Kα), cm^{-1}	37.5
no. of reflns measd	6967
$2\theta_{max}$, deg	50
no. of reflns [$I \geq 3\sigma(I)$]	4447
$R(F_o)$	0.047
$R_w(F_o)$	0.054
goodness of fit	1.14

X-ray Measurements and Structure Determination of *cis*-$\{(PPh_3)_2Pt[\overline{C(H)SCH_2CH_2S}]\}BF_4$ (2). Crystals were grown by slow diffusion of *n*-hexane into a solution of CH_2Cl_2 as pale yellow prisms. The space group $P2_1/n$ and the cell constants were determined at 295 K. Twenty-five reflections in the 2θ range 28–32° with Mo K_α radiation ($\lambda(K_\alpha)$ = 0.71069 Å) were used for cell dimensions. Data collection was done on a Philips PW1100 diffractometer. Three standard reflections measured at 150 reflection intervals did not reveal any crystal decomposition. All calculations were done with SHELX 76 package of crystallographic programms.[10] A ϕ scan absorption correction was applied to the data set.[11] A summary of crystal data and the details of the intensity data collection and refinement are shown in Table I. The structure was solved by Patterson–Fourier methods and refined by full matrix least-squares with anisotropic thermal parameters for all the non-hydrogen atoms, except for BF_4 molecules, which are disordered among two principal positions (occupancy factor 50%) and were refined isotropically. The hydrogens were introduced at calculated idealized positions (d(C–H) = 0.98 Å with U = 0.07 $Å^2$) and allowed to ride on the attached carbon atom. The final refinement cycle resulted in the conventional *R* factors, R = 0.047 and R_w = 0.054, based on the 4447 reflections with $I > 3\sigma(I)$ and the 418 variables. The maximum and minimum peaks in the final difference electron density map have heights of +1.2 and −0.6 e/$Å^3$ with the maximum peak in the immediate vicinity of the platinum atom. Scattering factors for neutral atoms were used and included terms for

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Table II. Atomic Coordinates and Thermal Parameters U_{eq} (Å^2) for *cis*-$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}BF_4$

atom	*x*	*y*	*z*	U_{eq}	PP[a]
Pt	0.19932(2)	0.13631(2)	0.05243(3)	0.0509(1)	
P(1)	0.2040(1)	0.2466(1)	0.0494(2)	0.0490(7)	
P(2)	0.3338(1)	0.1002(1)	0.0475(2)	0.0464(8)	
S(1)	0.1237(2)	0.0397(2)	0.0533(4)	0.101(2)	
S(2)	0.0104(3)	0.1284(2)	−0.0836(7)	0.154(3)	
C(1)	0.0694(5)	0.1184(4)	0.0461(9)	0.068(4)	
C(2)	0.0762(9)	0.0777(8)	−0.1605(12)	0.139(9)	
C(3)	0.1046(7)	0.0123(6)	−0.0942(11)	0.092(6)	
C(4)	0.2431(5)	0.2852(5)	0.1858(8)	0.052(3)	
C(5)	0.2455(8)	0.3539(6)	0.1961(11)	0.080(5)	
C(6)	0.2713(9)	0.3813(7)	0.3049(13)	0.095(6)	
C(7)	0.2929(7)	0.3441(7)	0.3975(12)	0.085(5)	
C(8)	0.2911(7)	0.2785(7)	0.3902(10)	0.082(5)	
C(9)	0.2644(6)	0.2482(6)	0.2848(8)	0.067(4)	
C(10)	0.1023(6)	0.2847(4)	0.0285(8)	0.055(3)	
C(11)	0.0731(6)	0.3168(4)	−0.0745(9)	0.057(3)	
C(12)	−0.0067(7)	0.3450(5)	−0.0800(9)	0.068(4)	
C(13)	−0.0565(7)	0.3400(6)	0.0147(13)	0.078(5)	
C(14)	−0.0255(7)	0.3085(5)	0.1097(11)	0.069(4)	
C(15)	0.0521(6)	0.2792(6)	0.1297(9)	0.068(4)	
C(16)	0.2600(6)	0.2754(5)	−0.0708(8)	0.056(4)	
C(17)	0.3286(7)	0.3184(7)	−0.0522(12)	0.084(5)	
C(18)	0.3711(9)	0.3343(8)	−0.1523(13)	0.100(6)	
C(19)	0.3488(9)	0.3099(9)	−0.2563(14)	0.111(7)	
C(20)	0.2801(9)	0.2719(8)	−0.2747(11)	0.094(6)	
C(21)	0.2396(8)	0.2516(6)	−0.1811(9)	0.073(4)	
C(22)	0.3291(5)	0.0424(4)	−0.0755(8)	0.050(3)	
C(23)	0.3388(6)	−0.0240(5)	−0.0652(10)	0.065(4)	
C(24)	0.3254(8)	−0.0641(7)	−0.1606(12)	0.086(5)	
C(25)	0.3002(8)	−0.0380(8)	−0.2702(14)	0.098(6)	
C(26)	0.2922(8)	0.0261(8)	−0.2844(11)	0.090(6)	
C(27)	0.3048(6)	0.0700(6)	−0.1901(9)	0.064(4)	
C(28)	0.4225(6)	0.1514(4)	0.0281(8)	0.052(3)	
C(29)	0.4775(6)	0.1401(5)	−0.0565(10)	0.068(4)	
C(30)	0.5462(7)	0.1812(8)	−0.0613(12)	0.095(6)	
C(31)	0.5606(8)	0.2303(7)	0.0144(14)	0.094(6)	
C(32)	0.5077(7)	0.2412(6)	0.0969(13)	0.092(6)	
C(33)	0.4393(7)	0.2046(5)	0.1050(10)	0.071(4)	
C(34)	0.3685(5)	0.0527(4)	0.1763(8)	0.047(3)	
C(35)	0.3176(6)	0.0472(4)	0.2686(8)	0.054(3)	
C(36)	0.3450(7)	0.0113(5)	0.3683(9)	0.065(4)	
C(37)	0.4200(8)	−0.0183(5)	0.3786(10)	0.071(4)	
C(38)	0.4716(7)	−0.0135(5)	0.2896(10)	0.072(4)	
C(39)	0.4449(6)	0.0233(5)	0.1889(9)	0.061(4)	
B	0.843(2)	0.890(1)	0.554(3)	0.133(8)*	
F(1)	0.845(3)	0.959(2)	0.609(4)	0.23(2)*	0.5
F(2)	0.880(2)	0.851(2)	0.646(3)	0.20(1)*	0.5
F(3)	0.794(3)	0.862(2)	0.467(5)	0.22(3)*	0.5
F(4)	0.929(1)	0.900(1)	0.497(2)	0.14(1)*	0.5
F(11)	0.834(2)	0.962(1)	0.536(3)	0.15(1)*	0.5
F(21)	0.891(2)	0.877(2)	0.442(3)	0.20(1)*	0.5
F(31)	0.884(2)	0.898(2)	0.660(3)	0.21(2)*	0.5
F(41)	0.783(2)	0.869(1)	0.533(3)	0.16(1)*	0.5

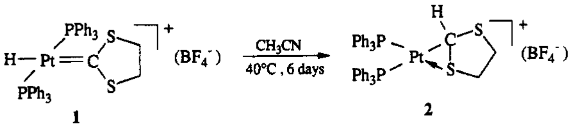
[a] Population parameters (PP) are reported when ≠ 1. [b] Values marked with an asterisk denote atoms refined isotropically.

anomalous scattering.[12] Final positional and equivalent isotropic thermal parameters are given in Table II. Lists of anisotropic thermal parameters and hydrogen atom coordinates are available as supplementary material.

Results and Discussion

The synthesis of the hydrido–carbene complex *trans*-$\{(PPh_3)_2PtH[CSCH_2CH_2S]\}BF_4$ (1) has been reported in a previous communication,[13] but a detailed procedure is given in the Experimental Section together with a full spectroscopic and analytical characterization. The preparation of 1 as well as of the other hydrido–carbene complexes of Pt(II) takes advantage of the ease with which the α-fluorines of the σ-bonded trifluoromethyl complex *trans*-$(PPh_3)_2Pt(H)(CF_3)$ undergo abstraction by acids such as HBF_4.[14] The reaction leads initially to the formation of the highly reactive intermediate *trans*-$[(PPh_3)_2Pt(H)(CF_2)]BF_4$,[14] which, on addition of 1,2-ethanediol, $HSCH_2CH_2SH$, converts to 1 in 80% yield. Complex 1 is stable in the solid state and in solution of dichloromethane. The ^1H NMR (CD_2Cl_2) shows the hydride resonance as a sharp triplet at δ −6.16 by coupling with the two equivalent ^{31}P nuclei ($^2J_{HP}$ 12.56 Hz), flanked by ^{195}Pt satellites ($^1J_{HPt}$ 700 Hz); however, this triplet resonance appears as a broad singlet (with broad ^{195}Pt satellites) when the proton NMR is recorded in CD_3CN. The $^{13}C\{^1H\text{-coupled}\}$ NMR (CD_2Cl_2) shows the carbene carbon resonance at δ 291.7 as a doublet by coupling with the *trans*-hydride ligand ($^2J_{CH}$ 40.9 Hz) with ^{195}Pt satellites ($^1J_{CPt}$ 647.9 Hz). It is worthwhile nothing that the carbene carbon resonance of 1 falls in the range (280–310 ppm) reported for other electrophilic dithiocarbene complexes.[15]

When 1 is heated at 40 °C in CH_3CN solvent, it slowly undergoes hydride to carbene migration to give almost quantitatively *cis*-$\{(PPh_3)_2Pt[C(H)SCH_2CH_2S]\}BF_4$ (2) (eq 1). Compound 2 is a pale yellow, air-stable solid, which is soluble in chlorinated solvents. It was characterized by its elemental analysis, IR, ^1H, $^{31}P\{^1H\}$, and ^{13}C NMR spectra (Experimental Section). The structure of 2 in the solid state was determined by an X-ray crystallographic analysis. An ORTEP[16] drawing of 2 is shown in Figure 1. Selected bond distances and angles are listed in Table III.



1 2

(1)

The Pt, S(1), C(1), P(1), and P(2) atoms lie in a distorted square plane. The Pt–S(1) and Pt–C(1) distances of 2.326(4) and 2.139(5) Å, respectively, are similar to the corresponding Pt–S and Pt–C distances of 2.328(6) and 2.12(1) Å, respectively, found in *cis*-$\{(Et_3P)_2Pt[C(H)CH_2CH_2CH_2S]\}PF_6$, which also has a metallacyclopropane geometry.[17] The C(1)–S(1) distance of 1.83(1) Å is in the range of S–C(alkyl) distances (range 1.80–1.84 Å).[14] The S(1)–C(3) distance of 1.77(2) Å and even more the C(1)–S(2) distance of 1.71(2) Å are relatively short S–C(alkyl) distances, but not nearly as short as the C═S double bond of 1.618(8) Å in the thioacetone ligand of $W(CO)_5$

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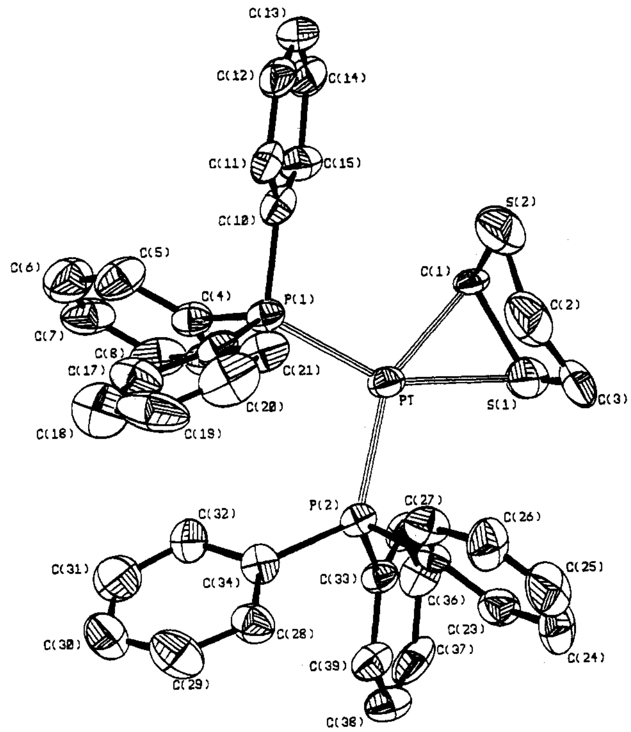

Figure 1. An ORTEP drawing of the cation from *cis*-{(PPh$_3$)$_2$Pt[C(H)SCH$_2$CH$_2$S]}BF$_4$ (2) with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

Table III. Selected Bond Distances (Å) and Angles (deg) for *cis*-{(PPh$_3$)$_2$Pt[C(H)SCH$_2$CH$_2$S]}BF$_4$

Bond Lengths			
Pt–P(1)	2.254(3)	Pt–P(2)	2.313(2)
Pt–S(1)	2.326(4)	Pt–C(1)	2.139(5)
P(1)–C(4)	1.81(1)	P(1)–C(10)	1.82(1)
P(1)–C(16)	1.81(1)	P(2)–C(22)	1.83(1)
P(2)–C(28)	1.81(1)	P(2)–C(34)	1.81(1)
S(1)–C(1)	1.83(2)	S(1)–C(3)	1.77(2)
S(2)–C(1)	1.71(1)	S(2)–C(2)	1.77(2)
C(2)–C(3)	1.58(2)		
Bond Angles			
S(1)–Pt–C(1)	48.3(3)	P(2)–Pt–C(1)	151.4(1)
P(2)–Pt–S(1)	103.3(1)	P(1)–Pt–C(1)	101.8(1)
P(1)–Pt–S(1)	150.1(1)	P(1)–Pt–P(2)	106.6(1)
Pt–P(1)–C(16)	110.9(3)	Pt–P(1)–C(10)	113.4(3)
Pt–P(1)–C(4)	115.6(3)	Pt–P(2)–C(34)	112.4(3)
Pt–P(2)–C(28)	125.6(3)	Pt–P(2)–C(22)	104.3(3)
Pt–S(1)–C(3)	108.2(4)	Pt–S(1)–C(1)	60.5(4)
C(1)–S(1)–C(3)	101.0(4)	C(1)–S(2)–C(2)	92.4(5)
S(1)–C(1)–S(2)	110.1(3)	Pt–C(1)–S(2)	119.3(2)
Pt–C(1)–S(1)	71.2(5)	S(2)–C(2)–C(3)	115(1)
S(1)–C(3)–C(2)	102(1)		

(S=CMe$_2$)[19] or the uncoordinated C=S double bond of 1.54(5) Å of the carbon disulfide ligand in (PPh$_3$)$_2$Pt(CS$_2$),[20] while for this latter complex the Pt-coordinated C=S bond distance is 1.72(5) Å.

The Pt–P(1) and Pt–P(2) bond distances of 2.254(3) and 2.313(2) Å, respectively, compare well with those of the aforementioned complex *cis*-{(Et$_3$P)$_2$Pt[C(H)CH$_2$CH$_2$CH$_2$S]}PF$_6$ (2.242(5) and 2.304(4) Å, respectively). As expected, the longer Pt–P(2) is a result of the stronger trans influence of C(1) compared to S(1).[21]

The S(1)–Pt–C(1) bond angle of 48.3(3)° in **2** is lower than that observed in *cis*-{(Et$_3$P)$_2$Pt[C(H)CH$_2$CH$_2$CH$_2$S]}PF$_6$ (60.6(6)°) and in {(PPh$_3$)Pd[CH$_2$S(Me)]Cl} (57.0(2)°),[22] causing probably the enlargement of the P(1)–Pt–P(2) bond angle (106.6(1)°). The 1,3-dithiolane ring has an envelope conformation (puckering parameters Q_2 = 0.81(1) Å and Φ = 28.9(5)°).[23]

A close contact distance of 2.38(6) Å between the C(1) proton and platinum is present. This value is between the values accepted for an agostic interaction (upper limit 2.2 Å)[24] and a weak interaction (2.4–2.6 Å).[24] Considering the nonequivalence of the torsion angles P(1)–Pt–C(1)–S(2) of 75.4 (1)° and P(2)–Pt–S(1)–C(3) of −83.3 (4)°, it seems that the smaller torsion (on the side of the C(1) proton) is in order to favor this Pt–H interaction to which a certain degree of covalent character (agostic interaction) could be ascribed.

The reaction in eq 1 was monitored by IR spectroscopy (in CH$_3$CN solvent) in the range 1500–2500 cm^{-1} and by ^{1}H NMR spectrometry (CD$_3$CN solvent) at 25 °C in the range δ −10 to +10. The IR spectra show only the slow disappearance of the Pt–H stretching at 2069 cm^{-1} of **1** with no other absorption being detected. In the ^{1}H NMR spectra the hydride resonance at δ −6.16 of **1** slowly disappears with a concomitant growth of the CH methine proton resonance at δ 4.67 as a doublet of doublets by coupling to two magnetically different phosphorus nuclei flanked by ^{195}Pt satellites. No other hydride resonance in the high field region (range −20 to 0 ppm) is detected, even on running the reaction at low temperature (230 K).

The platinum to carbene 1,2-hydrogen shift reported in eq 1 is clearly a CH$_3$CN-catalyzed process. The observed broadening of the hydride resonance of **1** in CD$_3$CN indicates that acetonitrile, owing to its good coordinating ability, binds to platinum in a fast exchange process. This would ultimately lead to the formation of the required *cis*-hydrido–carbene intermediate, as demonstrated for similar processes,[3] possibly a pentacoordinate complex of the type [(PPh$_3$)$_2$Pt(H)(CSCH$_2$CH$_2$S)(CH$_3$CN)]BF$_4$ (**I**). Since **I** could not be spectroscopically detected it is assumed that the lifetime of this species might be so short that it would not exist in sufficient concentration to be observed in the IR or in the ^{1}H NMR spectrum. However, a similar intermediate has been revealed in the reaction of **1** wit Cl$^-$ ions under FAB conditions (see below). The subsequent step involves hydride migration to the electrophilic carbene carbon in **I** and subsequent CH$_3$CN displacement by one S atom of the 1,3-dithiolane ring leading eventually to **2**.

This reaction mechanism is supported by a similar reaction carried out in the presence of Cl$^-$ ions. Thus, the reaction of **1** with PPN$^+$Cl$^-$ (in a ca. 45% molar excess) in CH$_2$Cl$_2$ at ambient temperature led to the isolation of

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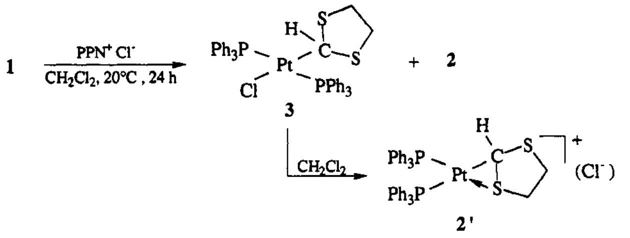
trans-$\{(PPh_3)_2PtCl[\overline{C(H)SCH_2CH_2S}]\}$ (**3**) and an inseparable mixture of **2** (or **2′**, see below) and PPN^+Cl^- (eq 2).



(2)

The trans geometry of **3** has been determined on the basis of its IR spectrum. This later shows ν (Pt–Cl) at 283 cm^{-1}, which indicates that chlorine is trans to a C(alkyl)group[21a] and shows also the absence of the typical strong absorption at ca. 550 cm^{-1} assigned to the first overtone of the asymmetric PC_3 deformation mode of PPh_3, which is indicative, according to Mastin's rule,[25] of a cis stereogeometry for bis(triphenylphosphine)platinum(II) complexes of the type $(PPh_3)_2Pt(X)(Y)$ (X, Y = anionic ligands). Complex **3** isomerizes to **2′** in CH_2Cl_2 solvent by intramolecular Cl^- displacement by one S atom of the dithiolane ring as indicated by its ^1H and ^{31}P NMR spectra, which closely match those of **2**. Thus, it is likely that the presence of Cl^- ions (as in eq 2) hampers to some extent the chloride ligand dissociation, but no kinetic data are yet available. It is worth noting that the analogous reaction of the parent hydrido–dioxycarbene complex *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})]BF_4$ with Cl^- ions leads to carbene ring fragmentation,[7b] contrasting markedly the behaviour exhibited by **1** in eq 2.

No reaction intermediates have been detected in the rearrangement of **1** to **2** and **3** reported in eq 2, even when monitoring the reaction by low temperature ^1H and $^{31}P\{^1H\}$ NMR spectroscopies. However, evidence of the involvement of a pentacoordinate species of the type $[(PPh_3)_2Pt(Cl)H(\overline{CSCH_2CH_2S})]$ as the primary intermediate in the reaction of **1** with Cl^- ions under FAB conditions, has been reported.[26]

Further studies on the chemical reactivity as well as of the redox properties of **1** and **2** are in progress.

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Supplementary Material Available: Tables of all bond distances and angles, anisotropic thermal parameters for the nonhydrogen atoms, and hydrogen atom coordinates (4 pages). Ordering information is given on any current masthead page.

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