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New C,P-Cyclometalated Compounds of Platinum(II) and Platinum(IV) Derived from Tri-*o*-tolylphosphine

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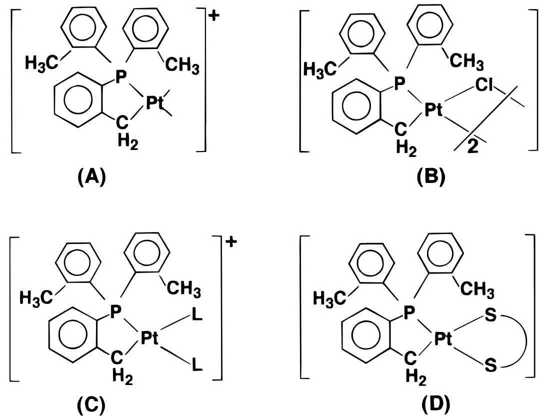
The reaction between [*trans*-$PtCl_2(PhCN)_2$] (PhCN = benzonitrile) and tri-*o*-tolylphosphine rendered [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (**1**), a new C,P-cyclometalated compound of Pt(II). The treatment of **1** with $AgClO_4$ (1: 2) in NCMe gave the mononuclear compound [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(NCMe)$_2$]ClO_4 (**2**). Solutions probably containing the cation [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(THF)$_2$]$^+$ (THF = tetrahydrofuran) reacted with sodium dimethyldithiocarbamate (NaS_2CNMe_2) and potassium ethyl xanthate (KS_2COEt) in 1:1 molar ratio yielding the mononuclear complexes [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CR)] (R: NMe_2 (**3**), OEt (**4**)). The molecular structure of **3** was determined by X-ray diffraction. The reactions of **3** and **4** with Cl_2, Br_2 and I_2 gave the mononuclear Pt(IV) complexes [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CR)X_2] (X: Cl, Br, I) (**5**−**10**). In each reaction a single product can be detected spectroscopically, indicating that the oxidative addition of halogens (X_2) to **3** and **4** proceeds stereoselectively. The molecular structure of compound **7**, determined by X-ray diffraction, revealed that the obtained isomer has the OC-6-42 structure with both halogen atoms in *cis* positions.

Introduction

Cyclometalation reactions with tertiary phosphines give organometallic compounds with a $\overline{\text{C-P-M}}$ structure. Two important factors which promote internal metalation in such complexes are (a) the presence of bulky substituents on the tertiary phosphine and (b) the possibility of forming five-membered rings on metalation.[1] P(*o*-tolyl)$_3$ is an adequate ligand for such processes since the value of the cone angle, crystallographically determined, is 198°[2] and the activation of one H of the CH_3 in the *o*-tolyl substituent leads to a five-membered ring.

Phosphines with one [P^tBu_2(*o*-tolyl)] or two [P^tBu(*o*-tolyl)$_2$] o-tolyl groups undergo cyclopalladation and cycloplatination involving the methyl fragment of one o-tolyl group.[3−5] Although tri-*o*-tolylphosphine undergoes side chain metalation on Mn[6] and Rh[7] complexes, as far as we know, only two palladium derivatives, [Pd{$CH_2C_6H_4P$(*o*-tolyl)$_2$}(μ-X)]$_2$ (X = I,[8a] CH_3COO[8b]), and one platinum derivative, [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$}(P(*o*-tolyl)$_3$)(Br)],[9] with cyclometalated P(*o*-tolyl)$_3$ have been reported, [Pd{$CH_2C_6H_4P$(*o*-tolyl)$_2$}(μ-I)]$_2$ being the initial product formed during arylation reactions of conjugated polyenes using palladium (II) acetate, tri-*o*-tolylphosphine, and triethylamine as catalyst. Recently Herrmann et al. have reported that these C,P-cyclometalated Pd(II) complexes are very active catalysts for the Heck or Suzuki reactions.[8b,c]

Chart 1



As an extension of our interest in cyclometalated derivatives,[10] we decided to explore the reactions of cycloplatination of P(*o*-tolyl)$_3$. In this paper we describe the synthesis of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (**1**), which we have used for the preparation of other Pt(II) and Pt(IV) complexes containing the "Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}" fragment [Pt($C^\frown P$) in the following; see Chart 1A].

Results and Discussion

(A) Synthesis and Characterization of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (1) and [Pt{CH_2-

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Table 1. $^{31}P\{^1H\}$ NMR[a] Data for Complexes 2−10

complex	δ(P) (ppm)	$^1J_{Pt-P}$ (Hz)
$[Pt(C\frown P)(NCMe)_2](ClO_4)$[b] (**2**)	17.19 (s)	4673.0
$[Pt(C\frown P)(S_2CNMe_2)]$[b] (**3**)	24.70 (s)	3969.4
$[Pt(C\frown P)(S_2COEt)]$[b] (**4**)	23.73 (s)	4083.8
$[Pt(C\frown P)(S_2CNMe_2)Cl_2]$[b] (**5**)	24.20 (s)	2609.5
$[Pt(C\frown P)(S_2CNMe_2)Br_2]$[b] (**6**)	21.87 (s)	2607.9
$[Pt(C\frown P)(S_2CNMe_2)I_2]$[b] (**7**)	19.60 (s)	2620.7
$[Pt(C\frown P)(S_2COEt)Cl_2]$[c] (**8**)	24.91 (s)	2691.6
$[Pt(C\frown P)(S_2COEt)Br_2]$[c] (**9**)	23.13 (s)	2692.5
$[Pt(C\frown P)(S_2COEt)I_2]$[b] (**10**)	19.60 (s)	2620.5

[a] $C\frown P = CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P$; external reference 85% H_3PO_4; $CDCl_3$, room temperature. [b] Recorded on a Varian XL-200. [c] Recorded on a Varian Unity 300.

$C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(NCMe)_2]ClO_4$ (2). Equimolar quantities of $[trans\text{-}PtCl_2(PhCN)_2]$ and tri-*o*-tolylphosphine react, in refluxing 2-methoxyethanol, giving the intramolecular coordination complex $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(\mu\text{-Cl})]_2$ (**1**) (Chart 1B) (eq 1).

$$2[trans\text{-}PtCl_2(PhCN)_2] + 2P(o\text{-tolyl})_3 \rightarrow [Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(\mu\text{-Cl})]_2 + 2HCl + 4PhCN \quad (1)$$

Complex **1** is insoluble in the usual organic solvents. Its IR spectrum shows two absorptions due to ν_{st}(Pt−Cl) at 249 and 255 cm^{-1}, consistent with a dinuclear formulation, $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(\mu\text{-Cl})]_2$ (**1**). Absorptions assignable to the $C\frown P$ ligand ($C\frown P$:$\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}$) are also observed (see Experimental Section).

Halide abstraction with $AgClO_4$ (1:2 molar ratio) in a donor solvent (L), at room temperature, affords the cationic solvento complexes $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(L)_2]^+$ (eq 2) (Chart 1C), which contain two solvent molecules, such as THF (tetrahydrofuran) or NCMe (acetonitrile) in *cis* positions. For L = NCMe, a solid stable at room temperature, $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(NCMe)_2]ClO_4$ (**2**) was obtained. When L = THF, no solid has been isolated, but solutions containing presumably the $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(THF)_2]^+$ species have been used as starting materials for the synthesis of new complexes.

$$[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(\mu\text{-Cl})]_2 + 2AgClO_4 \xrightarrow{L} 2[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(L)_2]^+ + 2ClO_4^- + 2AgCl \quad (2)$$

$$L = THF, NCMe$$

The IR spectrum of **2** (see Experimental Section) shows the following: (a) two absorptions assignable to the ClO_4^- (T_d) anion,[11] (b) several absorptions assignable to the $C\frown P$ ligand, and (c) two absorptions due to ν_{st}(C−N) (2288 (m), 2298 (m) cm^{-1}) of the acetonitrile groups, denoting their *cis* positions. The shift to higher energies of these frequencies with respect to that in the free ligand (2254 cm^{-1}) suggests that the acetonitrile groups are N-coordinated, acting as pure σ-donors.[12] In the ^1H NMR spectrum (Table 2) the two inequivalent NCMe ligands give two singlets at 2.22 and 2.55 ppm. The methylene group of the $C\frown P$ fragment gives one singlet at 3.39 ppm with the corresponding ^{195}Pt satellites ($^2J_{Pt-H}$: 101.25 Hz) which confirms the existence of the Pt−C σ-bond. The equivalence of these two diasterotopic hydrogen atoms agrees with the existence of a mirror plane in the molecule. Accordingly, the methyl groups of the two *o*-tolylphosphine's substituents appear as only one singlet at 2.55 ppm.

(B) Neutral C,P-Cyclometalated Pt(II) Complexes: $[Pt(C\frown P)(S_2CR)]$ ($C\frown P = -CH_2C_6H_4P(o\text{-tolyl})_2$; R = NMe_2 (3), OEt (4)). Solutions of $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(THF)_2]ClO_4$ in methanol or THF react with sodium dimethyldithiocarbamate (NaS_2CNMe_2) and potassium ethyl xanthate (KS_2COEt) in 1:1 molar ratio to give the mononuclear complexes $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2CNMe_2)]$ (**3**) and $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2COEt)]$ (**4**), in high yields, as air stable solids (Chart 1D) (eq 3).

$$[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(THF)_2]ClO_4 + MS_2CR \rightarrow [Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2CR)] + MClO_4 + 2THF \quad (3)$$

$$M = Na, R = NMe_2\ (\mathbf{3});\ M = K, R = OEt\ (\mathbf{4})$$

In spite of the similarity of both complexes, the isolation procedure is different in each case (see Experimental Section) due to the solubility of complex **4** in the most common solvents.

In the IR spectrum of **3**, the presence of only one absorption in the 950−1050 cm^{-1} region (975 cm^{-1}) due to ν(CS) indicates the bidentate binding of the "$S_2CNMe_2^-$" group.[13] An absorption at 1543 cm^{-1} corresponds to the ν_{st}(C−N), and suggests a pronounced degree of C−N double bond.[13] In the IR spectrum of **4**, the "S_2COEt^-" group is characterized by the presence of absorptions at 1239, 1123, and 1031 cm^{-1}.[13]

Structure of $[Pt(CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2CNMe_2)]$ (3). Figure 1 shows the molecular structure of **3** with the atom-numbering scheme. General crystallographic information is collected in Table 3. Final atomic positional parameters are listed in Table 4. Relevant bond distances and angles are listed in Table 5.

As expected, the platinum atom is located in a distorted square-planar environment formed by the two sulfur atoms of the dimethyldithiocarbamate group and the phosphorus and an alkyl carbon (C(10)) atom of the C,P-cyclometalated phosphine ligand.

The five-membered metallocycle is not planar. C(4) and C(10) are 0.176 and 0.252 Å apart from the best least-squares plane through Pt−P−C(4)−C(9)−C(10).[14] The small bite angle of the chelate ligands makes the corresponding angles smaller than 90°; S(1)−Pt−S(2) = 74.1(1)° and P−Pt−C(10) = 84.2(2)°. These parameters and the bond distances related with the platinum environment are similar to those found for other complexes containing these types of chelating groups.[3−5,8]

The Pt−S(1) bond length (2.392(2) Å) is slightly longer than the Pt−S(2) one (2.354(1) Å) because of the

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Table 2. ^{1}H NMR^a Data for Complexes 2−10

	Pt−CH$_2$			C$_6$H$_4$*Me*	C$_6$H$_4$	NCMe	S$_2$CNMe$_2$	S$_2$COEt	
compd	δ (ppm)	$^2J_{\mathrm{H-H}}$ (Hz)	$^2J_{\mathrm{Pt-H}}$ (Hz)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	δ (ppm)	$^3J_{\mathrm{H-H}}$ (Hz)
2	3.39 (s)		101.25	2.55 (s)	6.9−7.3 (m)	2.22 (s) 2.55 (s)			
3	3.38 (s) 3.44 (s)		85.70 94.30	2.42 (s) 2.78 (s)	6.9−7.3 (m)		3.23 (s) 3.24 (s)		
4	3.54 (s) 3.55 (s)		90.00 98.20	2.40 (s) 2.74 (s)	6.8−7.6 (m)			4.64 (q) 1.47 (t)	7.14
5	4.28 (d) 4.69 (d)	12.63	65.40 80.00	2.02 (s) 2.31 (s)	7.0−7.6 (m)		2.95 (s) 3.20 (s)		
6	4.38 (d) 4.82 (d)	12.45	68.00 79.00	2.00 (s) 2.32 (s)	7.0−7.6 (m)		2.92 (s) 3.19 (s)		
7	4.60 (d) 4.95 (d)	12.64	70.90 73.60	1.96 (s) 2.33 (s)	7.0−7.6 (m)		2.90 (s) 3.20 (s)		
8	4.23 (d) 4.69 (d)	12.25	64.40 80.04	2.04 (s) 2.30 (s)	7.0−7.6 (m)			4.58 (q) 1.45 (t)	7.04
9	4.32(d) 4.82 (d)	12.01	66.10 78.81	2.02 (s) 2.32 (s)	7.0−7.6 (m)			4.57 (q) 1.45 (t)	6.93
10	4.52 (d) 4.95 (d)	12.25	85.00 72.50	1.97 (s) 2.35 (s)	7.0−7.6 (m)			4.54 (q) 1.44 (t)	7.17

^{a}Solvent CDCl$_3$, room temperature, 300 MHz; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

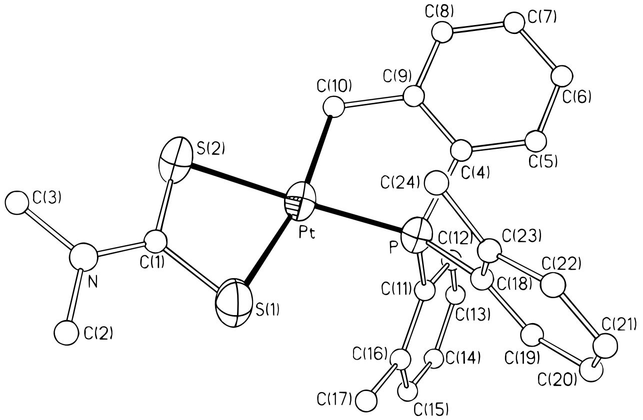

Figure 1. Molecular structure of [Pt(CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C,P*}(S$_2$CNMe$_2$)] (**3**).

different *trans* influence of the P and C donor atoms of the C,P-cyclometalated group.[15]

The [S$_2$CNMe$_2$$^-$] group is approximately planar. Bond angles around the N and C(1) atoms average 120°, as expected considering an sp^2 hybridization of both atoms; however the S(1)−C(1)−S(2) angle is only 112.8(3)° due to the coordination to the platinum center. The N−C(1) distance (1.336(7) Å) is not far from the C═N double bond distance (1.265 Å);[16] these structural features are common in chelating dithiocarbamate complexes.[17]

NMR Spectra of Complexes 3 and 4. The ^{1}H NMR spectra of **3** and **4** in CDCl$_3$ show a similar pattern due to the cyclometalated group "Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C,P*}" (see Table 2). At room temperature (20 °C) the following is observed: (a) the −CH$_2$− group appears as an AX system with the corresponding ^{195}Pt satellites, $^2J_{\mathrm{Pt-H}}$ being different and the H−H coupling constant not being observed. (b) The CH$_3$ groups of the *o*-tolylphosphine's substituents appear as two singlets indicating their inequivalence. Variable-temperature ^{1}H NMR spectra reveal the coalescence of both methyl groups and both methylenic protons of the "{CH$_2$C$_6$H$_4$P-(*o*-tolyl)$_2$-*C,P*}" ligand at 45 °C. At 50 °C both methyl groups are equivalent (**3**, 2.62 (s) ppm; **4**, 2.58 (s) ppm) and both methylenic protons are equivalent as well (**3**, 3.4 (s) ppm, $^2J_{\mathrm{Pt-H}} = 93.6$ Hz; **4**, 3.54 (s) ppm, $^2J_{\mathrm{Pt-H}} = 94.92$ Hz). These data indicate that at room temperature the molecular plane does not act as a mirror plane, i.e. the hindered rotation of the P−C$_{\mathrm{ipso}}$ bonds. Analysis of the proton ortho methyl resonances using the approximation to Eyring's equation[18]

$$\Delta G^{\ddagger} = 19.14T_{\mathrm{c}}(9.97 + \log T_{\mathrm{c}}/\Delta\nu)$$

leads to the $\Delta G^{\ddagger}$ at the coalescence temperature for the P−C$_{\mathrm{ipso}}$ bond rotation process in complexes **3** and **4** (**3**, $\Delta G^{\ddagger}_{318} = 63.53$ kJ mol^{-1}, $\Delta\nu = 108.34$ Hz; **4**, $\Delta G^{\ddagger}_{318} = 63.79$ kJ mol^{-1}, $\Delta\nu = 98.15$ Hz). Only a few cases in which restricted P−C$_{\mathrm{phenyl}}$ bond rotation is also evident have been reported,[9,19] and in most of them this process is hindered at low temperature but not at room temperature as in our cases.

The ^{1}H NMR spectra of **3** and **4** in CDCl$_3$ also show the signals due to the chelate S-donor ligands (see Table 2). The S$_2$CNMe$_2$$^-$ ligand gives two singlets at 3.23 and 3.24 ppm (**3**) even at 50 °C, indicating a high free energy of activation (ΔG‡) associated with C−N bond rotation in accord with its pronounced double-bond character in the dithiocarbamate ligand. This behavior is usual in dithiocarbamate Pt(II) and Pd(II) complexes.[17,20] The S$_2$COEt$^-$ ligand (**4**) gives its two characteristic signals: 4.64 (q), 1.50 (t); $^3J_{\mathrm{H-H}} = 7.14$ Hz).

(C) Neutral C,P-Cyclometalated Pt(IV) Complexes: [Pt($C^\frown P$)(S$_2$CR)X$_2$] ($C^\frown P$ = −CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$, R = NMe$_2$, OEt; X = Cl, Br, I). The reactions of **3** and **4** with X$_2$ (X = Cl, Br, I) (1:1 molar ratio) in dichloromethane at room temperature afford the air-stable complexes [Pt($C^\frown P$)(S$_2$CR)X$_2$] (R = NMe$_2$, X = Cl (**5**), X = Br (**6**), X = I (**7**); R = OEt, X = Cl (**8**), X = Br (**9**), X = I (**10**)) in high yields.

Oxidative addition reactions of halogens to square-planar d^8 organometallic complexes often result in the

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Table 3. Summary of Crystallographic Data

	3	7
formula	$C_{24}H_{26}NPPtS_2{\cdot}CHCl_3$	$C_{24}H_{26}I_2NPPtS_2{\cdot}{}^1/_2CH_2Cl_2$
M_r	738.043	914.941
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
systematic absences	$0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$	$0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$
a, Å	12.2980(10)	10.961(2)
b, Å	12.9748(10)	14.431(3)
c, Å	18.2293(18)	18.587(4)
β, deg	105.766(10)	91.39(3)
V, Å^3	2799.3(4)	2939(1)
Z	4	4
d_{calc}, g cm^{-3}	1.75	2.07
cryst size, mm	0.45 × 0.26 × 0.19	0.38 × 0.38 × 0.45
μ(Mo Kα), cm^{-1}	55.2	71.8
transm factors (min, max)	0.675, 0.965	0.485, 1.000
diffractometer	Siemens/Stoe AED2	Nicolet (Siemens) Autodiff
radiation (graphite monochromated)	Mo Kα ($\lambda_\alpha = 0.710\,73$ Å)	Mo Kα ($\lambda_\alpha = 0.710\,73$ Å)
T, °C	20 ± 1	20 ± 1
scan method	ω	ω
scan range, deg	$4 < 2\theta < 50$	$3 < 2\theta < 51$
no. of unique data	4858	5396
no. of unique data with $F_o{}^2 \geq 3\sigma(F_o{}^2)$	3996	3494
abs corr	ψ scans	ψ scans
no. of refined params	326	293
R^b	0.029	0.038
$R_w{}^c$	0.044	0.049
quality of fit indicator^d	0.95	0.96
weighting param g^e	0.0015	0.0013
largest shift/esd final cycle	0.001	0.001
final diff Fourier max peak, trough, e/Å^3	0.83, −0.96	1.39, −1.06

[a] **3**, $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2CNMe_2)]{\cdot}CHCl_3$; **7**, $[Pt\{CH_2C_6H_4P(o\text{-tolyl})_2\text{-}C,P\}(S_2CNMe_2)I_2]{\cdot}{}^1/_2CH_2Cl_2$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w\,(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [d] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$. [e] $w^{-1} = [\sigma^2\,(|F_o|) + g|F_o{}^2|]$.

formation of octahedral complexes.[21] Assuming that the $C^\frown P$ and S_2CR^- groups maintain their chelating function, these octahedral Pt(IV) complexes can exhibit three different structures (Chart 2). The dichloro complexes $[Pt(C^\frown P)(S_2CR)Cl_2]$ (R: NMe_2 (**5**), OEt (**8**)) show two absorptions at about 310 and 270 cm^{-1} (see Experimental Section) assignable to the ν(Pt−Cl) stretching vibrations, but this feature does not allow us to distinguish between any of the three possible isomers because two IR-active absorptions should be expected for each one of them (Chart 2).

In the IR spectra of complexes **5**−**7** the ν_{st}(C−N) absorptions appear at higher frequencies than in their precursor (complex **3**), showing a correlation between increasing oxidation state and the C−N stretching frequency as has been observed previously.[22]

The $^{31}P\{^1H\}$ NMR spectra of complexes **5**−**10** (see Table 1) show one singlet at about 20.0 ppm with the corresponding ^{195}Pt satellites, which indicates that only one diastereomer is present in each case. The smaller Pt−P coupling constant in these complexes ($^1J_{Pt-P}$ = 2600−2700 Hz) with respect to that in their Pt(II) precursors (**3** and **4**) is consistent with a higher oxidation state of the metal center.[23]

The ^{1}H NMR signals corresponding to the $C^\frown P$ fragment show, for all complexes, the same pattern (see Table 2): (a) two signals at ca. 2.0 ppm due to the methyl groups; (b) two signals for the diasterotopic H atoms of the methylene group, which appear as an AB system with the corresponding ^{195}Pt satellites, and (c) some multiplets corresponding to the aromatic hydrogens. The inequivalence of both methyl groups and both H atoms of $-CH_2-$ can be explained in two different ways: (a) complexes **5**−**10** show either an OC-6-42 or OC-6-32 geometry, which excludes the existence of any symmetry plane, or (b) these complexes show the geometry OC-6-14 but a hindered $P-C_{ipso}$ bond rotation process precludes the equatorial plane of the molecule to act as a mirror plane. In the last case, temperature-dependent ^{1}H NMR spectra should be expected as for complexes **3** and **4**. However we have observed that the ^{1}H NMR spectrum of complex $[Pt(C^\frown P)(S_2CNMe_2)I_2]$ (**7**) remain invariable even at 60 °C, suggesting the structure OC-6-42 or OC-6-32 as more probable. The X-ray study on complex $[Pt(C^\frown P)(S_2CNMe_2)I_2]$ (**7**) indicates an OC-6-42 geometry for it. The similarity of the IR and NMR spectra of these Pt(IV) complexes suggests the same geometry for all of them; i.e., the oxidative addition takes place in a stereoselective mode in all cases.

The most common mechanism in oxidative addition reactions of halogens (X_2) on square-planar platinum(II) complexes is the S_N2 type,[24] the process being initiated by end-on coordination of X_2 formed by donation of electron density from the metal to the X_2 molecule (**A**, Scheme 1). The basicity of the platinum center in $[Pt(C^\frown P)(S_2CR)]$ (**3**, **4**) becomes apparent considering their ability to form donor−acceptor Pt→M bonds.[25] The subsequent steps very often result in a *trans* addition of the halogen (Scheme 1, path 2) yielding

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Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C*,*P*}(S_2CNMe_2)]·$CHCl_3$

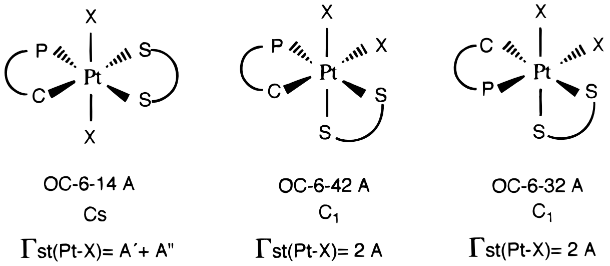
	x	*y*	*z*	*U*(eq)[a]
Pt	2446(1)	3060(1)	3161(1)	43(1)
P	3531(1)	2037(1)	4040(1)	40(1)
S(1)	1669(1)	4361(1)	3800(1)	61(1)
S(2)	1318(1)	4104(1)	2194(1)	62(1)
N	556(4)	5772(4)	2779(3)	66(2)
C(1)	1100(4)	4871(4)	2909(3)	54(2)
C(2)	434(6)	6419(6)	3407(5)	86(3)
C(3)	36(7)	6132(6)	1998(4)	88(3)
C(4)	4384(4)	1356(4)	3522(3)	44(2)
C(5)	5344(5)	794(4)	3862(3)	53(2)
C(6)	5919(5)	309(5)	3411(3)	60(2)
C(7)	5531(6)	394(5)	2630(4)	68(3)
C(8)	4585(5)	961(5)	2299(3)	62(2)
C(9)	3999(4)	1469(4)	2746(3)	48(2)
C(10)	2997(6)	2154(5)	2404(3)	62(2)
C(11)	2745(4)	1036(4)	4385(3)	41(2)
C(12)	2814(5)	12(4)	4148(3)	52(2)
C(13)	2220(5)	−763(5)	4369(4)	69(3)
C(14)	1517(6)	−547(6)	4831(4)	78(3)
C(15)	1432(5)	449(6)	5063(3)	67(2)
C(16)	2029(4)	1272(5)	4843(3)	51(2)
C(17)	1870(6)	2326(6)	5106(4)	71(3)
C(18)	4566(4)	2487(4)	4893(3)	46(2)
C(19)	4732(5)	1962(4)	5580(3)	54(2)
C(20)	5561(6)	2250(6)	6222(4)	72(3)
C(21)	6264(6)	3057(6)	6185(5)	80(3)
C(22)	6121(5)	3594(6)	5511(5)	80(3)
C(23)	5278(5)	3331(4)	4855(4)	60(2)
C(24)	5190(6)	3916(5)	4131(4)	84(3)
C(25)	1334(5)	6370(4)	6304(2)	158(7)
Cl(1)	1665(10)	5913(10)	7251(4)	120(4)
Cl(2)	2227(11)	7367(7)	6156(9)	255(11)
Cl(3)	1643(20)	5315(13)	5782(9)	153(6)
Cl(4)	2335(11)	7382(9)	6470(7)	161(5)
Cl(5)	2026(11)	5780(14)	7179(5)	181(6)
Cl(6)	1424(23)	5546(17)	5551(10)	223(11)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C*,*P*}(S_2CNMe_2)] (3)

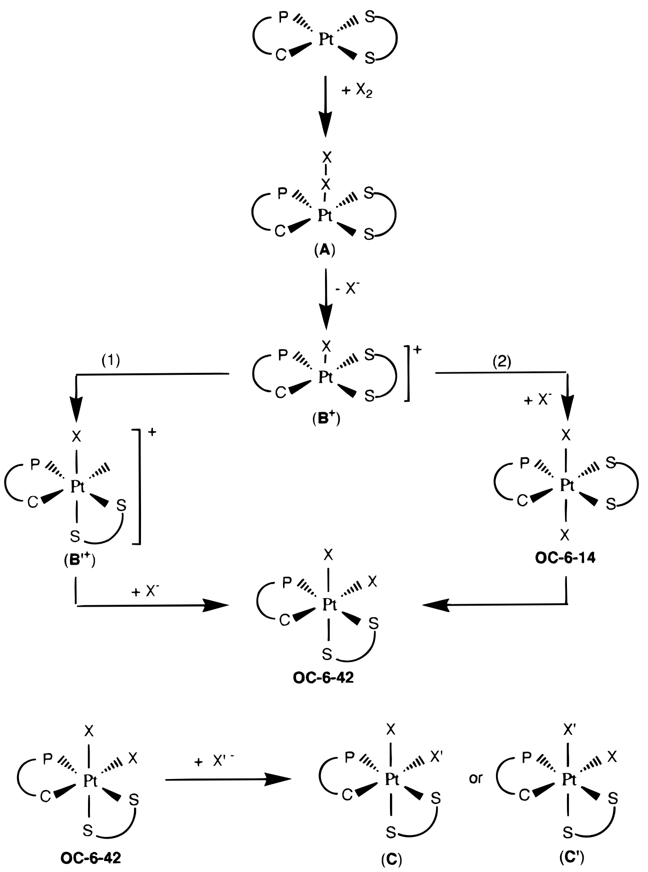
Pt−C(10)	2.063(7)	C(1)−S(1)	1.717(6)
Pt−P	2.223(1)	C(1)−S(2)	1.718(6)
Pt−S(1)	2.392(2)	C(1)−N	1.336(7)
Pt−S(2)	2.354(1)		
S(1)−Pt−S(2)	74.1(1)	S(2)−C(1)−N	123.1(5)
S(1)−Pt−P	108.2(1)	S(1)−C(1)−N	124.1(5)
P−Pt−C(10)	84.2(2)	C(1)−N−C(2)	121.2(5)
S(2)−Pt−C(10)	93.5(2)	C(1)−N−C(3)	121.0(6)
S(1)−C(1)−S(2)	112.8(3)	C(2)−N−C(3)	117.8(5)

Chart 2



the isomer OC-6-14. In our case, however, the couple of enantiomers OC-6-42 were solely obtained in all cases. These results mean that either the halogen molecule adds at once in a concerted fashion at *cis* positions or that isomerization must follow some of the proposed steps for the S_N2 mechanism.

Scheme 1



We tried to find some experimental evidence about the possible reaction mechanism by focusing our study on the iodination reaction of [Pt(C⁀P)(S_2CNMe_2)] (**3**). Assuming that the oxidative addition of halogen to [Pt(C⁀P)(S_2CNMe_2)] (**3**) takes place in a concerted fashion, iodination of **3** in the presence of chloride anions should exclusively give products derived from the already formed complex [Pt(C⁀P)(S_2CNMe_2)I_2] (**7**) by simple halide substitution (**C** or **C′**). In the reaction of [Pt(C⁀P)(S_2CNMe_2)I_2] (**7**) with NEt_3BzCl in a 1:1 molar ratio ([^{2}H]chloroform, room temperature) we observe the appearance of a single new product (**C** or **C′**; $^{31}P\{^1H\}$ NMR: δ 20.69, $^1J_{Pt-P} = 2634.4$ Hz) which means that halide substitution on **7** proceeds specifically at a certain position. This substitution reaction depends on the temperature and does not take place at −60 °C even in a 1:3 molar ratio. Because of that, we performed the iodination of **3** in the presence of NEt_3BzCl (1:3) at −78 °C in CD_2Cl_2. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture at this temperature shows signals corresponding to **7** and **C** (or **C′**) in the integrated ratios 0.926:1. The presence of **C** (or **C′**) as a reaction product allows us to accept the S_N2 mechanism including an additional isomerization step to explain the *cis* arrangement of the halogen atoms in the final product.

Aiming to know which intermediate species (OC-6-14 isomer or $\mathbf{B}^+$) undergoes further isomerization, we performed the reaction of [Pt(C⁀P)(S_2CNMe_2)] (**3**) with I_2 at −78 °C in CD_2Cl_2 in a NMR tube monitoring the progress of the reaction at −78, −65, −50, −35, −20, 0, and 20 °C by $^{31}P\{^1H\}$ NMR. At −78°C, the reaction mixture show the presence of two different products, the final one (**7**) and an intermediate (**X**) ($^{31}P\{^1H\}$: δ 16.04, $^1J_{Pt-P} = 2376$ Hz. ^{1}H: δ Pt−CH_2, 3.18 (d), 5.43 (d),

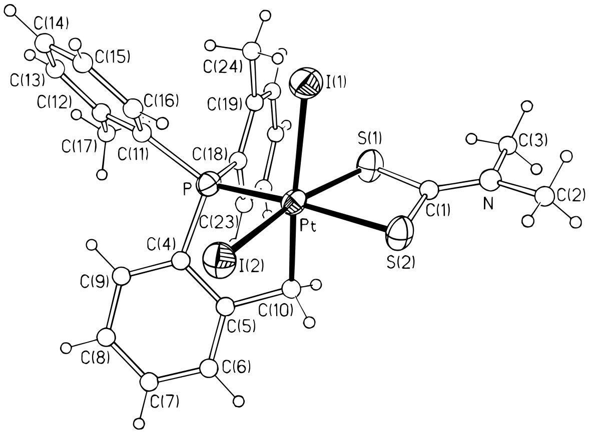


Figure 2. Molecular structure of [Pt(CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C*,*P*}(S$_2$CNMe$_2$)I$_2$] (**7**).

$^2J_{H-H} = 12.5$ Hz, $^2J_{Pt-H} = 75$ Hz; *o*-tolyl, 1.78 (s), 1.85 (s); S$_2$CNMe$_2$, 3.25 (s), 3.28 (s)). As temperature increases, the amount of **7** grows meanwhile the amount of (**X**) decreases with **7** being the only product in the reaction mixture at room temperature (20 °C). The possible conversion of **X** to **7** at low temperatures ($T < -60$ °C) even in the presence of NEt$_3$BzCl and the very different δ values observed for the signals corresponding to both H atoms of the Pt−CH$_2$ group in this species (**X**) suggest that this intermediate (**X**) can be either **A**, **B**$^+$, or **B′**$^+$ (Scheme 1) rather than the Pt(IV) isomer OC-6-14 whose isomerization probably would need higher temperatures[26] and in which both H atoms of the Pt−CH$_2$− group would have very similar chemical environments. However, we cannot determine the exact nature of the intermediate (**X**). From this observation we suggest that, in all likelihood, isomerization occur at the Pt(IV) cation (**B**$^+$, Scheme 1, path 1) rather than at the coordinatively saturated product OC-6-14.

In conclusion from our study on oxidation reactions of [Pt(C⌒P)(S$_2$CNMe$_2$)] and [Pt(C⌒P)(S$_2$COEt)] with chlorine, bromine, and iodine we can say that these reactions do not proceed in a concerted fashion but by an S$_N$2 mechanism including an isomerization step probably at the five-coordinated Pt(IV) cation intermediate to give a unique final product in each case with a *cis* arrangement of the halide ligands.

Molecular Structure of [Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C*,*P*}(S$_2$CNMe$_2$)I$_2$] (7). The stereogeometry of this platinum complex, as determined by single-crystal experiments, is illustrated in Figure 2 together with the atomic numbering scheme. General crystallographic information is collected in Table 3. Final atomic positional parameters are listed in Table 6. Relevant bond distances and angles are listed in Table 7.

The molecule shows a slightly distorted octahedral geometry around the platinum atom. One iodine atom [I(1)] and the carbon of the C⌒P group are in the axial sites, and the I(2), the bidentate dimethyldithiocarbamate ligand, and the P of the C⌒P group are located in the equatorial positions, with the angle between the line 1 (I(1), Pt, C(10)) and the perpendicular to the equatorial plane defined by the atoms I(2), S(1), S(2), Pt, and P being 7.50°.[14] Both P and S(2) atoms are located outside plane 1 at 0.1368 and 0.1740 Å, respectively.

Table 6. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for [Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C*,*P*}-(S$_2$CNMe$_2$)I$_2$]·$^1/_2$CH$_2$Cl$_2$

	x	*y*	*z*	*U*(eq)[a]
Pt	2572(1)	1196(1)	1372(1)	29(1)
I(1)	197(1)	1623(1)	1715(1)	47(1)
I(2)	2670(1)	2632(1)	472(1)	45(1)
P	3714(3)	1924(2)	2276(1)	30(1)
S(1)	2359(3)	−240(2)	1954(1)	40(1)
S(2)	1716(3)	149(2)	493(1)	40(1)
N	1153(9)	−1470(6)	1109(5)	39(3)
C(11)	3255(10)	2973(7)	2735(5)	31(3)
C(18)	4106(11)	1086(7)	2974(6)	39(4)
C(9)	5920(11)	2856(9)	1971(7)	46(4)
C(23)	5265(13)	657(9)	2945(7)	53(5)
C(6)	6270(10)	1694(8)	795(6)	40(4)
C(4)	5084(10)	2155(8)	1804(5)	37(4)
C(1)	1656(10)	−643(7)	1178(6)	37(4)
C(15)	1755(12)	4215(9)	2754(7)	49(4)
C(12)	3791(11)	3316(8)	3377(6)	38(4)
C(19)	3276(12)	854(8)	3515(6)	43(4)
C(10)	4306(11)	831(9)	1026(7)	47(4)
C(2)	458(14)	−1755(9)	468(7)	59(5)
C(5)	5254(10)	1567(8)	1215(6)	38(4)
C(17)	4890(12)	2878(9)	3766(7)	53(5)
C(16)	2239(10)	3443(7)	2431(6)	36(3)
C(14)	2255(13)	4527(9)	3382(8)	57(5)
C(7)	7113(12)	2386(10)	979(7)	56(5)
C(24)	2040(12)	1255(10)	3560(7)	58(5)
C(8)	6939(12)	2969(10)	1547(8)	54(5)
C(3)	1143(15)	−2109(9)	1728(7)	69(6)
C(13)	3266(12)	4082(8)	3694(7)	49(4)
C(20)	3661(16)	235(9)	4046(7)	63(5)
C(22)	5595(15)	19(10)	3478(8)	69(6)
C(21)	4816(19)	−173(11)	4028(8)	79(7)
Cl(1)	−1099(20)	4673(16)	−721(13)	214(9)
Cl(2)	809(18)	5576(14)	108(12)	190(7)
C(50)	−27(35)	5579(26)	−709(17)	142(18)

[a] See footnote *a* in Table 4.

Table 7. Selected Bond Lengths (Å) and Angles (deg) for [Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C*,*P*}(S$_2$CNMe$_2$)I$_2$] (7)

Pt−I(1)	2.764(1)	Pt−P	2.323(3)
Pt−I(2)	2.668(1)	Pt−S(1)	2.353(3)
Pt−C(10)	2.089(12)	Pt−S(2)	2.400(3)
I(1)−Pt−I(2)	91.4(1)	S(1)−Pt−S(2)	73.6(1)
I(1)−Pt−P	103.1(1)	P−Pt−S(1)	97.1(1)
I(1)−Pt−S(1)	89.2(1)	I(2)−Pt−P	94.2(1)
I(1)−Pt−S(2)	86.7(1)	I(2)−Pt−S(2)	94.7(1)
I(1)−Pt−C(10)	174.9(3)	P−Pt−C(10)	81.9(3)

Angles around the platinum are rather different from 90° because of the small bite angles of the chelate ligands. The Pt−I distances are similar to the observed ones in other Pt(IV) iodo complexes[27] and slightly different from each other, showing the stronger *trans* influence of the C(sp^3) σ-bond.[15] The Pt−C, Pt−P, and Pt−S distances are similar to the corresponding ones in the starting material (complex **3**). The metallacycle formed by the atoms Pt, C(10), C(5), C(4), and P is not planar, the atoms C(4) and C(10) being above and below the best least-squares-calculated plane 0.3826 and 0.5218 Å, respectively. The two *o*-tolyl groups are planar, and they are oriented by forming an angle of 112.43° between them and 57.115 and 84.80°, respectively, with the equatorial plane.

The S$_2$CNMe$_2$ ligand is basically planar and almost coplanar with the equatorial plane (interplanar angle 5.77°). Like in complex **3**, the structural parameters

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concerning the $Me_2NCS_2^-$ ligand point out to a high degree of C−N double-bond character.

Experimental Section

General Procedures and Materials. Elemental analyses were determined by using a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 4000−200 cm^{-1}). NMR spectra were recorded on either a Varian XL-200 or a Varian Unity 300 NMR spectrometer using the standard references. [*trans*-$PtCl_2(PhCN)_2$] was prepared by the literature method.[28]

Safety Note. *Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution!*

[Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (1). A mixture of [*trans*-$PtCl_2(PhCN)_2$] (2.0 g, 4.235×10^{-3} mol) and tri-*o*-tolylphosphine (1.29 g, 4.235×10^{-3} mol) in 2-methoxyethanol (25 mL) was refluxed for 30 min. The initial suspension dissolved to give a clear pale yellow solution, and then a white crystalline solid was deposited. After cooling, the solid was filtered off, washed with methanol and diethyl ether, and identified as complex **1** (yield 1.9 g, 84%). Anal. Calcd for $C_{42}Cl_2H_{40}P_2Pt_2$: C, 47.26; H, 3.78. Found: C, 47.54; H, 3.86. IR (cm^{-1}): $C\frown P$, 467 (vs), 479 (vs), 486 (vs), 527 (vs, sh), 564 (vs), 585 (vs), 750 (vs), 759 (vs), 784 (m), 806 (m), 1568 (m), 1584 (m), 1590 (m); ν(Pt−Cl), 249 (s), 255 (s).

[Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(NCMe)$_2$]ClO_4 (2). To a suspension of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (**1**) (0.6407 g, 0.6×10^{-3} mol) in acetonitrile (20 mL) was added $AgClO_4$ (0.2488 g, 1.2×10^{-3} mol), and the mixture was stirred for 4 h at room temperature. The AgCl precipitated was filtered off and washed with 5 mL of acetonitrile. Evaporation of the resulting solution to dryness followed by addition of OEt_2 to the residue afforded a white solid which was identified as **2** (yield 0.71 g, 87%). Anal. Calcd for $C_{25}ClH_{26}N_2O_4PPt$: C, 44.16; H, 3.85; N, 4.12. Found: C, 43.79; H, 3.66; N, 3.95. IR (cm^{-1}): $C\frown P$, 466 (s), 479 (s), 487 (s), 516 (m), 531 (s), 566 (s), 589 (s), 759 (s), 772 (s), 793 (s), 1568 (w), 1589 (w); NCMe, 2288 (m), 2298 (m), 2324 (m); ClO_4^-, 1083 (vs, br), 623 (s).

[Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CNMe_2)] (3). To a stirred suspension of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (**1**) (0.8544 g, 0.8×10^{-3} mol) in THF (40 mL) was added $AgClO_4$ (0.3317 g, 1.6×10^{-3} mol), and the mixture was stirred at room temperature for 4 h. The AgCl precipitated was filtered off, and the resulting solution was evaporated almost to dryness. The residue was treated with 30 mL of methanol, and the addition of $NaS_2CNMe_2{\cdot}2H_2O$ (0.2867 g, 1.6×10^{-3} mol) to the solution gave rise to a white solid, which was filtered off, recrystallized from CH_2Cl_2/*n*-hexane, and identified as **3** (yield 0.88 g, 89%). Anal. Calcd for $C_{24}H_{26}NPPtS_2$: C, 46.59; H, 4.24; N, 2.26. Found: C, 46.71; H, 3.89; N, 2.24. IR (cm^{-1}): $C\frown P$, 465 (s), 476 (s), 486 (s), 514 (m), 529 (m), 562 (s), 583 (s), 754 (vs), 765 (vs), 1583 (w); $^-S_2CNMe_2$, 1543 (vs) (ν(C−N)); 975 (vs) (ν(C−S)).

Synthesis of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2COEt)] (4). To the resulting solution of the treatment of [Pt{$CH_2C_6H_4P$-(*o*-tolyl)$_2$-*C,P*}(μ-Cl)]$_2$ (**1**) (0.5447 g, 0.51×10^{-3} mol) with $AgClO_4$ (0.2116 g, 1.02×10^{-3} mol) in THF (20 mL), after elimination of the AgCl, was added KS_2COEt (0.1636 g, 1.02×10^{-3} mol) and the mixture stirred for 15 min at room temperature. Then, the solution was evaporated to dryness and *n*-pentane (100 mL) was added to the residue. After filtration, the resulting solution was concentrated to 10 mL and cooled to ca. 5 °C. The yellow solid precipitated was filtered off, heated at 70 °C for 24 h, and identified as **4** (yield 0.474 g, 75%). Anal. Calcd for $C_{24}H_{25}OPPtS_2$: C, 46.52; H, 4.07. Found: C, 46.66; H, 4.08. IR (cm^{-1}): $C\frown P$, 458 (m), 477 (s), 487 (m), 505 (m), 586 (s), 758 (vs), 1567 (w), 1586 (w); $^-S_2COEt$, 1031 (vs), 1123 (vs), 1239 (vs).

[Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CNMe_2)X_2] (X = Cl (5), Br (6), I (7). X = Cl. To a pale yellow solution of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CNMe_2)] (**3**) (0.6 g, 0.9698×10^{-3} mol) in CH_2Cl_2 (20 mL) was added a slight excess of Cl_2 in CCl_4 (1.1×10^{-3} mol), and immediately the solution turned yellow. After 10 min of stirring at room temperature the solution was evaporated to dryness and OEt_2 (20 mL) was added to the residue to give a yellow solid, which was filtered off, dried, and identified as **5** (yield 0.515 g, 77%). Anal. Calcd for $C_{24}Cl_2H_{26}NPPtS_2$: C, 41.80; H, 3.80; N, 2.03. Found: C, 41.87; H, 3.87; N, 1.98. IR (cm^{-1}): $C\frown P$ group, 455 (s), 475 (s), 487 (s), 506 (m), 522 (s), 536 (s), 551 (s), 567 (m), 583 (m), 751 (vs), 759 (s), 767 (m), 1588 (w); $^-S_2CNMe_2$, 1561 (vs) (ν-(C−N)), 978 (w) (ν(C−S)); Pt−Cl, 272 (m), 311 (m).

Complexes 6 (X = Br) and **7 (X = I)** were prepared similarly.

Complex 6 (X = Br). **3** (0.2877 g, 0.465×10^{-3} mol) and Br_2 in CCl_4 (0.558×10^{-3} mol) were used. Yield: 0.323 g, 89%. Anal. Calcd for $Br_2C_{24}H_{26}NPPtS_2$: C, 37.03; H, 3.37; N, 1.80. Found: C, 37.36; H, 3.27; N, 1.71. IR (cm^{-1}): $C\frown P$ group, 455 (s), 475 (s), 487 (s), 507 (m), 523 (s), 536 (s), 551 (s), 567 (m), 583 (m), 751 (vs), 757 (s), 765 (m), 1636 (w); $^-S_2CNMe_2$, 1558 (vs) (ν(C−N)), 977 (w) (ν(C−S)).

Complex 7 (X = I). **3** (0.3036 g, 0.4907×10^{-3} mol) and I_2 (0.137 g, 0.54×10^{-3} mol) were used. Yield: 0.385 g, 90%. Anal. Calcd for $C_{24}H_{26}I_2NPPtS_2$: C, 33.04; H, 3.00; N, 1.60. Found: C, 32.93; H, 3.38; N, 1.46. IR (cm^{-1}): $C\frown P$ group, 454 (m), 472 (m), 487 (w), 505 (w), 519 (m), 536 (m), 550 (w), 567 (w), 580 (w), 748 (vs), 762 (s), 1584 (w); $^-S_2CNMe_2$, 1549 (vs) (ν(C−N)), 976 (w) (ν(C−S)).

[Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2COEt)X_2] (X = Cl (8), Br (9), I (10)). X = Cl. To a pale yellow solution of [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2COEt)] (**4**) (0.2497 g, 0.403×10^{-3} mol) in CH_2Cl_2 (25 mL) was added a little excess of Cl_2 in CCl_4 (0.462×10^{-3} mol). The mixture was stirred at room temperature for 5 min, and then the solution was evaporated to dryness. Addition of OEt_2 (20 mL) to the residue afforded a solid, which was identified as **8** (yield 0.223 g, 80%). Anal. Calcd for $C_{24}Cl_2H_{25}OPPtS_2$: C, 41.74; H, 3.65. Found: C, 41.71; H, 3.66. IR (cm^{-1}): $C\frown P$ group, 453 (s), 475 (s), 488 (s), 503 (w), 522 (s), 535 (s), 552 (m), 567 (w), 583 (m), 749 (s), 761 (vs),1567 (w), 1591 (m); $^-S_2COEt$, 1030 (s), 1298 (vs); Pt−Cl, 276 (m), 306 (m).

Complexes 9 (X = Br) and 10 (X = I) were prepared similarly.

Complex 9 (X = Br). **4** (0.2010 g, 0.32×10^{-3} mol) and Br_2 in CCl_4 (0.372×10^{-3} mol) were used. Yield: 0.2 g, 80%. Anal. Calcd for $Br_2C_{24}H_{25}OPPtS_2$: C, 36.98; H, 3.23. Found: C, 36.73; H, 3.50. IR (cm^{-1}): $C\frown P$ group, 453 (m), 474 (m), 487 (m), 502 (w), 521 (m), 535 (m), 552 (w), 567 (w), 582 (w), 758 (m, sh), 1565 (w), 1591 (m); $^-S_2COEt$, 1032 (s), 1291 (vs).

Complex 10 (X = I). **4** (0.1554 g, 0.25×10^{-3} mol) and I_2 (73 mg, 0.287×10^{-3} mol) were used. Yield: 0.157 g, 72%. Anal. Calcd for $C_{24}H_{25}I_2OPPtS_2$: C, 33.00; H, 2.88. Found: C, 32.62; H, 2.96. IR (cm^{-1}): $C\frown P$ group, 454 (m), 474 (m), 486 (m), 503 (m), 521 (m), 536 (m), 551 (m), 567 (m), 580 (m), 744 (m), 1567 (w), 1591 (w); $^-S_2COEt$, 1032 (s), 1288 (vs).

Crystallographic Studies. [Pt{$CH_2C_6H_4P$(*o*-tolyl)$_2$-*C,P*}(S_2CNMe_2)]·$CHCl_3$ (3). Important crystal data and data collection parameters for complex **3** are listed in Table 3. The complex [Pt{CH_2-C_6H_4P(*o*-tolyl)$_2$-*C,P*}(S_2CNMe_2)]·$CHCl_3$ crystallizes in space group $P2_1/c$ with $Z = 4$. A parallelepiped-shaped crystal mounted on the tip of a glass fiber with epoxy cement was used for geometric and intensity data collection. Four circle diffractometer data were taken at 293 ± 1 °C. Lattice dimensions and type were determined by routine procedures and verified by oscillation photography. Cell constants were refined from 2θ values of 48 reflections including Friedel pairs ($27.7 < 2\theta < 29.5°$). During intensity

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[28] (a) Hartley, F. R. *Organomet. Chem. Rev. A* **1970**, 6, 119. (b) Uchiyama, T.; Toshiyasu, Y.; Nakamura, Y.; Miwa, T.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 181.

data collection, three monitor reflections were measured at regular intervals. These check reflections did not vary appreciably in intensity during the course of data collection. For the diffractometer data a measured absorption correction was applied, based on 10 complete Ψ-scans of reflections with diffractometer angle χ near 90°.

The structure of compound **3** was solved by direct methods and developed and refined in series of alternating difference Fourier maps and least-squares analyses using all data and the program SHELXTL-PLUS.[29] The chlorine atoms of the chloroform solvent were disordered over two sites (occupancy 0.5) sharing the same C atom. The C−Cl distances were fixed at 1.77 Å. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions and refined as riding atoms [C−H = 0.96 Å and U = 0.0872 Å^3]. Residuals and other final refinement parameters are listed in Table 3.

[Pt{CH$_2$C$_6$H$_4$P(*o*-tolyl)$_2$-*C,P*}(S$_2$CNMe$_2$)I$_2$]·$^1/_2$CH$_2$Cl$_2$ (7). Important crystal data and data collection parameters for complex **7** are listed in Table 3. Diffraction data were measured by Crystalytics Co.[30] The complex [Pt{CH$_2$-C$_6$H$_4$P(*o*-tolyl)$_2$-*C,P*}(S$_2$CNMe$_2$)I$_2$]·$^1/_2$CH$_2$Cl$_2$ crystallizes in space group $P2_1/c$ with $Z = 4$. A parallelepiped-shaped crystal mounted on the tip of a glass fiber with epoxy cement was used for geometric and intensity data collection. Four-circle diffractometer data were taken at 293 ± 1 °C. Lattice dimensions and type were determined by routine procedures and verified by oscillation photography. Cell constants were refined from 2θ values of 15 reflections including Friedel pairs (20 < 2θ < 30°). During intensity data collection, six monitor reflections were measured at regular intervals. These check reflections did not vary appreciably in intensity during the course of data collection. For the diffractometer data a measured absorption correction was applied, based on 6 complete Ψ-scans of reflections with diffractometer angle χ near 90°.

The structure of compound **7** was solved by direct methods and developed and refined in series of alternating difference Fourier maps and least-squares analyses using all data and the program SHELXTL-PLUS.[29] The solvent molecule lays near an inversion center and is disordered over two positions. The occupancy of the atoms of the solvent molecule was fixed at 0.5. All non-hydrogen atoms except for those of the solvent were refined anisotropically. All hydrogen atoms except for the solvent one were included in calculated positions and refined as riding atoms [C−H = 0.96 Å and U = 0.0832 Å^3]. A difference map following convergence showed two peaks higher than 1 e/Å^3 (1.39 and 1.21 e/Å^3). These two peaks lay very close to the platinum atoms (0.91 and 0.95 Å) and had no chemical significance. Residuals and other final refinement parameters are listed in Table 3.

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Supporting Information Available: Tables of anisotropic thermal parameters, H positional and thermal parameters, and complete bond distances and bond angles (8 pages). Ordering information is given on any current masthead page.

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[29] SHELXTL-PLUS: *Software Package for the Determination of Crystal Structures*, Release 4.0; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

[30] Crystalytics Co., P.O. Box 82286, Lincoln, NE.