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Structural and Mechanistic Look at the Orthoplatination of Aryl Oximes by Dichlorobis(sulfoxide or sulfide)platinum(II) Complexes

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Structural and mechanistic aspects of orthoplatination of acetophenone and benzaldehyde oximes by the platinum(II) sulfoxide and sulfide complexes $[PtCl_2L_2]$ (**2**, L = $SOMe_2$ (**a**), *rac*-SOMePh (**b**), *R*-SOMe(C_6H_4Me-4) (**c**), and SMe_2 (**d**)) to afford the corresponding platinacycles *cis*-(*C,S*)-[Pt^{II}(C_6H_3-2-CR′=NOH-5-R)Cl(L)] (**3**, R, R′ = H, Me) have been investigated. The reaction of acetophenone oxime with sulfoxide complex **2a** in methanol solvent occurs noticeably faster than with sulfide complex **2d** due to the fact that the sulfoxide is a much better platinum(II) leaving ligand than the sulfide. Evidence is presented that the orthoplatination is a multistep process. The formation of unreactive dichlorobis(*N*-oxime)platinum(II) cations accounts for the rate retardation by excess acetophenone oxime and suggests the importance of pseudocoordinatively unsaturated species for the C–H bond activation by Pt^{II}. A comparative X-ray structural study of dimethyl sulfoxide platinacycle **3b** (R = R′ = Me) and its sulfide analogue **3e** (R = H, R′ = Me), as well as of SOMePh complex **3c** (R = H, R′ = Me), indicated that they are structurally similar and a sulfur ligand is coordinated in the cis position with respect to the σ-bound phenyl carbon. The differences concern the Pt–S bond distance, which is notably longer in the sulfide complex **3e** (2.2677(11) Å) as compared to that in sulfoxide complexes **3b** (2.201(2)–2.215(2) Å) and **3c** (2.2196(12) Å). Whereas the metal plane is practically a plane of symmetry in **3b** due to the H-bonding between the sulfoxide oxygen and the proton at carbon ortho to the Pt–C bond, an *S*-bonded methyl of SOMePh and SMe_2 is basically in the platinum(II) plane in complexes **3c** and **3e**, respectively. There are intra- and intermolecular hydrogen bond networks in complex **3b**. An interesting structural feature of complex **3c** is that the two independent molecules in the asymmetric unit of the crystal reveal an extremely short Pt–Pt contact of 3.337 Å.

Introduction

Carbon−hydrogen bond cleavage by Pt^{II} [1−10] and Pd^{II} [11] sulfoxide complexes $[MX_2(RR'SO)_2]$ (X = acido ligand) to afford the corresponding cyclometalated compounds has recently attracted considerable attention. Platinum(II) sulfoxide metalacycles, in particular, have been shown to be promising for creation of the centers with central carbon[12]

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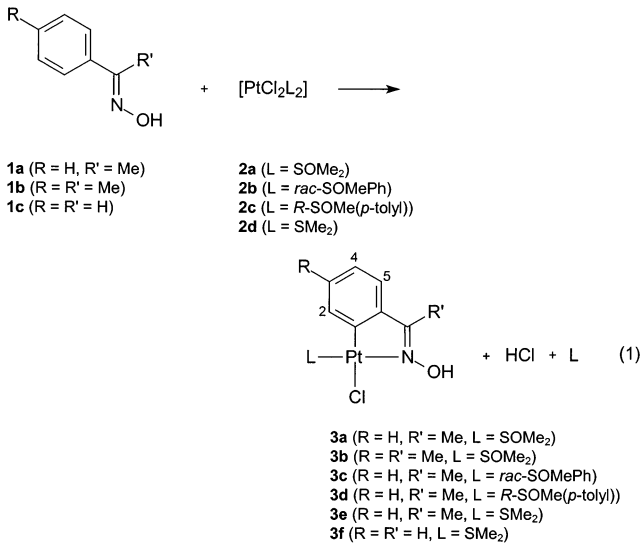
and planar chirality,[13] for the modeling of biologically relevant systems such as DMSO reductase,[14] and for the efficient catalysis of hydrolysis of pesticides of the parathion family.[15] Broad potential applications of these compounds preserve substantial interest in further exploring the synthetic capacity of the Pt^{II} sulfoxide complexes in the preparation of platinacycles via direct C−H bond cleavage and their structural studies, as well as stimulating a search for efficient, structurally similar metalating agents, such as alkyl sulfide chloro complexes of platinum(II). Accordingly, in this paper we report the results of comparative structural, kinetic, and mechanistic studies of cyclometalation of aryl oximes by compositionally related complexes $[Pt^{II}Cl_2L_2]$, where L = SOMeR and SMe_2 (eq 1). Additional interest in the compounds investigated arises from the fact that the ligands involved, viz. oximes[16,17] and sulfoxides,[18,19] have been the subjects of intensive research in recent years.



Experimental Section

Methods. Spectrophotometric and kinetic measurements were carried out on a Shimadzu UV-160A spectrophotometer equipped with a CPS-240A cell positioner/temperature controller or a Hitachi 150-20 instrument with a thermostated circulating water cell compartment. ^{1}H NMR spectra were recorded on CXP-200 Bruker and Varian UNITY 300 instruments with a residual solvent signal as internal standard. Spectra for **2d**, **3e**, and **3f** were recorded on a Bruker 300 MHz spectrometer. The δ scale is used; J is in Hz throughout.

Reagents. Sulfoxides used in this work were purchased from Fluka and dimethyl sulfide from Merck. Sulfoxide complexes **2a**−**c** were obtained according to the procedure of Price et al.[20] The dimethyl sulfide analogue, which is a mixture of cis and trans isomers, was synthesized according to the procedure of Hill et al.[21] $[PtCl_2(SMe_2)_2]$: ^{1}H NMR ($CDCl_3$) cis 2.56 ($^3J_{PtH}$ = 50); trans 2.45 ($^3J_{PtH}$ = 42). Acetophenones 4-RC_6H_4COMe (R = H, Me) were purchased from Lancaster and then converted into the corresponding oximes 4-$RC_6H_4C(Me)$═NOH.[22] Benzaldehyde oxime was purchased from Acros. Complexes **3a**,**b** were prepared from the corresponding oximes and *cis*-$[PtCl_2(SOMe_2)_2]$ in refluxing methanol as was described previously.[3,14] The crystal of **3b** for the X-ray study was obtained by slow evaporation of a methanol solution of **3b**. All other reagents used in this work were of the highest quality available.

Synthesis of Complex 3c: (A) Via C−H Activation. *cis*-$[PtCl_2(SOMePh)_2]$ (0.0986 g, 1.8×10^{-4} mol) was refluxed with acetophenone oxime (0.03 g, 2.2×10^{-4} mol) in 6 mL of methanol for 48 h. The volume of the yellow solution was reduced to 2 mL by using a rotary evaporator and this solution was kept at ca. −5 °C for 3 days. The yellow-orange crystals that formed were filtered, washed with methanol, and air-dried. Yield of **3c** 29% (0.026 g). **(B) Via Sulfoxide Exchange.** Complex **3a** (42 mg, 0.098 mmol) was refluxed with 0.168 g (0.98 mmol) of *rac*-SOMePh in 15 mL of MeOH for 13 h. The reaction mixture was then concentrated 2-fold and allowed to stand at ca. −5 °C for 4 days. Orange needlelike crystals formed which were separated, washed rapidly with cold methanol, and dried in the air. Yield 45% (0.022 g). One of these crystals was selected for an X-ray crystal study. Anal. Calcd for $C_{15}H_{16}ClNO_2PtS$: C, 35.68; H, 3.19; N, 2.77. Found: C, 35.12; H, 3.05; N, 2.86. ^{1}H NMR ($CDCl_3$): 2.43 (s, 3H, CCH_3, $^4J_{PtH}$ = 6.4), 3.74 (s, 3H, SCH_3, $^3J_{PtH}$ = 18.7), 7.05−7.18 (m, 3H, H3−H5),[23] 7.55−7.65 (m, 3H, H3′−H5′), 7.75 (dd, 1H, H2, J_{HH} = 7.4, $^3J_{PtH}$ = 41.2), 8.18−8.28 (m, 2H, H2′,H6′), 10.53 (s, 1H, OH, $^3J_{PtH}$ = 6.4).

Synthesis of Complex 3d: Via C−H Activation. Synthesis of **3d** was carried out as described for **3c** in 19% yield. No attempts were made to optimize the yield. Anal. Calcd for $C_{16}H_{18}ClNO_2PtS{\cdot}H_2O$: C, 35.8; H, 3.7; N, 2.6. Found: C 35.4, H 3.1, N 2.7. ^{1}H NMR ($CDCl_3$): 2.39 (s, 3H, CCH_3, $^4J_{PtH}$ = 5.8), 2.43 (s, 3H, $ArCH_3$), 3.65 (s, 3H, SCH_3, $^3J_{PtH}$ = 19.4), 7.00−7.15 (m, 3H, H3−H5), 7.34, 7.38, 8.02, 8.06 (AA′BB′, 4H, C_6H_4), 7.67 (dd, 1H, H2, J_{HH} = 7.6, $^3J_{PtH}$ = 51.2), 10.48 (s, 1H, OH, $^3J_{PtH}$ = 6.2).

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Table 1. Crystal Data for Orthometalated Platinum(II) Oxime Complexes

	3b	3b	3c	3e
chemical formula	$C_{11}H_{16}ClNO_2PtS$	$C_{11}H_{16}ClNO_2PtS$	$C_{15}H_{16}ClNO_2PtS$	$C_{10}H_{14}ClNOPtS$
fw	456.85	456.85	504.89	426.82
temp, K	120	293	293	293
space group	$Pna2_1$	$Pna2_1$	$P2_1/c$	$P2_12_12_1$
λ(Mo Kα)/ Å	0.71073	0.71073	0.71073	0.71073
a/Å	7.52710(10)	7.652(2)	16.054(3)	5.7635(12)
b/Å	36.3103(4)	36.583(7)	10.654(2)	8.8443(18)
c/Å	19.6160(2)	19.742(4)	19.212(4)	24.195(5)
α/deg	90	90	90	90
β/deg	90	90	92.20(4)	90
γ/deg	90	90	90	90
V/Å^3	5361.27(11)	5526(2)	3283.4(11)	1233.3(4)
Z	16	16	8	4
D_c/g cm^{-3}	2.264	2.196	2.043	2.293
μ/mm^{-1}	10.813	10.490	8.839	11.736
R^a ($I > 2(\sigma)I$)	0.0413	0.0677	0.0318	0.0227
wR^b	0.0996	0.0771	0.0652	0.0390

[a] $R = [(\sum\Delta F)/(\sum F_o)]$. [b] $wR = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Synthesis of Complex 3e. The complex was prepared by refluxing a mixture of *cis*- and *trans*-[$PtCl_2(SMe_2)_2$] (0.200 g, 0.52 mmol) and acetophenone oxime (0.086 g, 0.64 mmol) in methanol (25 mL) for 96 h. At selected time intervals a small sample of the reaction mixture was removed, the methanol evaporated, and a ^{1}H NMR spectrum recorded in $CDCl_3$. After 96 h 88% conversion of **2d** to the desired product (**3e**) was observed. No detectable amount of an intermediate could be identified. The solvent was removed in vacuo and the residue was column chromatographed on SiO_2 with methanol as eluent. Crystals suitable for X-ray analysis were grown by slow evaporation of a methanol solution of the complex. Anal. Calcd for $C_{10}H_{14}ClNOPtS$: C, 28.14; H, 3.31; N, 3.28. Found: C, 28.50; H, 3.40; N, 3.23. ^{1}H NMR ($CDCl_3$): 2.30 (s, 3H, CCH_3, $^4J_{PtH} = 7$), 2.72 (s, 6H, SCH_3, $^3J_{PtH} = 52$), 7.10 (m, 3H, H3−H5), 7.35 (dd, 1H, H2, $J_{HH} = 5$ and 2, $^3J_{PtH} = 54$), 10.29 (s, 1H, OH, $^3J_{PtH} = 8$).

Synthesis of Complex 3f. The complex was prepared by refluxing a mixture of *cis*- and *trans*-[$PtCl_2(SMe_2)_2$] (0.206 g, 0.53 mmol) and benzaldehyde oxime (0.092 g, 0.76 mmol) in methanol (25 mL) for 20 days. At selected time intervals a small sample of the reaction mixture was removed, the methanol evaporated, and a ^{1}H NMR spectrum recorded in $CDCl_3$. The reaction proceeds through a clearly distinguishable intermediate that is formed in a high concentration with respect to the other complexes in solution. After 16 days 56% conversion of **2d** into the desired product **3f** was observed in solution. The product **3f** was isolated by column chromatography as described for **3e**. Anal. Calcd for $C_9H_{12}ClNOPtS$: C, 26.19; H, 2.93; N, 3.39. Found: C, 26.57; H, 3.14; N, 3.21. ^{1}H NMR ($CDCl_3$): 2.72 (s, 6H, SCH_3, $^3J_{PtH} = 54$), 7.1 (m, 2H, aromatic), 7.2 (m, 1H, aromatic), 7.32 (m, 1H, aromatic), 8.15 (s, 1H, N=CH), 10.25 (s, 1H, OH, $^3J_{PtH} = 9$), in all cases the aromatic protons were poorly resolved multiplets and hence no specific assignments could be made. The intermediate *trans*-[$PtCl_2(SMe_2)$(benzaldehyde oxime)]: ^{1}H NMR ($CDCl_3$): 2.43 (s, 6H, SCH_3, $^3J_{PtH} = 44$), 7.5 (m, 3H, aromatic), 7.9−8.0 (m, 2H, aromatic), 8.38 (s, 1H, N=CH, $^3J_{PtH} = 24$), OH not resolved.

Crystallography: Data Collection and Structure Determination. A summary of the crystal data is given in Table 1.

Complex 3b. The measurements have been performed on a Nonius Kappa CCD diffractometer. The data were processed with the software described elsewhere.[24] The structures were solved by direct method and refined by full-matrix least-squares method on F^2 with the SHELX-97 program package.[25] The non-hydrogen atoms have been refined anisotropicaly. The aromatic hydrogens were placed in the calculated positions and refined with a riding model. The methyl and oxime hydrogens were refined isotropically. The isotropic thermal parameters for H atoms of the aromatic and methyl groups were increased by a factor of 1.2 and 1.5, respectively.

Complexes 3c and 3e. The intensity data were collected on a SMART CCD diffractometer fitted with a rotating anode. In both structures the first 50 frames were collected again after completion of the data collections to check for decay. No decay was observed in any of the structures. All reflections were merged and integrated with SAINT.[26] Corrections were applied for Lorentz, polarization, and absorption with use of multiscans.[27] Both structures were solved by direct methods and refined through consecutive least-squares cycles with the SHELXTL program package,[25] with $\sum(|F_o| - |F_c|)^2$ being minimized. All non-H atoms were refined with anisotropic displacement parameters, whereas the H atoms were constrained to their parent sites by using a riding model. The graphics were done with DIAMOND.[28]

Kinetic Measurements. Stock solutions of complex *cis*-[$PtCl_2(SOMe_2)_2$] (ca. 4.3×10^{-3} M) were prepared in methanol solvent. An aliquot of such a solution (ca. 0.2 mL) was introduced into a quartz cuvette with a 1 cm path length, followed by the addition of the required amount of acetophenone oxime dissolved in MeOH. The total concentration of *cis*-[$PtCl_2(SOMe)_2$] in the cell was 4.3×10^{-4} M. The UV−vis spectra were recorded every 10 and 90 min during the first and second steps, respectively. For the kinetic calculations, the wavelength of 320 nm was selected where the absorbance changes were significantly large to ensure accurate calculations. All calculations were performed with a SigmaPlot 4.0 package.

Results and Discussion

Two Approaches to Pt^{II} Sulfoxide Complexes. The cycloplatination of aryl oximes by Pt^{II} dimethyl sulfoxide

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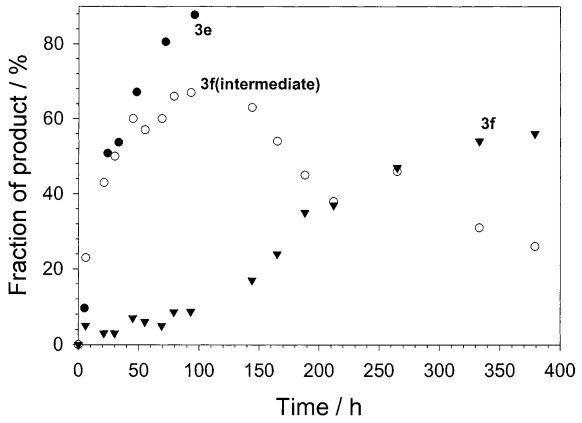

Figure 1. The progress of cycloplatination of acetophenone (●) and benzaldehyde oxime (▼) by $[PtCl_2(SMe_2)_2]$ in refluxing methanol. Open circles (○) show accumulation and consumption of the intermediate in the case of **1c**. For experimental details, see the Experimental Section.

complexes is well documented.[3,14] This approach was used to synthesize metalacycle **3b** for an X-ray structural study. Compounds **3c** and **3d** with asymmetric sulfoxides were synthesized by direct cycloplatination of acetophenone oxime by the corresponding complex in refluxing methanol (eq 1), as was first described for dimethylaminomethylferrocene.[13] Complex **3c** was also obtained by substitution of $SOMe_2$ by an excess of SOMePh (eq 2).

$$\mathbf{3a} + \mathrm{SOMePh} \rightarrow \mathbf{3c} + \mathrm{SOMe_2} \qquad (2)$$

Cycloplatination of Acetophenone and Benzophenone Oximes by $[PtCl_2(SMe_2)_2]$. The knowledge in cycloplatination of aryl oximes by *cis*-$[PtCl_2(SOMe_2)_2]$[3,14] was extended to a mixture of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$. When refluxed in methanol, acetophenone oxime undergoes gradual metalation to afford complex **3e** in an 88% conversion in 4 days. This is in fact much slower as when *cis*-$[PtCl_2(SOMe_2)_2]$ is used as a metalating agent. Complex **3e** was isolated by column chromatography and characterized by the analytical and ^{1}H NMR data. Its composition, and geometry, was also confirmed by a single-crystal X-ray structural investigation (see below). The accumulation of **3e** proceeds without the formation of a detectable amount of an intermediate, Figure 1. This contrasts with the behavior of benzaldehyde oxime. The cycloplatination of the latter by $[PtCl_2(SMe_2)_2]$ occurs significantly slower than that of **1a** and proceeds with the formation of an appreciable amount of an intermediate (Figure 1).

The geometry of this intermediate is predicted to be *trans*-$[PtCl_2(SMe_2)(\mathbf{1c})]$ based on the following arguments made from the ^{1}H NMR data. Integration of the well-defined N=CH peak with respect to the methyl resonance of the sulfide showed that a 1 to 6 ratio prevailed, confirming the substitution of one of the thioether ligands. The $^3J_{PtH}$ coupling constant of the DMS resonance in the intermediate equals 44 Hz compared to the 42 and 50 Hz of the trans and cis isomers of **2d**, respectively. This seems to indicate that the DMS ligand is coordinated trans to the oxime nitrogen in the intermediate. This argument is furthermore in accordance with the chemical shifts observed for the intermediate complex at δ 2.43 compared to δ 2.45 and 2.56 respectively of the trans and cis isomers of **2d**. For a specific resonance, such as the methyls in SMe_2, the coupling constants are most affected by the ligand in the trans position, while the chemical shift is more sensitive to changes in the cis position. From the coupling constants and chemical shifts reported above for the intermediate it is clear that these correspond best to a molecule exhibiting a trans configuration. No other intermediates or geometrical isomers could be identified unambiguously. The formation of exclusively the trans isomer can be rationalized by kinetic arguments. The trans effect of DMS in related systems[29−31] is estimated to be ca. 300 times larger than that of Cl^- and hence the DMS in the trans isomer is expected to be more labile toward substitution than that in the corresponding cis isomer. This intermediate then undergoes a slow cyclometalation step substituting one of the chloro ligands and yielding the final product where the N atom of the oxime ligand is trans with respect to the DMS ligand.

The ^{1}H NMR spectra of dimethyl sulfide complexes **3e** and **3f** are similar to those of the corresponding dimethyl sulfoxide complexes **3a**,**b** reported previously.[14] In particular, the methyl resonances from $SOMe_2$ and SMe_2 appear as one singlet with the ^{195}Pt satellites, which is a bit surprising, since the Pt^{II} plane is not a plane symmetry for the sulfide complex **3e** in the solid state (see below). This fact is indicative of free rotation around the Pt−S bond making the methyl groups of SMe_2, which are already chemically equivalent, also magnetically equivalent.

X-ray Structural Data for Complexes 3b, 3c, and 3e. Selected geometrical parameters for all three structures are given in Tables 1 and 2. The numbering schemes and displacement ellipsoids are shown in Figures 2, 4, and 5 for **3b**, **3c**, and **3e**, respectively. Compound **3b** crystallizes in the orthorhombic space group $Pna2_1$ with four crystallographically independent molecules in the asymmetric unit. Similar geometric parameters were obtained at 120 and 293 K, and therefore the low-temperature data will be used in further discussion. The interatomic distances and bond angles are very similar in all four molecules. The platinum atoms have a square-planar geometry with the N atom of the oxime ligand trans to DMSO.

In the four independent molecules the Pt−S bond lengths range from 2.201(2) to 2.215(2) Å and are in accordance with the 2.19−2.22 Å range observed for related Pt^{II} complexes.[32−35] The mean Pt−C and Pt−Cl bond distances of 2.026 and 2.416 Å, respectively, are typical of related Pt^{II} compounds.[1,36] The sulfur atom is tetrahedral and the

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Table 2. Selected Bond Distances (in Å) and Bond Angles (in deg) for Complexes **3b**, **3c**, and **3e**[a]

bond length	**3b**[b]	**3c1**	**3c2**	**3e**
Pt−C(1)	2.021(9)	2.010(4)	2.011(4)	1.998(4)
Pt−N(1)	2.002(7)	2.010(3)	2.018(4)	2.013(3)
Pt−S(1)	2.215(2)	2.2192(12)	2.2199(11)	2.2677(11)
Pt−Cl(1)	2.416(2)	2.3806(13)	2.4099(13)	2.4114(11)
S(1)−C(1A)	1.785(9)	1.797(5)	1.787(5)	1.797(5)
S(1)−C(1B)	1.776(8)	1.798(5)	1.789(4)	1.805(4)
S(1)−O(2)	1.477(6)	1.465(4)	1.469(3)	
N(1)−C(7)	1.319(11)	1.295(6)	1.302(6)	1.287(5)
N(1)−O(1)	1.397(9)	1.384(4)	1.377(5)	1.387(4)
C(1−6)avg	1.399(12)	1.383(7)	1.384(7)	1.392(7)
C(6)−C(7)	1.450(12)	1.451(7)	1.464(6)	1.473(5)
C(7)−C(8)	1.494(12)	1.487(6)	1.483(6)	1.484(6)

bond angle	**3b**	**3c1**	**3c2**	**3e**
C(1)−Pt-N(1)	80.0(3)	79.11(17)	79.49(17)	78.99(14)
C(1)−Pt−S(1)	99.8(3)	95.84(13)	94.14(12)	93.81(11)
N(1)−Pt−S(1)	175.5(2)	170.94(11)	171.62(12)	172.77(10)
C(1)−Pt−Cl(1)	169.7(3)	169.64(13)	168.57(12)	169.11(11)
N−Pt−Cl(1)	89.7(2)	90.80(11)	89.49(12)	90.12(10)
S−Pt−Cl(1)	90.45(7)	93.85(5)	96.53(5)	97.07(4)
C(1A)−S−C(1B)	100.9(4)	100.9(2)	101.9(2)	98.0(2)
C(1A)−S−Pt	106.6(3)	112.6(2)	113.11(19)	110.78(17)
C(1B)−S−Pt	110.6(3)	105.85(15)	105.08(14)	105.83(16)
C(7)−N−O(1)	116.3(7)	116.4(4)	116.9(4)	116.3(4)
C(7)−N−Pt	119.1(6)	119.7(3)	119.1(3)	120.1(3)
O(1)−N−Pt	124.5(5)	123.6(3)	123.9(3)	123.6(3)
C(2)−C(1)−Pt	130.8(7)	129.4(3)	130.3(3)	129.2(3)
C(6)−C(1)−Pt	111.7(6)	112.3(3)	113.2(3)	113.5(3)
[C(1)−C−C(6)]avg	119.98(8)	120.0(6)	120.0(5)	120.0(5)
C(5)−C(6)−C(7)	121.4(8)	123.3(5)	123.7(4)	122.6(4)
C(1)−C(6)−C(7)	117.1(7)	116.8(4)	115.4(4)	115.5(4)
N−C(7)−C(6)	111.8(8)	111.5(4)	112.8(4)	111.6(4)
N−C(7)−C(8)	121.5(8)	123.1(5)	122.6(5)	123.8(4)
C(6)−C(7)−C(8)	126.7(8)	125.4(5)	124.6(5)	124.5(4)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] These values refer to the Pt1 crystallographically independent molecule.

S−C and S−O distances are in the range 1.760−1.794 and 1.468−1.478 Å, respectively. Each unit has an intramolecular C(*n*2)−H···O(*n*2) (n = 1−4, indicating molecules 1−4, respectively) interaction between the aromatic proton and the sulfoxide oxygen, which stabilizes the coordination of DMSO. The geometric parameters of these C(*n*2)−H···O(*n*2) hydrogen bonds are given in Table 5S.

The intermolecular interactions in structure **3b** are worth mentioning. The short contacts O(11)···O(31) and O(21)···O(41) of 2.839(9) and 2.817(9) Å suggest O−H···O binding between the oxime OH groups within the Pt(1)−Pt(3) and Pt(2)−Pt(4) pairs, respectively (Figure 3). The Pt(1) oxime group is involved in the bifurcated hydrogen bonding comprised of the intramolecular interaction with Cl(1) and the intermolecular one directed at the neighboring Pt(3) oxime oxygen. The same H-bond network is observed for the Pt(2) and Pt(4) pair, viz. the Pt(4) oxime participates in the bifurcated O−H···Cl and O−H···O bonding. The intermolecular contacts of the C−H···O type provide extra binding of the complexes in the crystal. The geometric parameters of these contacts agree well with the data reported elsewhere.[24] The Pt(1) and Pt(2) units have a glide plane *a*. Besides, the Pt(3) and Pt(4) units are related by the 2_1 screw axis and are also bound via the C−H···O interactions. The hydrogen bond network occurs both at low and room temperatures.

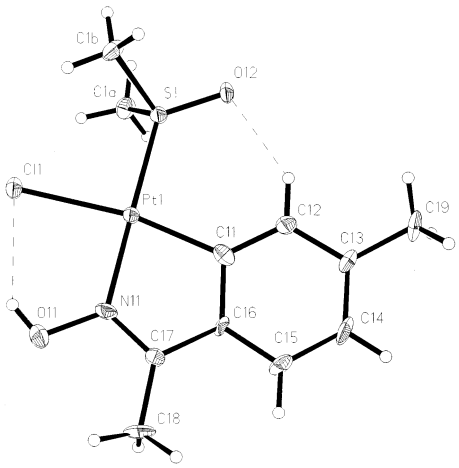

Figure 2. Numbering scheme for complex **3b**; the ellipsoids denote 30% probability. Molecule 1 of four crystallographically independent molecules are shown, molecules 2−4 are identical. In the numbering scheme the first digit refers to the number of the molecule and the second digit refers to the number of the atom in the molecule.

Complex **3c** crystallizes with two independent molecules in the asymmetric unit in $P2_1/c$. The molecules exhibit a distorted square-planar geometry with the N atom of the oxime ligands trans to methylphenylsulfoxide. The Pt−Cl bond lengths for molecules 1 and 2 of **3c** are noticeably different, viz. 2.3806(13) and 2.4099(13) Å, respectively, due to the packing effects (chemically equivalent). An interesting feature of complex **3c** is that the two independent molecules reveal an extremely short Pt−Pt separation of 3.337 Å. This is clearly seen in Figure 6. The separation is even shorter than the 3.53 Å reported by Chassot et al. for the bisplatinacycle *cis*-bis(2-phenylpyridine)platinum(II).[37]

Complex **3e** crystallizes as a racemic twin in the noncentric space group $P2_12_12_1$. The crystal structure of **3e** exhibits a distorted square-planar geometry with the N atom of the oxime ligand trans to the sulfide. All bond distances within the coordination polyhedron are typical of the ligands involved, with 1.998(4), 2.013(3), 2.2677(11), and 2.4114(11) Å being observed for the Pt−N, Pt−C, Pt−S, and Pt−Cl bonds, respectively. The geometrical parameters in the oxime and sulfide ligands are all typical of these ligands. A strong intramolecular interaction between the chloro ligand and the oxime hydroxyl hydrogen keeps the ligand locked in a planar configuration with respect to the coordination plane. There does not seem to be any interactions between the individual molecules in the structure, either through a hydrogen bonding network or Pt−Pt interactions, so it can be assumed that the packing is governed by the van der Waals interactions alone.

The Pt−C and Pt−N bond distances are similar in the crystal structures of all three complexes reported here. All

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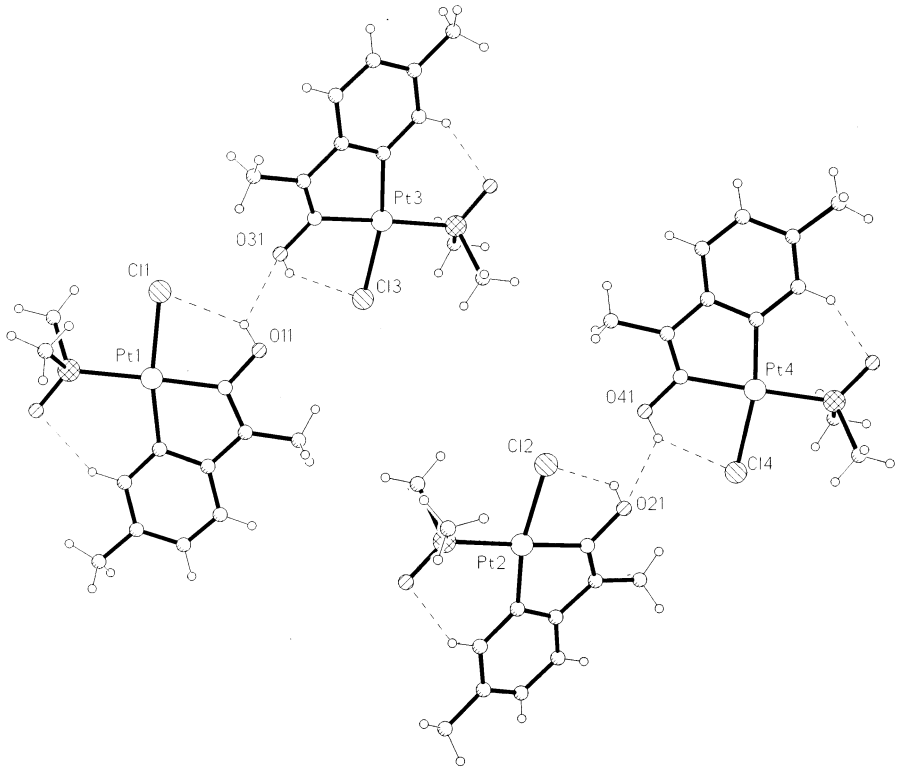

Figure 3. Hydrogen bond network in complex **3b**.

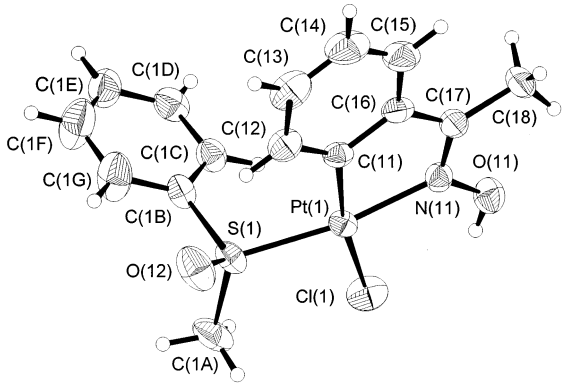

Figure 4. Numbering scheme for complex **3c**; the ellipsoids denote 30% probability. Molecule 1 of two crystallographically independent molecules are shown, molecule 2 is identical. In the numbering scheme the first digit refers to the number of the molecule and the second digit refers to the number of the atom in the molecule.

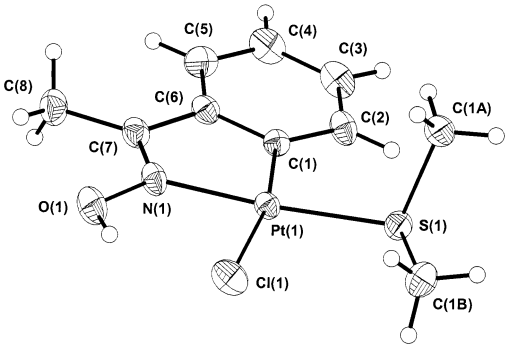

Figure 5. Crystal structure of complex **3e**; the ellipsoids denote 30% probability.

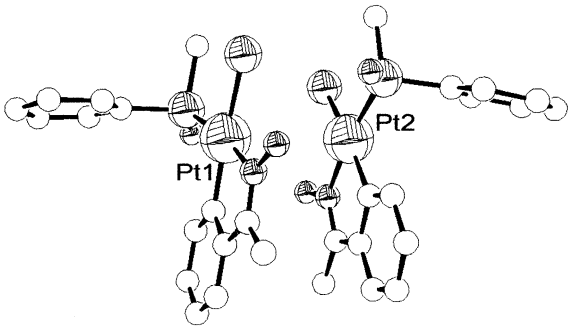

Figure 6. The asymmetric unit of **3c** with two independent molecules showing the Pt−Pt separation of 3.337 Å.

exhibited a distinct planar geometry making intermolecular interactions feasible; this was indeed established for **3b** and **3c**. Small bite angles of ca. 80° were observed for all seven molecules of the three complexes and are characteristic of the five-membered chelates formed by the cyclometalated oxime ligands. The Pt−S(sulfide) bond is significantly longer (2.268 Å) than the Pt−S(sulfoxide) bonds (2.201−2.220 Å), but this is not reflected in the Pt−N bonds. It is however much shorter than in the structurally related Pt^{IV} sulfide complex (2.333 Å),[14] as well as in the cyclometalated sulfide Pt^{II} complex in which sulfur is trans to the sp^2-carbon (2.336 Å).[38] It is worth noting that the Pt−S(sulfide) bond trans to the methyl group in the platina(IV)cycle is significantly longer at 2.441−2.469 Å.[39] The geometrical parameters in the oxime and sulfide ligands are all typical of these ligands.

Kinetics of Cycloplatination of Acetophenone Oxime by *cis*-[$PtCl_2(SOMe_2)_2$]: UV−Vis and ^{1}H NMR Data. The

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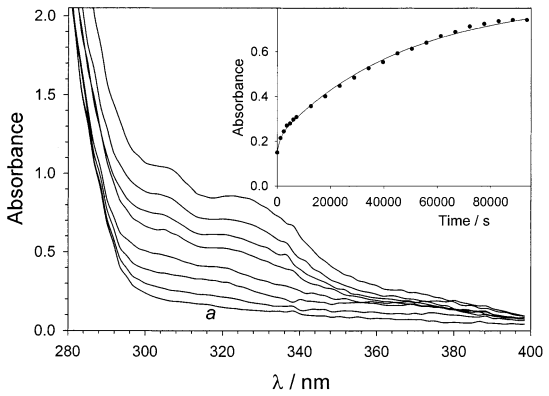

Figure 7. Spectral changes accompanying the formation of complex **3a** on cycloplatination of acetophenone oxime by *cis*-[$PtCl_2(SOMe_2)_2$] at 55 °C in MeOH (0.01 M $NaClO_4$). Spectrum a was recorded at time $t = 0$ after addition of the oxime; other spectra were obtained at $t = 20$, 120, 210, 570, 840, 1200, and 1560 min, respectively. The inset shows the biphasic nature of the reaction by following the absorbance change at 320 nm; the solid line is the theoretical curve calculated by using the rate constants k_{XY} and k_{YZ} from Table 3 at [PhCMe═NOH] = 0.0045 M and $a_0 = 0.88 \pm 0.02$, $a_1 = 0.077 \pm 0.008$, $a_2 = 0.65 \pm 0.01$ (eq 3, see text for details).

progress of reaction 1, studied spectrophotometrically in methanol at 55 °C with [**1a**] ≫ [**2a**] to ensure pseudo-first-order conditions, is shown in Figure 7. The reaction leads gradually to complex **3a** as suggested by the absorption maximums developing at 303 and 319 nm.[14] The change in absorbance at 320 nm is shown in the inset to Figure 7. Although pseudo-first-order conditions have been met, the reaction obviously does not follow first-order kinetics. The $\log(a_o/(a_o - x))$ versus time plots were always curved, indicating a multistep process, and hence no pseudo-first-order rate constants *k*(obs) could be calculated. The inset shows that the reaction between **1a** and **2a** is at least biphasic. At 55 °C the faster first step is over in a matter of 90 min whereas it takes ca. 25 h to accomplish the second step of the reaction. The absorbance versus time plot was quantified by using the algorithm for consecutive irreversible first-order reactions X → Y → Z with the rate constants k_{XY} and k_{YZ}, respectively.[40] In excess of **1a** complete displacement of the reaction toward the products is assumed. The rate constants k_{XY} and k_{YZ} were calculated by fitting the data as in Figure 7 to eq 3 to get an impression on how they depend on the concentration of incoming aryl oxime.

$$A = a_0 + a_1 e^{-k_{XY}t} + a_2 e^{-k_{YZ}t} \quad (3)$$

The values of k_{XY} and k_{YZ} in Table 3 show that the rate of the first step decreases on increasing the concentration of **1a**, whereas the rate of the second step is oxime independent. The assignment of steps 1 and 2 has been made on the basis of the ^{1}H NMR data obtained in this work and previous reports on kinetics of interaction of the complex *cis*-[$PtCl_2(SOMe_2)_2$] with various amines.[41−45]

Table 3. Rate Constants k_{XY} and k_{YZ} for Steps 1 and 2 in Scheme 1, Respectively, of Cycloplatination of Acetophenone Oxime by *cis*-[$PtCl_2(SOMe_2)_2$] (4.3×10^{-4} M)[a]

[PhCMe═NOH] × 10^3/M	$k_{XY} \times 10^4/s^{-1}$	$k_{YZ} \times 10^5/s^{-1}$
4.5	9 ± 2	1.8 ± 0.2
18.0	4.7 ± 0.8	1.6 ± 0.3
22.5	3.9 ± 0.5	1.38 ± 0.04
27.0	3.2 ± 0.4	1.78 ± 0.07
31.5	2.5 ± 0.7	1.87 ± 0.15
36.0	2.1 ± 0.3	2.3 ± 0.3

[a] Obtained by fitting the absorbance versus time plots to the rate equation $A = a_0 + a_1 e^{-k_{XY}t} + a_2 e^{-k_{YZ}t}$ (methanol, 55 °C).

The ^{1}H NMR spectrum of *cis*-[$PtCl_2(SOMe_2)_2$] recorded in CD_3CN has a single resonance at δ 3.56, $^3J_{PtH} = 21.7$ Hz, indicative of equivalent coordinated DMSO ligands. In d_4-methanol, an extra resonance from free DMSO at δ 2.59 is observed together with two "^{195}Pt-coupled" resonances at δ 3.51 and 3.44 ($^3J_{PtH} = 23.1$ and 24.5 Hz, respectively). Equal integral intensities of the latter signal and of free DMSO suggest the solvolysis according to eq 4 with $K_{MeOH} = 7.0 \times 10^{-3}$ M at 60 °C.

$$cis\text{-}[PtCl_2(SOMe_2)_2] + MeOH \overset{K_{MeOH}}{\rightleftharpoons} cis\text{-}[PtCl_2(SOMe_2)(MeOH)] + SOMe_2 \quad (4)$$

Addition of a 1.5-fold excess of acetophenone oxime to the solution of *cis*-[$PtCl_2(SOMe_2)_2$] in methanol eliminates instantaneously the δ 3.44 resonance and gives rise to a new signal at δ 3.19 ($J_{PtH} = 18.8$ Hz) that was ascribed to the coordinated $SOMe_2$ in the Pt^{II} complex with the N-bound oxime ligand (complex **A** in Scheme 1). The formation of **A** as the only detectable intermediate in the related systems was reported.[1,4,46] Complex **A** must be in equilibrium with **B** to account for a decrease in k_{XY} in excess of **1a**. Structurally related species with two alicyclic primary amines were characterized.[41] The rate constants for the substitution of DMSO in *cis*-[$PtCl_2(SOMe_2)_2$] by pyridines are close to 20 M^{-1} s^{-1} in dimethoxyethane.[42] This implies that at the 0.01 M concentration of the incoming ligand half of the Pt^{II} will be N-complexed by **1a** in a matter of ca. 3 s, i.e., the substitution of the first DMSO ligand by oxime is very fast on the cycloplatination time-scale.

The methyl signal at δ 2.46 ($J_{PtH} = 7.1$ Hz) from the cycloplatinated acetophenone oxime develops gradually. The C−H bond cleavage via cyclometalation by Pd^{II} and Pt^{II} complexes requires pseudocoordinatively unsaturated intermediates.[47] The chloro ligand, which is cis to the oxime C−H bond, is a candidate for achieving the cis coordinative unsaturation in a form of cationic intermediate **C**. The vacant

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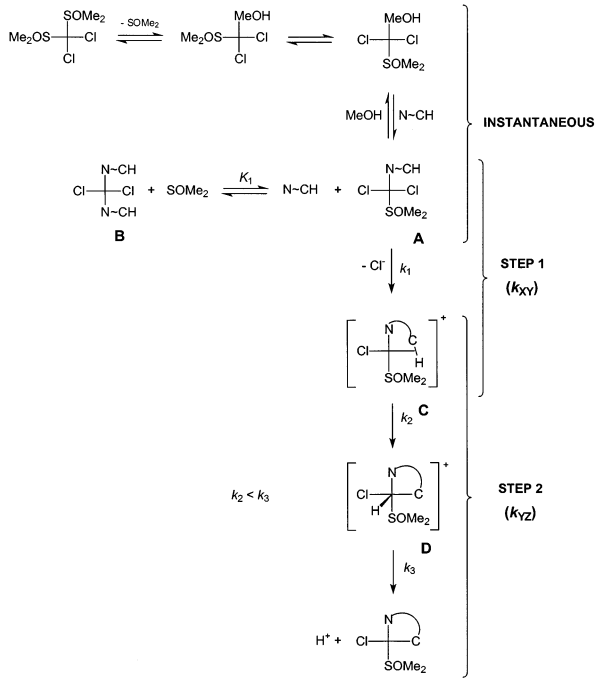
Scheme 1



site can actually be occupied by a solvent molecule or, as shown in Scheme 1, by the intact ortho C−H bond via the η^2-*C,H*[48] or agostic interaction.[49] Therefore, if step 1 (k_{XY}) involves the equilibrium K_1 (Scheme 1), the expression for k_{XY} is given by eq 5, which is in a qualitative agreement with the experimental observations. It shows that k_{XY} should decrease with increasing the concentration of incoming oxime and this is in fact observed.

$$k_{XY} = \frac{k_1 K_1[\mathrm{DMSO}]}{K_1[\mathrm{DMSO}] + [\mathbf{1a}]} \qquad (5)$$

Step 2 (k_{YZ}) is slower than step 1 and is independent of the oxime concentration, suggesting that it is intramolecular in nature and, hence, involves the C−H bond cleavage. Platinum(II) complexes have a significant affinity to the proton or, alternatively, of platinum(IV) to the hydride.[14,48,50−52] Therefore, the C−H bond cleavage may occur to a significant extent as oxidative addition to afford intermediate **D** in which the proton is still bound to Pt^{II} (or hydride to Pt^{IV}). Oxime-independent step 2 should thus be associated with a slower C−H bond cleavage (k_2) followed by a faster collapse of H-bonded intermediate **D** into the final cycloplatinated product (k_3). Such a mechanism of the benzene C−H bond activation by the $[(N{-}N)Pt^{II}Me(H_2O)]^+BF_4^-$ complex (N−N = ArN=C(Me)C(Me)=NAr, Ar = 2,6-$Me_2C_6H_3$) studied in detail recently[48] is very likely operative in this system. We prefer to consider **C** as the η^2-*C,H* rather than η^2-*C,C* bound intermediate,[53,54] since the latter is sterically less favorable on the assumption that the benzene fragment, by analogy with binding of alkenes, is coordinated perpendicular to the Pt^{II} plane. It should be pointed out that step 2 involves two processes driven by the rate constants k_2 and k_3. The latter should be faster. Otherwise hydride intermediate **D** could be accumulated in a significant amount and be detected by the ^{1}H NMR technique. This is not the case under the conditions used.

Further support for the mechanism in Scheme 1 has recently been obtained by isolating intermediates **A** and **B** as acetophenone oxime and benzaldehyde oxime complexes, respectively.[55] Both were characterized by X-ray crystallography. Remarkably, the *coordinated* oximes have different geometry, viz. *Z* and *E* in **A** and **B**, respectively. This observation explains nicely why complex **B** must be unreactive.

$[PtCl_2(SMe_2)_2]$ versus $[PtCl_2(SOMe_2)_2]$ as a Metalating Agent. Cycloplatination of oximes by $[PtCl_2(SMe_2)_2]$ is obviously feasible, but it reacts significantly slower than its dimethyl sulfoxide analogue **2a**. This fact makes kinetic studies with **2d** difficult. The results of previous investigations of the substitution of sulfur-containing ligands in the $[PtCl_2(SMe_2)_2]$ and $[PtCl_2(SOMe_2)_2]$ complexes[42,43] indicate that slower rates for **2d** are due to the fact that SMe_2 is by a factor of ca. 1000 a worse leaving ligand compared to DMSO. For the same reason, in contrast to **2a**, *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ do not undergo solvolysis in d_4-methanol. No resonance from free SMe_2 was observed by the ^{1}H NMR technique but from the coordinated ligand at δ 2.53 and 2.42 ($^3J_{PtH}$ = 50 and 41 Hz, respectively), suggesting that the coordination of oximes with Pt^{II} is more difficult to achieve for the sulfide complexes. Interestingly, **1c** reacts appreciably slower than **1a** and the transient species is observed for the former incoming organic ligand only. The basicity of **1a** must be higher than that of **1c** because of the methyl group at the C=N carbon. Therefore, **1a** may react faster to form an intermediate similar to **A** (Scheme 1), since it is well-documented that more basic pyridines replace SMe_2 faster in both *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$.[43]

Conclusion. It is shown in this study that cycloplatination of aryl oximes via the sp^2-C−H bond metalation is feasible with use of the bis-sulfoxide and -sulfide dichloro platinum(II) complexes. The cycloplatination by a mixture of *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ is considerably slower than that by the corresponding sulfoxide complexes. This is due to the absence of solvolysis of the dimethyl sulfide complexes in methanol and slower substitution of SMe_2 in the coordination sphere of Pt^{II} by the entering oximes. Cycloplatination of both acetophenone and benzaldehyde oxime by *cis*- and *trans*-$[PtCl_2(SMe_2)_2]$ produces a single isomer with the S and C donor atoms in a cis configuration. The X-ray structural investigations of sulfoxide platinacycles **3b** and **3c** revealed

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an interesting example of the hydrogen bond network and a rare very short Pt−Pt separation.

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Supporting Information Available: Listings of atom coordinates, bond distances and angles, thermal parameters, anisotropic refinements, and hydrogen atom coordinates for **3b**, **3c**, and **3e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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