trans-Chloromethylbis(dimethyl sulfoxide)platinum(II): X-ray Structure, Mechanism of Isomerization, and Its Use as a Precursor to Organoamine Complexes of Variable Geometrical Configurations

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An unusual 2:1 aggregate between the complex *trans*-[PtCl(CH_3)($DMSO)_2$] (**1**; DMSO = dimethyl sulfoxide) and the organotin compound bis(μ_3-oxo)bis(μ-chloro)bis(μ-dimethyltin(IV))bis(chlorodimethyltin(IV)) [Cl($CH_3)_2$-SnOSn($CH_3)_2$Cl]$_2$ has been isolated and characterized by X-ray analysis. The crystals belong to the triclinic space group $P\bar{1}$ with lattice constants $a = 9.373(2)$ Å, $b = 9.576(1)$ Å, $c = 14.087(3)$ Å, $\alpha = 70.29(1)°$, $\beta = 72.50(1)°$, $\gamma = 72.21(2)°$, and $Z = 2$. Least-squares refinement of the structure led to an R factor of 2.37%. ^{1}H, ^{13}C, and ^{195}Pt NMR measurements revealed that in chloroform solution complex **1** gives a mixture of four different species, which have been unambiguously identified as the starting complex **1** in equilibrium with *cis*-[PtCl(CH_3)-($DMSO)_2$] and the two corresponding isomeric aqua-species *cis* and *trans*-[PtCl(CH_3)(DMSO)(OH_2)]. The ^{195}Pt NMR magnetization transfer technique allowed determination of the rate of interconversion among the various complexes, showing that the direct *trans*−*cis* isomerism between the [PtCl(CH_3)($DMSO)_2$] species is negligible and that the geometrical interconversion occurs through a water-catalyzed pathway. The exchange between free and coordinated DMSO in *cis*- and *trans*-[PtCl(CH_3)($DMSO)_2$] has been measured by ^{1}H NMR magnetization transfer experiments. The molecule of DMSO in the position *trans* to a methyl group was found to be 10-fold more labile than that *trans* to another sulfur bonded dimethyl sulfoxide. The reactivity of complex **1** in chloroform with a series of monodentate nitrogen ligands having widely different electronic and steric properties has been investigated by ^{1}H NMR spectroscopy. The utility of this system as precursor for the synthesis of *cis*- and *trans*-[PtCl(CH_3)(DMSO)(am)] is discussed together with the evidence for the factors promoting the prevalence of a geometrical configuration.

Introduction

The chemistry of sulfoxide complexes with transition metal ions has received considerable attention due to the importance of their use as labile synthetic precursors[1] and potential antitumor agents[2] and to their role as catalytic intermediates. A great deal of work has been addressed to the study of the reactivity and the clarification of the mechanism of substitution in square-planar complexes of platinum(II) containing dimethyl sulfoxide as the coordinating molecule. As a ligand it exhibits a quite large *trans* effect[3] and a relatively weak *trans* influence.[4] It can be considered a poor nucleophilic agent,[5] resembling ethene. Acting as a leaving group, sulfoxides display a mutual labilization effect. It is well-established that a single dimethyl sulfoxide is difficult to remove,[6] while the presence of a second molecule, even when in the *cis* position, enhances the reactivity, and this property has been investigated from a kinetic point of view[7] and exploited in inorganic synthesis.[8] Analogous organometallic species of the type *cis*-[Pt($R)_2$($DMSO)_2$] (R = Me, aryl group; DMSO = dimethyl sulfoxide), reported by Eaborn *et al.*,[9] behave in a similar way, and both sulfoxide ligands can be easily replaced by bidentate chelating ligands. The mech-

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anism of these reactions has been investigated in great detail and provides the first example of a dissociative activation pathway for the nucleophilic substitution process in square-planar platinum(II) complexes.[10]

Despite the large amount of data available for the structural characterization and the reactivity of complexes containing two sulfoxide molecules spanning mutual *cis* positions, there are scarce reports on complexes containing two sulfoxide ligands in *trans* configuration and, to the best of our knowledge, none involving organometallic species. This stereochemistry is adopted only in the case of sterically hindered ligands such as diisoamyl sulfoxide.[11] Usually the *trans* isomer prefers to interconvert into the more stable *cis* species, and only in some instances has been it possible to isolate these intermediates.[12] For example, enriched solutions of *trans*-$[PtCl_2(Pr^n{}_2SO)_2]$ have been prepared by photochemical isomerization of the stable *cis* isomer.[13] The complexes *trans*-$[PtCl_2(DMSO)_2]$ and *trans*-$[PtCl_2(Et_2SO)_2]$[14] have been obtained by a bridge splitting reaction or by immediately precipitating the compound prepared from a proper labile precursor.[15]

Following these considerations, we thought it of interest to study the solution behavior of the organometallic complex *trans*-$[PtCl(CH_3)(DMSO)_2]$ as a simple model compound using NMR spectroscopy in an aprotic solvent. In this paper we report also the unusual X-ray structure of a cocrystallization product between the polynuclear tin(IV) compound bis(μ_3-oxo)bis(μ-chloro)bis(μ-dimethyltin(IV))bis(chlorodimethyltin(IV)) and the complex under investigation. The application of this compound as a useful synthon for the preparation of asymmetric organometallic species containing four different groups coordinated to the metal center is discussed.

Experimental Section

Materials. K_2PtCl_4 was obtained from Strem and was purified by dissolving it in water and filtering. Tetramethyltin was received from Aldrich, and its purity was checked by ^{1}H NMR. Dimethyl sulfoxide was purified by liquid chromatography on alumina under argon and stored over molecular sieves. The solvents used, except those for NMR measurements, were purified and dried by standard techniques. All of the other reagents were the best commercially available materials and were used as received or were purified by distillation or crystallization when needed. Microanalysis was performed by Analytical Laboratories, Engelskirchen. Elemental analyses were consistent with theoretical formulas.

Preparation of Complexes. The title complex, *trans*-$[PtCl(CH_3)(DMSO)_2]$ (**1**), was prepared according to Eaborn *et al*.[9] The complex was purified by several crystallizations from dichloromethane/diethyl ether mixtures.

The neutral complexes of the type $[PtCl(CH_3)(DMSO)(am)]$ (am = *n*-propylamine (Pr^nNH_2), pyridine (py), 2-methylpyridine (2-Mepy), 2,6-dimethylpyridine (2,6-Me_2py), 2-methylquinoline (2-Mequin), 5-aminoquinoline (5-AQ-*N1*), 3,8-bis(dimethylamino)acridine, or acridine orange (AO)) were prepared by following essentially the same procedure. An 80.2 mg (0.2 mmol) sample of complex **1** was dissolved in the minimum amount of dichloromethane (~10 mL) and reacted under stirring with the stoichiometric amount of the proper nitrogen ligand. After 30 min, pentane was added and the reaction mixture was cooled to allow precipitation. The solid precipitate was collected, washed with several small portions of cold pentane, and dried under vacuum. The yields were almost quantitative.

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(*n*-propylamine)platinum(II), *cis*(*C,N*)-[PtCl(CH_3)(DMSO)(Pr^nNH_2)] (2).** ^{1}H NMR: δ 3.49 (br s, $^2J_{PtH}$ = 58 Hz, 2H, NH_2), 3.41 (s, $^3J_{PtH}$ = 26 Hz, 6H), 2.92 (m, J_{av} = 7 Hz, 2H), 1.69 (m, J_{av} = 7 Hz, 2H), 0.98 (t, J_{av} = 7 Hz, 3H), 0.79 (s, $^2J_{PtH}$ = 83 Hz, 3H). Anal. Calcd for $C_6H_{18}ClNOPtS$: C, 18.83; H, 4.74; N, 3.66. Found: C, 19.21; H, 4.61; N, 3.80.

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(pyridine)platinum(II), *cis*(*C,N*)-[PtCl(CH_3)(DMSO)(py)] (3).** ^{1}H NMR: δ 8.73 (m, $^3J_{PtH}$ = 42 Hz, J_{av} = 5 Hz, 2H, H_2), 7.88 (m, J_{av} = 7 Hz, 1H, H_4), 7.45 (m, J_{av} = 7 Hz, 2H, H_3), 3.52 (s, $^3J_{PtH}$ = 26 Hz, 6H), 0.90 (s, $^2J_{PtH}$ = 83 Hz, 3H). Anal. Calcd for $C_8H_{14}ClNOPtS$: C, 23.85; H, 3.50; N, 3.48. Found: C, 24.02; H, 3.55; N, 3.30.

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-methylpyridine)platinum(II), *cis*(*C,N*)-[PtCl(CH_3)(DMSO)(2-Mepy)] (4).** ^{1}H NMR: δ 8.64 (dd, $^3J_{PtH}$ = 42 Hz, J_{av} = 5 Hz, 1H, H_6), 7.73 (m, J_{av} = 7 Hz, 1H), 7.36 (m, J_{av} = 7 Hz, 1H), 7.26 (m, J_{av} = 5 Hz, 1H), 3.51 (s, $^3J_{PtH}$ = 27 Hz, 6H), 3.00 (s, $^4J_{PtH}$ = 8.7 Hz, 6H, Me), 0.74 (s, $^2J_{PtH}$ = 84 Hz, 3H). Anal. Calcd for $C_9H_{16}ClNOPtS$: C, 25.93; H, 3.87; N, 3.36. Found: C, 25.80; H, 3.78; N, 3.48.

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2,6-dimethylpyridine)platinum(II), *trans*(*C,N*)-[PtCl(CH_3)(DMSO)(2,6-Me_2py)] (5).** ^{1}H NMR: δ 7.59 (t, $^3J_{HH}$ = 7 Hz, 1H, H_4), 7.14 (d, $^3J_{HH}$ = 7 Hz, 2H, H_3), 3.24 (s, $^3J_{PtH}$ = 37 Hz, 6H), 3.08 (s, $^4J_{PtH}$ = 7.3 Hz, 6H, Me), 0.71 (s, $^2J_{PtH}$ = 75 Hz, 3H). Anal. Calcd for $C_{10}H_{18}ClNOPtS$: C, 27.88; H, 4.21; N, 3.25. Found: C, 28.01; H, 4.11; N, 3.09.

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-methylquinoline)platinum(II), *trans*(*C,N*)-[PtCl(CH_3)(DMSO)(2-Mequin)] (6).** ^{1}H NMR: δ 9.78 (d, J_{av} = 9 Hz, 1H), 8.21 (d, J_{av} = 9 Hz, 1H), 7.85 (m, 2H), 7.57 (t, J_{av} = 8 Hz, 1H), 7.41 (d, J_{av} = 8 Hz, 1H), 3.30 (s, $^4J_{PtH}$ = 6.7 Hz, 3H), 3.22 (s, $^3J_{PtH}$ = 35 Hz, 3H), 3.16 (s, $^3J_{PtH}$ = 35 Hz, 3H), 0.88 (s, $^2J_{PtH}$ = 76 Hz, 3H). Anal. Calcd for $C_{13}H_{18}ClNOPtS$: C, 33.44; H, 3.89; N, 3.00. Found: C, 33.8; H, 3.95; N, 2.85.

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(5-aminoquinoline-*N1*)platinum (II), *cis*(*C,N*)-[PtCl(CH_3)(DMSO)(5-AQ-*N1*)] (7).** ^{1}H NMR: δ 9.02 (d, $^3J_{PtH}$ = 46 Hz, J_{av} = 5 Hz, 1H, H_2), 8.60 (d, J_{av} = 8 Hz, 1H, H_4), 8.34 (d, J_{av} = 8 Hz, 1H, H_8), 7.66 (m, J_{av} = 8 Hz, 1H, H_7), 7.37 (dd, $^3J_{HH}$ = 8 Hz, $^3J_{HH}$ = 5 Hz, 1H, H_3), 6.87 (d, J_{av} = 8 Hz, 1H, H_6), 4.35 (br s, 2H, NH_2), 3.60 (s, $^3J_{PtH}$ = 26 Hz, 3H), 3.56 (s, $^3J_{PtH}$ = 26 Hz, 3H), 0.79 (s, $^2J_{PtH}$ = 84 Hz, 3H). Anal. Calcd for $C_{12}H_{17}ClN_2OPtS$: C, 30.81; H, 3.66; N, 5.99. Found : C, 31.03; H, 3.5; N, 6.01.

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(3,6-bis(dimethylamino) acridine)platinum(II), *trans*(*C,N*)-[PtCl(CH_3)(DMSO)(AO)] (8).** ^{1}H NMR: δ 8.65 (d, $^4J_{HH}$ = 2 Hz, 2H, $H_{2,9}$), 8.34 (s, 1H, H_{10}), 7.69 (d, $^3J_{HH}$ = 9 Hz, 2H, $H_{5,6}$), 7.06 (dd, $^3J_{HH}$ = 9 Hz, $^4J_{HH}$ = 2 Hz, 2H, $H_{4,7}$), 3.23 (s, 12H, NMe_2), 2.90 (s, $^3J_{PtH}$ = 31 Hz, 6H), 1.13 (s, $^2J_{PtH}$ = 76 Hz, 3H). Anal. Calcd for $C_{20}H_{28}ClN_3OPtS$: C, 40.78; H, 4.79; N, 7.13. Found: C, 41.10; H, 4.61; N, 7.00.

Some of the complexes (am = *tert*-butylamine (Bu^tNH_2), diisopropylamine ($Pr^i{}_2NH_2$), triethylamine (Et_3N), 4-(dimethylamino)pyridine (4-(NMe_2)py), 2-chloropyridine (2-Clpy), 2-phenylpyridine (2-Phpy), and acridine (Acr)) were prepared *in situ* by following the same general procedure. An 8 mg (0.02 mmol) sample of complex **1** dissolved in 0.5 mL of chloroform-*d* was reacted with the stoichiometric amount of the proper nitrogen ligand in an NMR tube. All of the complexes were characterized by ^{1}H NMR spectroscopy. Some of the signals were not assignable or resolvable due to the overlap with signals of the corresponding isomer and/or the free ligand.

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(*tert*-butylamine)platinum(II), *cis*(*C,N*)-[PtCl(CH_3)(DMSO)(Bu^tNH_2)] (9A).** ^{1}H NMR: δ 3.59 (v br s, $^2J_{PtH}$ = 60 Hz, 2H, NH_2), 3.41 (s, $^3J_{PtH}$ = 27 Hz, 6H), 1.41 (s, 9H), 0.80 (s, $^2J_{PtH}$ = 83 Hz, 3H).

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(*tert*-butylamine)platinum(II), *trans*(*C,N*)-[PtCl(CH_3)(DMSO)(Bu^tNH_2)] (9B).** ^{1}H NMR: δ 3.26 (s, $^3J_{PtH}$ = 39 Hz, 6H), 1.39 (s, 9H), 0.47 (s, $^2J_{PtH}$ = 74 Hz, 3H).

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***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(diisopropylamine)-platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(Pr$^i_2$NH$_2$)] (10A).** ^{1}H NMR: δ 3.57 (m, 2H), 3.41 (s, $^3J_{PtH}$ = 26 Hz, 6H), 1.47 (d, $^3J_{HH}$ = 7 Hz, 6H), 1.36 (d, $^3J_{HH}$ = 7 Hz, 6H), 0.74 (s, $^2J_{PtH}$ = 84 Hz, 3H).

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(diisopropylamine)-platinum(II), *trans*(*C,N*)-[PtCl(CH$_3$)(DMSO)(Pr$^i_2$NH$_2$)] (10B).** ^{1}H NMR: δ 3.54 (m, 2H), 3.23 (s, $^3J_{PtH}$ = 39 Hz, 6H), 1.42 (d, $^3J_{HH}$ = 6 Hz, 6H), 1.32 (d, $^3J_{HH}$ = 6 Hz, 6H), 0.45 (s, $^2J_{PtH}$ = 75 Hz, 3H).

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(triethylamine)platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(Et$_3$N)] (11).** ^{1}H NMR: δ 3.48 (s, $^3J_{PtH}$ = 28 Hz, 6H), 3.14 (q, $^3J_{HH}$ = 7 Hz, 6H), 1.28 (t, $^3J_{HH}$ = 7 Hz, 9H), 0.76 (s, $^2J_{PtH}$ = 85 Hz, 3H).

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(4-(dimethylamino)-pyridine) platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(4-(NMe$_2$)py)] (12).** ^{1}H NMR: δ 8.18 (m, $^3J_{PtH}$ = 41 Hz, J_{av} = 7 Hz, 2H, H$_2$), 6.47 (m, J_{av} = 7 Hz, 2H, H$_3$), 3.49 (s, $^3J_{PtH}$ = 25 Hz, 6H), 3.07 (s, 6H, NMe$_2$), 0.88 (s, $^2J_{PtH}$ = 84 Hz, 3H).

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-chloropyridine)-platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(2-Clpy)] (13A).** ^{1}H NMR: δ 8.68 (m, $^3J_{PtH}$ = 43 Hz, 1H), 7.84 (m, 1H), 7.59 (m, 1H), 7.40 (m, 1H), 3.54 (s, $^3J_{PtH}$ = 28 Hz, 3H), 3.53 (s, $^3J_{PtH}$ = 29 Hz, 3H), 0.78 (s, $^2J_{PtH}$ = 83 Hz, 3H).

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-chloropyridine) platinum(II), *trans*(*C,N*)-[PtCl(CH$_3$)(DMSO)(2-Clpy)] (13B).** ^{1}H NMR: δ 8.75 (m, $^3J_{PtH}$ ~ 15 Hz, 1H), 7.79 (m, 1H), 7.53 (m, 1H), 7.38 (m, 1H), 3.33 (s, $^3J_{PtH}$ = 34 Hz, 3H), 3.24 (s, $^3J_{PtH}$ = 39 Hz, 3H), 0.77 (s, $^2J_{PtH}$ = 78 Hz, 3H).

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-phenylpyridine)-platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(2-Phpy)] (14A).** ^{1}H NMR: δ 8.94 (dd, J_{av} = 6 Hz, $^3J_{PtH}$ = 42 Hz, 1H, H$_6$), 8.06 (m, 2H), 7.92 (m, 1H), 7.60 (m, 1H), 7.53 (m, 3H), 7.44 (m, 1H), 3.47 (s, $^3J_{PtH}$ = 27 Hz, 3H), 3.23 (s, $^3J_{PtH}$ = 27 Hz, 3H), 0.29 (s, $^2J_{PtH}$ = 84 Hz, 3H).

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(2-phenylpyridine) platinum(II), *trans*(*C,N*)-[PtCl(CH$_3$)(DMSO)(2-Phpy)] (14B).** ^{1}H NMR: δ 9.01 (m, $^3J_{PtH}$ < 20 Hz, 1H, H$_6$), 8.16 (m, 2H), 3.00 (s, $^3J_{PtH}$ = 40 Hz, 3H), 2.19 (s, $^3J_{PtH}$ = 36 Hz, 3H), 0.54 (s, $^2J_{PtH}$ = 75 Hz, 3H).

***cis*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(acridine)platinum(II), *cis*(*C,N*)-[PtCl(CH$_3$)(DMSO)(Acr)] (15A).** ^{1}H NMR: δ 9.69 (d, J_{av} = 9 Hz, 2H), 9.04 (s, 1H), 8.05 (m, 4H), 7.63 (d, J_{av} = 8 Hz, 2H), 3.68 (s, $^3J_{PtH}$ = 27 Hz, 6H), 0.70 (s, $^2J_{PtH}$ = 83 Hz, 3H).

***trans*(*C,N*)-Chloromethyl(dimethyl sulfoxide)(acridine)platinum-(II), *trans*(*C,N*)-[PtCl(CH$_3$)(DMSO)(Acr)] (15B).** ^{1}H NMR: δ 9.94 (d, J_{av} = 9 Hz, 2H), 9.01 (s, 1H), 8.08 (d, J_{av} = 8 Hz, 2H), 8.01 (t, J_{av} = 9 Hz, 2H), 7.60 (d, J_{av} = 8 Hz, 2H), 3.10 (s, $^3J_{PtH}$ = 34 Hz, 6H), 1.07 (s, $^2J_{PtH}$ = 72 Hz, 3H).

Instrumentation. The NMR spectra were recorded on Bruker ARX 300, AMX 400, and WH 400 NMR spectrometers. The ^{1}H magnetization transfer measurements were performed on a Bruker ARX-300 NMR spectrometer. The probe tuning was optimized before beginning the measurements. The 180° pulse was determined by nulling the signal. The T_1 values were estimated from $5T_1-\pi-t-\pi/2$ measurements. The magnetization transfer measurements were performed using the pulse sequence $5T_1-\pi$(selective)$-t-\pi/2$(general), with t values of 0.0001, 0.001, 0.002, 0.004, 0.008, 0.016, 0.032, 0.064, 0.100, 0.200, 0.500, 1.000, 2.000, and 10.000 s. A Gaussian shaped pulse (256 points, 47 dB, 20 ms) was used for the selective ^{1}H π-pulse.

The ^{195}Pt magnetization transfer measurements were performed on a Bruker ARX-300 NMR spectrometer operating at 64.2 MHz, and referenced to Ξ 21.4, with high frequency taken as being positive. The probe tuning was optimized before beginning the measurements. The 180° pulse was determined by nulling the signal. The T_1 values were estimated from $5T_1-\pi-t-\pi/2$ measurements. The magnetization transfer measurements were performed using the pulse sequence $5T_1-\pi$(selective)$-t-\pi/2$(general) pulse sequence, with t values of 0.000003, 0.001, 0.002, 0.004, 0.008, 0.016, 0.032, 0.064, 0.100, 0.200, and 1.0 s. A Gaussian shaped pulse (256 points, 29 dB, 1 ms) was used for the selective ^{195}Pt π-pulse.

Variable temperature measurements were obtained by using a Bruker standard accessory. The temperature within the probe was checked by the methanol or ethylene glycol method.[16]

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Table 1. Crystallographic Data

formula	$C_9H_{27}Cl_3O_3PtS_2Sn_2$	V, Å^3	1105.5(4)
fw	786.25	Z	2
cryst syst	triclinic	ρ_{calcd}, g/cm^3	2.362
space group	$P\bar{1}$	T, °C	23
a, Å	9.373(2)	μ, cm^{-1}	9.106
b, Å	9.576(1)	R	0.024
c, Å	14.087(3)	R_w[a]	0.058
α, deg	70.29(1)		
β, deg	72.50(1)		
γ, deg	72.21(2)		

[a] $w = [\sigma^2(F_o^2) + (0.0372P)^2 + 0.45P]^{-1}$ with $P = [\max(0,F_o^2) + 2F_c^2]/3$.

X-ray Data Collection and Structure Refinement. A colorless crystal was mounted on a glass fiber, and the corresponding X-ray diffraction measurements were performed at room temperature with a Siemens R3m/v automatic four-circle diffractometer using graphite-monochromated Mo Kα radiation. Cell parameters were obtained by least-squares refinement of the setting angles of 25 accurately centered reflections with $15° \le 2\theta \le 30°$. Data collection was performed up to $2\theta = 55°$ by the variable-speed $w-2q$ scan method, measuring 5928 reflections of which 4843 were unique (R_{int} = 2.37%). The intensities of three standard reflections, monitored after every 197 measurements, showed only statistical fluctuations. The reflection intensities were corrected for Lorentz−polarization and absorption effects.[17]

The structure was solved by standard Patterson methods and subsequently completed by a combination of least-squares technique and Fourier syntheses by using SHELXTL-PLUS.[18] Subsequently the model refinement was carried out with SHELXL-93[19] by full-matrix least-squares technique based on F^2. A set of 2505 reflections was considered and observed by the threshold $F_o \ge 7\sigma(F_o)$, with resolution up to 0.9 Å.

The hydrogen atoms, even though most of them appeared on the difference syntheses, were generated in calculated positions by considerations based on stereochemistry with an unique fixed isotropic thermal parameter (U_{iso} = 0.080 Å^2), and during the refinement they were allowed to ride on their respective parent carbons, which type determines the fixed length of the corresponding C−H bonds. The structure model, with all non-hydrogen atoms anisotropic, was refined by minimizing the function $\sum w(F_o^2 - F_c^2)^2$ with convergence to $R = \sum|F_o - F_c|/\sum|F_o| = 0.024$ and $R' = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2} = 0.046$ with the final weighting scheme $w^{-1} = [\sigma^2(F_o^2) + (0.0372P)^2 + 0.45P]$ with $P = (\max(0,F_o^2) + 2F_c^2)/3$ and by considering an extinction parameter refined to 0.0021(2).

The last difference map showed some significant electron density residuals (maximum = 1.25 e Å^{-3}) at about 1 Å from the platinum and tin atoms. Neutral-atom scattering factors and anomalous dispersion corrections, automatically used by the program, come from ref 20.

Data reduction and drawings were performed with the Siemens SHELXTL-PLUS package, while the final geometrical calculations were carried out with the PARST program[21] on a DEC MicroVax/3400 computer.

Table 1 reports the details of the crystallographic measurements. Results are given in Table 2.

Results and Discussion

The synthesis of the complex *trans*-[PtCl(CH$_3$)(DMSO)$_2$] was reported by Eaborn *et al.*[9] by reacting *cis*-[PtCl$_2$(DMSO)$_2$] with a 2-fold quantity of tetramethyltin as methylating agent. The reaction is conducted in dimethyl sulfoxide as solvent at 80 °C for an average time of 24 h, and the yields (ranging from 20 to

(17) Kopfmann, G.; Huber, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *24*, 348.
(18) *SHELXTL-PLUS*, Version 4.2; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1991.
(19) Sheldrick, G. M. *SHELXL-93, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1994.
(20) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C.
(21) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95 (version locally modified).

Table 2. Selected Bond Distances (Å), Bond Angles (deg) and Torsion Angles (deg)

Bond Distances			
Pt−C(1)	2.049(7)	Pt−Cl(1)	2.416(2)
Pt−S(1)	2.261(2)	Pt−S(2)	2.257(2)
S(1)−O(1)	1.470(5)	S(1)−C(2)	1.767(7)
S(1)−C(3)	1.774(8)	S(2)−O(2)	1.473(5)
S(2)−C(4)	1.776(8)	S(2)−C(5)	1.787(8)
Sn(1)−O(3)	2.047(5)	Sn(1)−C(8)	2.088(8)
Sn(1)−O(3)′	2.102(5)	Sn(1)−C(9)	2.104(8)
Sn(1)−Cl(2)	2.890(3)	Sn(1)···Cl(3)′	3.293(3)
Sn(1)···Sn(1)′	3.295(1)	Sn(2)−O(3)	2.029(5)
Sn(2)−C(7)	2.094(8)	Sn(2)−C(6)	2.096(7)
Sn(2)−Cl(3)	2.521(2)	Sn(2)−Cl(2)	2.736(2)
Sn(2)···Cl(1)	3.442(2)		
Angles			
C(1)−Pt−S(2)	89.7(2)	C(1)−Pt−S(1)	89.6(2)
S(2)−Pt−S(1)	176.80(7)	C(1)−Pt−Cl(1)	178.2(3)
S(2)−Pt−Cl(1)	90.04(7)	S(1)−Pt−Cl(1)	90.76(6)
Pt−Cl(1)−Sn(2)	124.41(7)	O(1)−S(1)−C(2)	107.9(3)
O(1)−S(1)−C(3)	108.1(4)	C(2)−S(1)−C(3)	101.5(4)
O(1)−S(1)−Pt	120.2(2)	C(2)−S(1)−Pt	107.4(3)
C(3)−S(1)−Pt	110.0(3)	O(2)−S(2)−C(4)	107.4(4)
O(2)−S(2)−C(5)	107.8(4)	C(4)−S(2)−C(5)	102.3(5)
O(2)−S(2)−Pt	119.4(2)	C(4)−S(2)−Pt	109.8(3)
C(5)−S(2)−Pt	108.8(3)	O(3)−Sn(1)−C(8)	111.2(3)
O(3)−Sn(1)−C(9)	110.0(3)	C(8)−Sn(1)−C(9)	135.1(4)
O(3)′−Sn(1)−C(9)	102.6(3)	O(3)−Sn(1)−Cl(2)	74.5(2)
O(3)−Sn(2)−C(7)	106.5(3)	O(3)−Sn(2)−C(6)	104.1(3)
C(7)−Sn(2)−C(6)	147.8(3)	O(3)−Sn(2)−Cl(3)	86.5(2)
C(7)−Sn(2)−Cl(3)	93.7(3)	C(6)−Sn(2)−Cl(3)	97.7(2)
O(3)−Sn(2)−Cl(2)	78.4(2)	C(7)−Sn(2)−Cl(2)	88.4(3)
C(6)−Sn(2)−Cl(2)	88.4(2)	Cl(3)−Sn(2)−Cl(2)	164.70(8)
Cl(1)···Sn(2)−C(7)	77.0(3)	Cl(1)···Sn(2)−C(6)	72.2(2)
Cl(1)···Sn(2)−O(3)	176.3(2)	Cl(1)···Sn(2)−Cl(3)	94.23(8)
Cl(1)···Sn(2)−Cl(2)	101.00(7)	Sn(2)−Cl(2)−Sn(1)	80.56(6)
Sn(2)−O(3)−Sn(1)	126.5(3)	Sn(2)−O(3)−Sn(1)′	128.3(3)
Sn(1)−O(3)−Sn(1)′	105.2(2)		
Torsion Angles			
S(1)−Pt−S(2)−O(2)	74(1)	Cl(1)−Pt−S(2)−O(2)	178.8(3)
S(1)−Pt−S(2)−C(4)	−161(1)		

45%) depend on both the time and the control of the temperature. The original assignment[9] of the *trans* geometry was based on the presence of a single band for the ν_{PtCl} stretching frequency in the IR spectrum (275 cm^{-1}) and of a simple pattern for the coordinated dimethyl sulfoxide in the ^1H NMR spectrum.

Crystal Structure. Several attempts at growing crystals of pure samples of complex **1** from different solvents, were unsuccessful. Crystals suitable for X-ray analysis were obtained on cooling a solution of the crude reaction product in dichloromethane.

The solid state analysis reveals that the platinum(II) complex **1** cocrystallizes with the polynuclear tin(IV) compound bis(μ-3-oxo)bis(μ-chloro)-bis(μ-dimethyltin(IV))bis(chlorodimethyltin(IV)) $[Cl(CH_3)_2SnOSn(CH_3)_2Cl]_2$. The crystal structure of the title compound is constituted by two platinum complexes that are interacting with a central distannoxane moiety through a Pt−Cl−Sn interaction (Figure 1). While the molecular structure of *trans*-$[PdCl_2(DMSO)_2]$ has been known for many years,[22] this determination is, to the best of our knowledge, the first study on the crystal structure of a *trans*-(dimethyl sulfoxide)-platinum(II) compound. The platinum atom displays, at first glance, a square-planar coordination. The weighted least-squares plane through the Pt and the four atoms of the coordination sphere indicates that this portion of the molecule slightly deviates from planarity toward a tetrahedral arrangement of the metal (deviations (Å): Pt, 0.0060(5); C(1), 0.072(1); S(1), −0.052(2); S(2), −0.058(2); Cl(1), 0.003(2)). The Pt complex

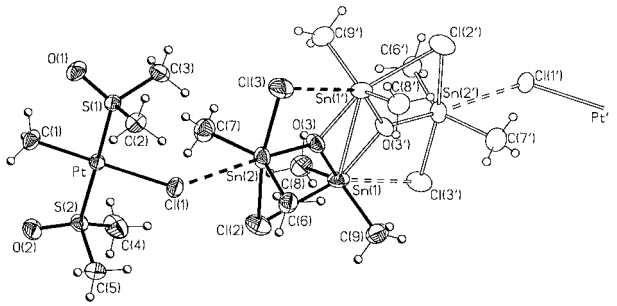

Figure 1. ORTEP drawing of the 2:1 aggregate between *trans*-$[PtCl(CH_3)(DMSO)_2]$ and $[Cl(CH_3)_2SnOSn(CH_3)_2Cl]_2$, showing the labeling of the non-H atoms. Thermal ellipsoids are drawn at the 40% probability level.

geometry is close to the mirror symmetry with the sulfoxide O(1) and O(2) atoms almost lying on the coordination mean plane. As can be seen from the O(1)−S(1)−Pt−C(1) and O(2)−S(2)−Pt−C(1) torsion angles, 3.0(4) and 2.9(4)°, respectively, both the oxygen atoms are oriented toward the methyl group $C(1)H_3$. Such an orientation avoids the hindering effects of the DMSO methyl groups on $C(1)H_3$ and, at the same time, favors short (O(1)···C(1) = 3.09(1) Å and O(2)···C(1) = 3.07(1) Å) interactions. Both DMSO ligands are coordinated through the S atom to the metal center, as expected.

The Pt−S(1) and Pt−S(2) bond distances, 2.261(2) and 2.257(2) Å, respectively (mean 2.259(2) Å), are shorter than the corresponding mean value 2.292(3) Å reported for the complex *trans*-dichlorobis(di-*n*-propyl sulfoxide)platinum(II)[23] that is the unique example of a *trans*-bis(sulfoxide)platinum(II) compound reported so far. Since in both complexes relevant steric repulsions of the sulfoxide groups are not seen with the other two adjacent ligands, this difference in the *trans* Pt−S distances seems to be due entirely to the different electron-donor ability of the alkyl substituents on the sulfur atom. Unfortunately, the lack of other structural data does not allow one to ascertain whether this trend is confirmed and to search for a correlation between the electron-donating characteristics of the substituents and the ground-state *trans* influence of various sulfoxides.

A number of investigations on the *trans* influence of sulfoxides did not show significant lengthening of the *trans* Pt−Cl bonds, which varied in the limits of the statistical significance.[4] Further investigations[24] suggested that in $[PtCl_3L]^-$ complexes the Pt−Cl bond *trans* to L becomes weaker in the order PEt_3 > DMSO >ethylene > amines, Cl^-. However, when a statistically more consistent set of data is considered,[25] it is confirmed that the *trans* influence of DMSO relative to chloride is very weak (the mean Pt−Cl bond length increases from 2.299(2) Å, when *trans* to Cl, O, or N ligands, to 2.312(1) Å, when *trans* to S). It is interesting therefore to look at the *trans* influence relative to the Pt−DMSO bond. Inspection of the Pt−S bond distances of almost 50 compounds[25] having only one S bonded sulfoxide per metal atom gives an average of 2.207(3) Å, spanning in a rather wide range (from 2.168(2) to 2.257(8) Å). The Pt−S distances observed for the two *trans* sulfur bonded DMSO groups (2.261−2.257 Å) are considerably longer than those observed for Pt−DMSO distances *trans* to oxygen-bonded DMSO in the tetrakis(dimethyl sulfoxide)-platinum(II) cation (2.205−2.208 Å)[26] and still longer than those *trans* to chloride (2.185−2.233 Å) and *trans* to nitrogen (2.209−2.224 Å) . Only the Pt−S distances *trans* to a strong σ-donor

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(25) Caligaris, M.; Carugo, O. *Coord. Chem. Rev.* **1996**, *153*, 1−23.
(26) Elding, L. I.; Oskarsson, A. *Inorg. Chim. Acta* **1987**, *130*, 209.

Pt−C(phenyl) bond are considerably longer (2.315−2.324 Å).[27] Thus, a *trans* influence order for platinum of O < N ≅ Cl < S < C can be derived, if *cis* effects and packing forces are considered of minor importance as compared to the *trans* influence.

The Pt−C(1) bond (2.049(7) Å) is comparable with the corresponding distance (2.056(5) Å) found in the cation [Pt(CH$_3$)(1,10-phenanthroline)(DMSO)]$^+$ [28] where a pyridine nitrogen is in the *trans* position with respect to the methyl group, while it is somewhat shorter than the distances usually reported in other *trans*-chloromethylplatinum complexes.[29] The C(1)−Pt-S(1) and C(1)−Pt−S(2) bond angles, like other bond angles at the metal center, are nearly the ideal values denoting the absence of steric strains in the Pt fragment. The tetrahedral-distorted arrangement and the geometric features of the sulfurs (mean values: S−O = 1.471(5) Å and S−C = 1.776(8) Å) agree with the values reported for other Pt−DMSO complexes.[25] The Pt−Cl bond length (2.416(2) Å) is significantly longer than the distances usually reported, because of both the strong *trans* influence of the opposite methyl group and the interaction with one tin atom of the distannoxane system (Cl(1)−Sn(2) = 3.442-(2) Å). This interaction and the ensuing presence of the stannoxane seem to play a crucial role in the formation and in the stabilization of the crystal lattice.

A molecular structure of the distannoxane fragment has been already reported in the literature.[30] It reflects the well-known property of the association of organotin units by oxygen bridges and consists of [ClMe$_2$SnOSnMe$_2$Cl]$_2$ dimeric units with crystallographic inversion point at the center. The central part of the unit consists of a four-membered Sn(1)O(3)Sn(1′)O(3′) ring. On this plane the other two exocyclic tins Sn(2) and Sn-(2′) are aligned. All tin atoms display a distorted arrangement between the octahedral and trigonal-bipyramidal limiting geometries. The presence of a square-planar platinum(II) moiety in the lattice does not seem to produce significant effect on bond distances and bond angles of the distannoxane fragment (the highest angle difference regards C(6)−Sn(2)−C(7): 147.8-(3)° *vs* 140.6(9)°, respectively).

The molecular packing (Figure SI 1, Supporting Information)) is mainly determined by van der Waals interactions and by weak intermolecular hydrogen bonds.

NMR Measurements. The ^{1}H NMR spectrum of [PtCl-(CH$_3$)(DMSO)$_2$] in CDCl$_3$ at 273 K is shown in Figure 2a. The spectrum showed signals due to DMSO at δ 3.49 ($^3J_{PtH}$ = 36 Hz), 3.42 ($^3J_{PtH}$ = = 24 Hz), 3.34 ($^3J_{PtH}$ = 36 Hz), 3.32 ($^3J_{PtH}$ = 36 Hz), 3.21 ($^3J_{PtH}$ = 8 Hz), and 2.58, and Pt−Me signals at δ 1.17, ($^2J_{PtH}$ = 73 Hz), 0.98 ($^2J_{PtH}$ = 80 Hz), and 0.93 ($^2J_{PtH}$ = 86 Hz). The ^{195}Pt NMR spectrum of the same solution showed signals at δ 645, 629, 422, and 151, see Figure 3. The ^{13}C NMR spectrum is closely similar to the proton spectrum. In fact it exhibits different series of slightly broad signals: (i) a singlet at δ −1.8 ($^1J_{PtC}$ = 660 Hz) for a methyl group and a singlet with satellite peaks at δ 44.4 ($^2J_{PtC}$ = 59 Hz) consistent with a S bonded dimethyl sulfoxide; (ii) a singlet at δ 0.5 (no coupling constant was detected even at low temperature) and two different singlets at δ 46.4 ($^2J_{PtC}$ = 70 Hz) and 44.1 ($^2J_{PtC}$ = 19 Hz) for two different S bonded dimethyl sulfoxides; (iii) only a minor species is detected at δ 45.9 (no coupling constants were observable); (iv) a singlet at δ 40.9 due to free dimethyl sulfoxide.

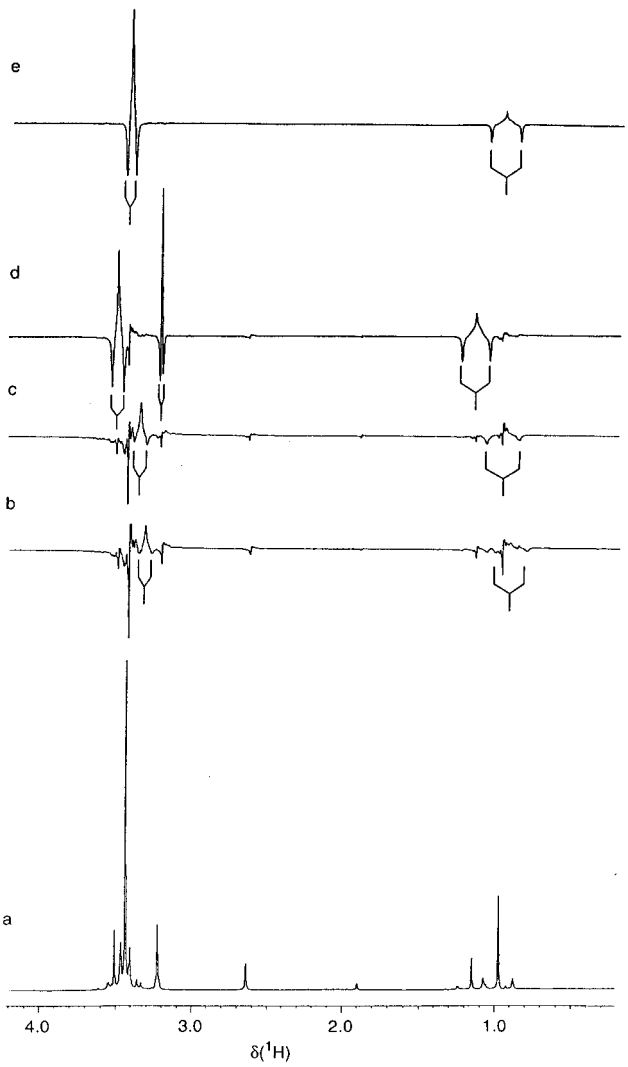

Figure 2. (a) 300.13 MHz ^{1}H NMR spectrum of [PtCl(CH$_3$)(DMSO)$_2$] in CDCl$_3$ at 273 K. (b−e) Difference spectra between spectrum a and spectra recorded with ^{195}Pt decoupling (b) at δ 645, (c) at δ 629, (d) at δ 422, and (e) at δ 151.

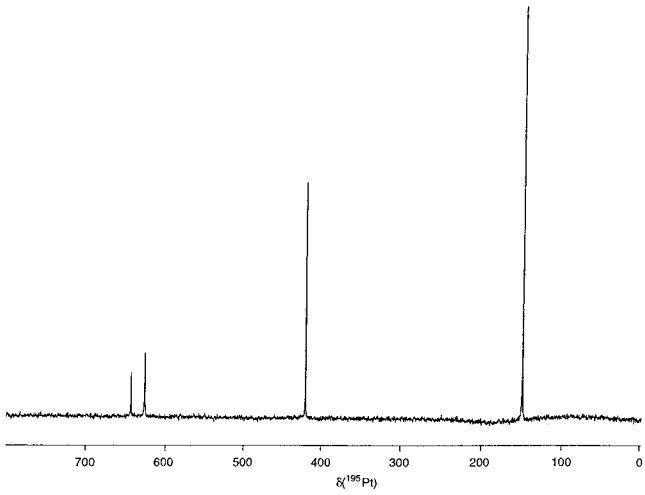

Figure 3. 64.2 MHz ^{195}Pt NMR spectrum of [PtCl(CH$_3$)(DMSO)$_2$] in CDCl$_3$ at 296 K.

The ^{195}Pt NMR signals were tied to the ^{1}H NMR signals by selective ^{195}Pt decoupling (see Figure 2), and the results are summarized in Table 3. Clearly there are four species present. The major species has been unambiguously identified. The X-ray structure clearly demonstrates that *trans*-[PtCl(CH$_3$)-(DMSO-*S*)$_2$] is present in the crystal. When some of these

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(29) (a) Goel, A. B.; Goel, S.; van Derveer, D. *Polyhedron* **1984**, *3*, 373. (b) Bardi, R.; Piazzesi, A. M. *Inorg. Chim. Acta* **1981**, *17*, 249.
(30) Harrison, P. H.; Begley, M. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *186*, 213, and references cited therein.

Table 3. ^{1}H and ^{195}Pt NMR Data for the Four Species Present in a Solution of $[PtCl(CH_3)(DMSO)_2]$ in $CDCl_3$ at 273 K

compound	δ (DMSO), ppm ($^3J_{PtH}$, Hz)	δ (Pt−CH_3), ppm ($^2J_{PtH}$, Hz)	δ (^{195}Pt),[a] ppm
trans-$[PtClMe(DMSO)_2]$	3.42 (24)	0.98 (80)	151
cis-$[PtClMe(DMSO)_2]$	3.49 (36); 3.21 (8)	1.17 (73)	422
cis-$[PtClMe(DMSO)(OH_2)]$	3.34 (36)	0.98 (87)	629
trans-$[PtClMe(DMSO)(OH_2)]$	3.32 (36)	0.93 (83)	645

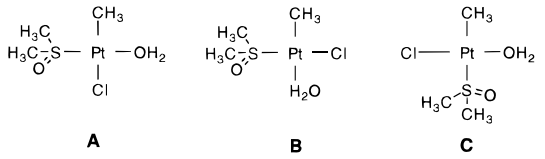
[a] The corresponding shifts relative to $[PtCl_6]^{2-}$ are, in parentheses, δ 151 (−4352), 422 (−4082), 629 (−3876), and 645 (−3860).

crystals are dissolved in $CD_2Cl_2/CDCl_3$ at 190 K, only one species is detected in the ^{1}H NMR spectrum at low temperature at δ 3.42 ($^3J_{PtH}$ = 24 Hz) and 0.98 ($^2J_{PtH}$ = 80 Hz). On warming to room temperature, the other three species appear in the ^{1}H NMR spectrum. Decoupling the ^{195}Pt at δ 151 removes ^{195}Pt coupling from these signals (see Figure 2e, where the effect of ^{195}Pt decoupling is shown as a difference spectrum).

When the ^{195}Pt NMR signal at δ 422 is decoupled, coupling is removed from the DMSO ^{1}H NMR signals at δ 3.49 and 3.21, and the methyl signal at δ 1.17 (see Figure 2d). Both of these DMSO signals show substantial $^3J_{PtH}$ coupling constants, showing that they are both S bonded. Therefore, this species is *cis*-$[PtCl(CH_3)(DMSO\text{-}S)_2]$. The *trans*-influence of methyl and chloride permits the assignment of the DMSO signals.[31] The DMSO signal at δ 3.49, $^3J_{PtH}$ = 36 Hz, must arise from DMSO *trans* to chloride, and that at δ 3.21, $^3J_{PtH}$ = 8 Hz, is due to DMSO *trans* to methyl.

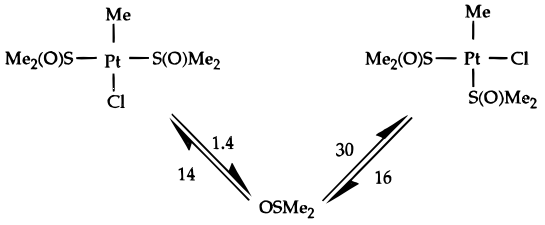
There are a number of possibilities for the remaining two minor species. Each one has only one type of DMSO bonded to the platinum, and the $^3J_{PtH}$ coupling constants show that the DMSO ligands are S bonded. The two possible dimers $[Pt_2(CH_3)_2(DMSO\text{-}S)_2(\mu\text{-}X)_2]$ (X = Cl, OH) can be rejected as the ^{1}H and ^{13}C NMR spectra of the compounds would show $[A_3X]_2$ (for the Me−Pt) and $[A_6X]_2$ (for the DMSO) signals due to the $[^{195}Pt_2(CH_3)_2(DMSO\text{-}S)_2(\mu\text{-}X)_2]$ isotopomer, and no such signals were detected.[32] The most reasonable interpretation is that the two compounds are isomers of $[PtCl(CH_3)(OH_2)(DMSO)]$.[33] Addition of DMSO to the solution leads to the disappearance of the signals of the aqua species. This hypothesis is further supported by the observation that the ^{195}Pt NMR spectrum of a sample of complex in D_2O exhibits a completely reversed pattern for the intensities of the peaks; see Figure SI 2 (Supporting Information). The signals have moved to low frequency, presumably as a result of a solvent shift. The major signals are at δ 611 and 602 and are probably the two isomers of $[PtCl(CH_3)(OH_2)(DMSO)]$ observed in $CDCl_3$. The signal at δ 112 is probably due to *trans*-$[PtCl(CH_3)(DMSO)_2]$. New unassigned signals are observed at δ 824 and 540. Easy hydrolysis of the dialkyl $[Pt(CH_3)_2(DMSO)_2]$ complex has already been reported.[35]

There are three isomers possible, **A**−**C**. Isomer **C** can be eliminated as $^3J_{PtH}$ for the DMSO protons is comparable to that found in both *cis*- and *trans*-$[PtCl(CH_3)(DMSO)_2]$ for the DMSO *trans* to Cl or DMSO. In *cis*-$[PtCl(CH_3)(DMSO)_2]$, the large *trans*-influence of the methyl group on the *trans* DMSO causes the $^3J_{PtH}$ coupling constant to be 8 Hz.



Magnetization transfer measurements were performed on *trans*- and *cis*-$[PtCl(CH_3)(DMSO)_2]$ in $CDCl_3$ at 298 K, using ^{1}H NMR spectroscopy. The signal at δ 2.58 due to free DMSO was inverted and the transfer to the sites at δ 3.42 and 3.21 monitored. No transfer to the DMSO signal at δ 3.49 was detected, showing that the DMSO *trans* to chloride in *cis*-$[PtCl(CH_3)(DMSO)_2]$ does not exchange at a significant rate. The signals at δ 3.32 and 3.34 were too weak to observe if transfer occurred and partially obscured at 298 K by the broadened signals due to the major *cis*- and *trans*-$[PtCl(CH_3)(DMSO)_2]$ isomers. No direct exchange was detected between *cis*- and *trans*-$[PtCl(CH_3)(DMSO)_2]$. The results of the analysis are shown in Scheme 1.

Scheme 1. Results of the ^{1}H Magnetization Transfer Measurements on $[PtCl(CH_3)(DMSO)_2]$ at 298 K (Rates (s^{-1}) for Exchange of DMSO)



The most interesting feature that emerges from the rate data in Scheme 1 is the great dependence of the lability of the various S-bonded DMSO upon the nature of the *trans* group. The sequence is as follows: CH_3 > DMSO ≫ Cl. The somewhat high *trans* labilizing effect of a molecule of DMSO toward another *trans* DMSO is not unexpected, in view of the known experimental difficulty in synthesizing bis(dimethyl sulfoxide) complexes of *trans* geometry.

Magnetization transfer measurements were performed on $[PtCl(CH_3)(DMSO)_2]$ in $CDCl_3$ at 298 K, using ^{195}Pt NMR spectroscopy. The aim was to check for the involvement of the minor aqua-species in the exchange. The signals at δ 151, 422, and 629 were selectively inverted in three separate magnetization transfer experiments. The three sets of data were combined and were analyzed using the previously published program.[36] As the exchange is fast compared with T_1 of the ^{195}Pt, the relaxation is averaged over the sites. However, the ^{195}Pt T_1 values were determined at 273 K, and the ratio of the values was imposed on the fitting program. The derived rate constants were found to be insensitive to the relative values chosen for the T_1 (^{195}Pt). No significant rate of exchange was detected between the sites at δ 151 and 422. The results are summarized in Scheme 2.

(31) Pregosin, P. S. *Annu. Rep. NMR Spectrosc.* **1986**, *17*, 285.
(32) $J(^{195}Pt^{195}Pt)$ is expected to be larger than 100 Hz; see: (a) Boag, N. M.; Browning, J.; Crocker, C.; Goggin, P. L.; Goodfellow, R. J.; Murray, M.; Spencer, J. L. *J. Chem. Res., Synop.* **1978**, 228. (b) Kiffen, A. A.; Masters, C.; Visser, J. P. *J. Chem. Soc., Dalton Trans.* **1975**, 1311. (c) Huis, R.; Masters, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1796.
(33) Although the solvents for the synthesis were dried, the NMR solvents were not, and the ^{1}H NMR spectrum has a signal attributable to water at δ = 1.60.
(34) The corresponding shifts relative to $[PtCl_6]^{2-}$ are δ 824 (−3682), 611 (−3894), 602 (−3903), 540 (3964), and 112 (−4391).
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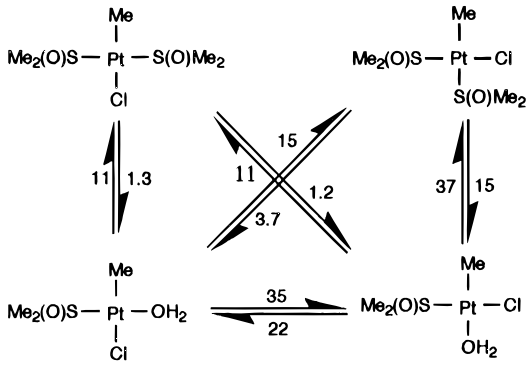
Table 4. Selected ^{1}H NMR Data for Platinum(II) Complexes of the Type [Pt(Me)Cl(DMSO)(am)] in Chloroform-*d*[a]

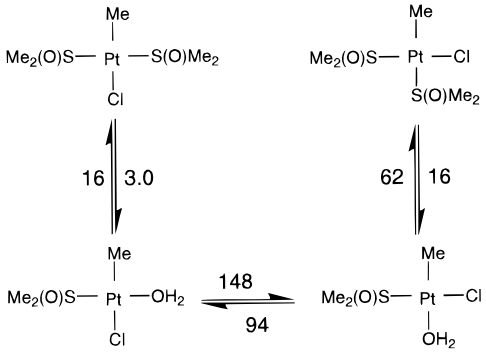
complex	am	δ(Pt−CH$_3$), ppm ($^2J_{PtH}$, Hz)	δ(Me$_2$SO), ppm ($^3J_{PtH}$, Hz)	δ(aromatics),[b] ppm ($^3J_{PtH}$, Hz)	others
2 (*cis-C,N*)	Pr^{n}NH$_2$	0.79 (83)	3.41 (26)		3.49 (58)[c] (NH$_2$)
3 (*cis-C,N*)	py	0.90 (83)	3.52 (26)	8.73 (42)	
4 (*cis-C,N*)	2-Mepy	0.74 (84)	3.51 (27)	8.64 (42)	3.00 (8.7)[d] (Me)
5 (*trans-C,N*)	2,6-Me$_2$py	0.71 (75)	3.24 (37)		3.08 (7.3)[d] (Me)
6 (*trans-C,N*)	2-Mequin	0.88 (76)	3.16 (35)		3.30 (6.7)[d] (Me)
			3.22 (35)		
7 (*cis-C,N*)	5-AQ-*N1*	0.79 (84)	3.60 (26)	9.02 (46)	4.35 (NH$_2$)
			3.56 (26)		
8 (*trans-C,N*)	AO	1.13 (76)	2.90 (31)		3.23 (NMe$_2$)
9A (*cis-C,N*)	Bu^{t}NH$_2$	0.80 (83)	3.41 (27)		3.59 (60)[c] (NH$_2$)
9B (*trans-C,N*)	Bu^{t}NH$_2$	0.47 (74)	3.26 (39)		
10A (*cis-C,N*)	Pr$^i_2$NH	0.74 (84)	3.41 (26)		
10B (*trans-C,N*)	Pr$^i_2$NH	0.45 (75)	3.23 (39)		
11 (*cis-C,N*)	Et$_3$N	0.76 (85)	3.48 (28)		
12 (*cis-C,N*)	4-(NMe$_2$)py	0.88 (84)	3.49 (25)	8.18 (41)	3.07 (NMe$_2$)
13A (*cis-C,N*)	2-Clpy	0.78 (83)	3.54 (28)	8.68 (43)	
			3.53 (29)		
13B (*trans-C,N*)	2-Clpy	0.77 (78)	3.33 (34)	8.75 (∼15)	
			3.24 (39)		
14A (*cis-C,N*)	2-Phpy	0.29 (84)	3.47 (27)	8.94 (42)	
			3.23 (27)		
14B (*trans-C,N*)	2-Phpy	0.54 (75)	3.00 (40)	9.01 (<20)	
			2.19 (36)		
15A *cis-C,N*)	Acr	0.70 (83)	3.68 (27)		
15B (*trans-C,N*)	Acr	1.07 (72)	3.10 (34)		

[a] Chemical shifts are reported in parts per million units downfield from Me$_4$Si. [b] H$_6$ on the pyridine ring. [c] $^2J_{^{195}Pt^1H}$. [d] $^4J_{^{195}Pt^1H}$.

Scheme 2. Results of the ^{195}Pt Magnetization Transfer Measurements on [PtCl(CH$_3$)(DMSO)$_2$] at 298 K (rates in s^{-1})



Scheme 3. Alternative Exchange Mechanism Compatible with ^{195}Pt Magnetization Transfer Measurements on [PtCl(CH$_3$)(DMSO)$_2$] at 298 K (rates in s^{-1})



The kinetic data in Schemes 1 and 2 permit the assignment of the compounds with ^{195}Pt chemical shifts at δ 645 and 629. The ^{1}H NMR magnetization transfer data shows that the DMSO *trans* to methyl in *cis*-[PtCl(CH$_3$)(DMSO)$_2$] is lost at 16 s^{-1}, while the ^{195}Pt NMR data shows that *cis*-[PtCl(CH$_3$)(DMSO)$_2$] is converted to the compound with δ(^{195}Pt) 629 at 15 s^{-1}. It is therefore probable that this compound is **B**. This leaves the compound with δ(^{195}Pt) of 645 to be **A**. The rate of exchange between *trans*-[PtCl(CH$_3$)(DMSO)$_2$] and **A** and **B** of (1.3 + 1.2) s^{-1} is close to double that of the rate of DMSO leaving *trans*-[PtCl(CH$_3$)(DMSO)$_2$]. This arises as either DMSO can leave *trans*-[PtCl(CH$_3$)(DMSO)$_2$] and convert it to **A** or **B**, but only one DMSO exchanges with free DMSO.

The magnetization transfer data are not very sensitive to the presence of exchange between *trans*-[PtCl(CH$_3$)(DMSO)$_2$] and **B** and between *cis*-[PtCl(CH$_3$)(DMSO)$_2$] and **A**. The data can also be fitted with the rates in Scheme 3 with only a small increase in the error between the experimental and calculated data. Attempts to fit the data with **A** and **B** reversed gave a far worse fit.

A comparison of Schemes 2 and 3 shows that the calculated rates are sensitive to the exchange mechanisms assumed in the analysis and should not be taken as being accurate. The problem arises as a result of the rapid exchange between **A** and **B**. The significance of the result is not the absolute rate constants but that DMSO exchange and isomerization of [PtCl(CH$_3$)(DMSO)$_2$] is strongly catalyzed by adventitious water in the solvent. The absolute rates will depend on the quantity of water present.

Reactivity toward Nitrogen Ligands. The addition of the equimolar amount of a nitrogen ligand am to a dichloromethane or chloroform solution of complex **1** led to the rapid substitution of one sulfoxide ligand yielding the species [PtCl(CH$_3$)(DMSO)(am)] containing four different groups coordinated to the platinum(II) center. This neutral reaction product is the only species obtained, even in the presence of a large excess of added ligand. Depending on the electronic and steric properties of the ligand, different patterns of behavior can be recognized: (i) fast build-up of a stable isomer; (ii) fast formation of an isomer that interconverts very slowly; (iii) the formation of an equilibrium mixture containing both isomers and the starting material. Some of these complexes (**2**−**8**) have been isolated as solids and fully characterized by elemental analyses and ^{1}H NMR spectroscopy. All of the other compounds (**9**−**15**) were prepared directly *in situ* and characterized by ^{1}H NMR spectroscopy. Table 4 reports the most relevant NMR data. Again, three different isomers are possible, and for the sake of comparison we refer to the same geometrical arrangement used for the aqua species (**A**−**C**, see structure diagram). Isomer **C**

can be ruled out as the $^3J_{PtH}$ coupling constants for the coordinated dimethyl sulfoxide are in the range 25−40 Hz, which is well above the usual values observed for a DMSO ligand *trans* to a methyl group. The assignment to the **A** isomer (amine *cis* to the methyl group, *cis*(*C*,*N*)) or to the **B** isomer (amine *trans* to the methyl group, *trans*(*C*,*N*)) can be made, in the case of pyridine or substituted pyridines, on the basis of the magnitude of the values observed for the $^3J_{PtH}$ coupling constants on the H_6 hydrogen of the aromatic ring. This criterion has been applied recently to the complex $[Pt(CH_3)(phen)(DMSO)]^+$ (phen = 1,10-phenanthroline) to distinguish the H_2 proton (*trans* to the methyl group, $^3J_{PtH}$ = 16.5 Hz) from the H_9 proton (*trans* to DMSO) which shows satellite peaks due to ^{195}Pt coupling at a much higher frequency ($^3J_{PtH}$ = 44 Hz).[37] For example, in the case of the ligand 2-Clpy, the isomer **B** (*trans*(*C*,*N*)) can be recognized from the H_6 peak at δ 8.75 with a $^3J_{PtH}$ coupling constant of about 15 Hz. A further distinction between isomers **A** and **B** can be made on the basis of the values of the coupling constants of the coordinated dimethyl sulfoxide, whether in *trans* position to an amine (*cis*(*C*,*N*)) or to a chloride (*trans*(*C*,*N*)). These $^3J_{PtH}$ values for the **A** isomers (*cis*(*C*,*N*)) are all characterized by values ranging from 25 to 29 Hz. In this latter configuration, the bond axis $CH_3-Pt-Cl$ of the starting *trans*-$[PtCl(CH_3)(DMSO)_2]$ complex is maintained and therefore the $^2J_{PtH}$ coupling constants for the methyl groups, all in the range 83−85 Hz, give a further indication of the geometry of the compounds.

The ^{1}H NMR spectra of the complexes containing the ligands 2-Clpy, 2-Phpy, 2-Mequin, and 5-AQ-*N1* exhibit a double peak for the coordinated DMSO. These findings suggest that, as expected, the torsion angle between the coordination plane and the plane of the ligand must be significantly high (the values of torsion angles for platinum−pyridine complexes are all within the range 45−60°)[38] and that the rotation of the ligand around the Pt−N bond is slow in the NMR time scale. Under these circumstances the two methyl groups become diastereotopic and give two distinct resonances.

In the case of the most sterically hindered ligands, such as 2-Mequin, AO, 2,6-Me_2py, and Acr, the **B** isomer is the only detectable species in solution. The presence of a methyl group and/or of a condensed aromatic ring in both of the *ortho* positions with respect to the donor nitrogen atom seems to be a prerequisite for the isolation of complexes in a *trans*(*C*,*N*) configuration. With less sterically demanding ligands such as 2-Clpy an equilibrium mixture containing unreacted complex **1** and both of the two isomers of $[PtCl(CH_3)(DMSO)(am)]$ is obtained, even in the presence of a slight excess of the ligand. With less bulky ligands, such as pyridine, the only product obtained in solution soon after mixing the reagents is the stable *cis*(*C*,*N*) complex. Thus, the configuration of the reaction product between complex **1** and aliphatic or heterocyclic nitrogen bases depends strongly upon the steric requirements of the entering ligand. A similar pattern of behavior has already been observed by several groups for the reaction of *cis*-$[PtCl_2(DMSO)_2]$ with nitrogen-donor ligands.[39] A kinetic study of these reactions by Annibale *et al.*[40] has revealed that the conversion to the most stable isomer is a multistep displacement process which takes place with complete retention of the configuration. We have no detailed kinetic data for the isomerization of these organoamine compounds, except the observation through the NMR spectra that, as time goes on, the *trans*(*C*,*N*) configuration tends to convert slowly to the *cis*(*C*,*N*) analogue. Considering the complexity of the starting system, made up by *cis* and *trans* sulfoxide and aqua complexes in mutual fast exchange, it is difficult to recognize which of the four is the most reactive species. However, the kinetic data from Schemes 1−3 suggest that the lability of the sulfoxide *trans* to the methyl group in the compound *cis*-$[PtCl(CH_3)(DMSO)_2]$ is very high and would lead to the fast formation of the *trans*(*C*,*N*) isomer in the reaction with a nitrogen ligand. This kinetically favored product isomerizes in a subsequent step to the more stable *cis*(*C*,*N*) compound. The isomerization process could be catalyzed by DMSO or water, and its rate is essentially related to the steric properties of the entering nitrogen ligand.

Conclusions

The molecular structure of the title compound has shown that the *trans*-influence of a sulfur bonded DMSO, taking as index the Pt−S lengthening of another *trans* bonded DMSO, is significantly higher than that of chloride or of ligands with oxygen or nitrogen donor ligands but still less than that of a σ Pt−C bond. This order of ground state destabilization is reflected in the lability of the *trans* dimethyl sulfoxide, as shown by magnetization transfer experiments. The facile removal of the molecule of dimethyl sulfoxide *trans* to a methyl group or to another DMSO from the coordination sphere of the metal leads to the formation of aqua-species that were found to be key intermediates in the *trans* to *cis* conversion of **1**. The mechanism of isomerization of square-planar platinum(II) complexes has received extensive investigation and usually occurs through associative catalytic or dissociative pathways.[41] The discovery of a water-catalyzed pathway for $[PtCl(CH_3)(DMSO)_2]$ introduces a new possibility and calls for a careful analysis of the role of water in ligand exchange and isomerization processes involving square-planar complexes.

The complex *trans*-$[PtCl(CH_3)(DMSO)_2]$ offers a convenient key for accessing a series of new organometallic species of the type $[PtCl(CH_3)(DMSO)(am)]$ containing four different groups. The relative stability of the two obtained isomers depends mainly on the steric requirements imposed by the entering ligand. Again, the role of the water and/or of the leaving sulfoxide in catalyzing the isomerization process is of central interest in the understanding of the reactivity of such organometallic complexes, and it is currently under investigation.

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Supporting Information Available: Figures SI 1 and SI 2 showing the unit cell of the 2:1 aggregate and the ^{195}Pt spectrum of compound **1** in D_2O, respectively, text detailing complete crystallographic work, and tables giving structure determination parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates (11 pages). Ordering information is given on any current masthead page.

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