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Cycloplatination of aryl and ferrocenyl oximes by *cis*-$[PtCl_2(OSMe_2)_2]$ affording expected platinum(II) and unexpected platinum(IV) products

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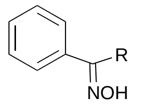
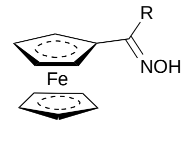
Acetophenone, benzamide, ferrocenyl methyl ketone and ferrocenecarboxamide oximes reacted with *cis*-$[PtCl_2(dmso)_2]$ (dmso = dimethyl sulfoxide) in refluxing methanol to afford the expected platina(II)cycles *N,S-trans*-[Pt(C–N)Cl(dmso)], where C–N stands for the corresponding cycloplatinated organic ligand. The highest yield of 51% was observed in the case of the acetophenone oxime complex. The structures of the complexes were established on the basis of analytical and ^1H NMR data, and confirmed by an X-ray diffraction analysis of the platinated ferrocenyl methyl ketone oxime. A cyclic voltammetry study of the latter indicated that cyclometallation decreases the redox potential of the ferrocene unit by *ca.* 200 mV. The reaction of a bulkier analog of acetophenone oxime, *viz.* 2-methyl-1-phenylbutan-1-one oxime, resulted in the formation of the unexpected platinum(IV) complex *fac*-$[Pt(C{-}N)Cl_3(SMe_2)]$ revealing a unique combination of oxidative cycloplatination and dmso-deoxygenation processes which occur under rather mild conditions. The composition of the platinum(IV) compound was established by X-ray crystallography. The Pt–Cl bond distance *trans* to the phenyl carbon [2.464(4) Å] is rather large. As a result, the *trans* chloro ligand undergoes rapid solvolysis in aqueous solution, causing a pH drop. The deoxygenation of dimethyl sulfoxide that occurs within the metal co-ordination sphere can be viewed as a model of the action of the metal-dependent redox enzyme dimethyl sulfoxide reductase.

Recently, we reported on a number of novel reactions of cycloplatinated compounds including the photoinduced addition of *NN*-dimethylbenzylamine chloro-bridged platinacycles to azobenzenes,[1] the exchange of cycloplatinated ligands leading to homo- and hetero-leptic bis(metallacycles)[2] and utilization of orthoplatinated acetophenone oximes as mimetics of metallopeptidases.[3] The development of the chemistry of platinacycles is strongly impeded by the fact[4] that the synthesis of key starting compounds occurs usually in low yields. In particular, the yields of orthoplatinated *NN*-dimethylbenzylamine[5] and acetophenone oxime[6] in reactions with $K_2[PtCl_4]$ do not exceed 20 and 10%, respectively. Thus, we are seeking a universal platinating agent that would allow us to make the preparation of the corresponding compounds inexpensive and less laborious. A recent report on cycloplatination of dimethylaminomethylferrocene by *cis*-$[PtCl_2(dmso)_2]$ (dmso = dimethyl sulfoxide) in refluxing methanol[7] suggested that this procedure might be a general routine. More recent works describing the preparation of five- and six-membered indole-fused platinacycles[8a] and cycloplatination of ferrocenyl ketimines[8b] using the same reagent evidenced the same. Here we report on the results of attempted cycloplatination by *cis*-$[PtCl_2(dmso)_2]$ of a number of aryl and ferrocenyl oxime derivatives, namely acetophenone, benzamide, acetylferrocene and aminocarbonylferrocene oximes (**I**, **II**, **IV** and **V**, respectively), the isolation and characterization of the corresponding expected square-planar platinum(II) complexes **1a**, **2a**, **4a** and **5a** and crystal structural and electrochemical investigation of platinacycle **4a** derived from acetylferrocene oxime. In the case of a more sterically hindered oxime, *viz.* 2-methyl-1-phenylbutan-1-one oxime **III**, the same reaction provided the unexpected octahedral platinum(IV) derivative by a route which involves (*i*) cycloplatination, (*ii*) oxidation of Pt^{II} to Pt^{IV}, as well as (*iii*) deoxygenation of dmso to afford co-ordinated dimethyl sulfide. The structure of the latter compound (**7**) has also been confirmed by X-ray crystallography.



R = Me (**I**), NH_2 (**II**), CHMeEt (**III**)



R = Me (**IV**), NH_2 (**V**)

Experimental

Methods

Infrared spectra were recorded on a Mattson Polaris Fourier-transform instrument in KBr discs, ^1H NMR spectra on CXP-200 Bruker and Varian Gemini-300 instruments with a residual solvent signal as internal standard. Electrochemical measurements were made in a three-electrode cell with a glassy carbon working electrode at 25 °C. A potential sweep was generated with an IPC-3 instrument interfaced with a personal computer. The working electrode was polished with a diamond paste and then sonicated for 1–2 min in an Ultrasonic type 07 bath before each new measurement. Potentials are *versus* the saturated calomel electrode (SCE) throughout.

Reagents

The complex *cis*-$[PtCl_2(dmso)_2]$ was obtained according to the procedure of Price *et al.*[9] Benzamide oxime **II** was prepared from benzonitrile and hydroxylamine as described more than a century ago[10] [^{1}H NMR (CD_2Cl_2): δ 4.93 (br s, NH_2), 7.35–7.45 (m, H^3–H^5) and 7.55–7.65 (m, H^2, H^6)]. Ferrocenyl methyl ketone oxime was prepared from acetylferrocene and hydroxylamine as described elsewhere.[11] Methanol (Chimed) used as a reaction medium was refluxed over CaH_2 for 2 h and then distilled.

Preparations

2-Methyl-1-phenylbutan-1-one oxime III. 2-Methyl-1-phenylbutan-1-one was prepared as described elsewhere[12] from 2-methylbutanoic acid (Aldrich) by converting it into the acid chloride followed by treatment with the Grignard reagent made of bromobenzene in the presence of zinc chloride. 2-Methyl-1-phenylbutan-1-one (1.6 g, 0.01 mol) and $NH_2OH{\cdot}HCl$ (0.8 g, 0.011 mol) were dissolved in absolute ethanol–pyridine (1 : 1, 10 cm^3) and refluxed for 2 h using a condenser capped with a drying tube filled with $CaCl_2$ until the starting ketone disappeared according to TLC (Silufol, eluent *n*-hexane–ethyl acetate 9 : 1). The solvent was removed in vacuum to give a transparent oil which began to crystallize slowly. The oil was treated twice with distilled water, dried by rotary evaporation of the residual water with added absolute benzene and diethyl ether followed by addition of *n*-hexane. Treatment of the oil with a glass stick afforded colorless crystals. The latter were separated, dissolved in absolute MeOH and purified by preparative TLC on silica gel (eluent *n*-hexane–ethyl acetate 9 : 1). The solvent was removed in vacuum and the crystals formed (0.9 g, 52%) dried. M.p. 81–82 °C. ^{1}H NMR ($CDCl_3$): δ 0.92 (t, CH_2CH_3), 1.22 (d, $CHCH_3$), 1.56 and 1.71 (two spt, CH_2CH_3), 3.55 (sxt, $CHCH_3$) and 7.3–7.4 (m, aryl, OH). IR: *ca.* 3200vs (br, NOH), 2962s, 2873s, 1625m, 1453s, 1437, 933, 766 and 700 cm^{-1}.

Ferrocenecarboxamide oxime V. Cyanoferrocene (1.3 g, 6 mmol) was dissolved in EtOH (30 cm^3) and the solution was mixed with $NH_2OH{\cdot}HCl$ (0.4 g, 6 mmol) and K_2CO_3 (0.8 g, 6 mmol) in water (15 cm^3). The mixture was heated (70 °C) with stirring for 3 h. It became homogeneous and changed from dark yellow to crimson. The reaction progress was followed by TLC on Silufol using benzene–acetone (3 : 2 v/v) as eluent [R_f(**V**) = 0.3, R_f(cyanoferrocene) = 0.8]. The mixture was cooled to ambient temperature and filtered from the unchanged cyanoferrocene. The filtrate was extracted three times with diethyl ether and the combined organic layers were washed with water and dried over Na_2SO_4. The solvent was removed in vacuum and the residue purified by preparative TLC on silica gel using benzene–acetone (7 : 3 v/v) as eluent. A bright orange band was removed [R_f(**V**) = 0.6] and washed with MeOH to yield 0.274 g of spectroscopically pure material (19%). ^{1}H NMR (CD_3OD): δ 4.26 (s, cyclopentadienyl, 5 H), 4.35 (t, 2 H), 4.68 (t, 2 H) and 4.92 (s, NH_2, OH). M.p. 181–182 °C.

Complex 1a: cycloplatination of acetophenone oxime. The complex *cis*-[$PtCl_2$(dmso)$_2$] (0.1 g, 0.23 mmol) in MeOH (16 cm^3) was stirred by a magnetic bar with gentle heating for 2–2.5 h. Acetophenone oxime (0.032 g, 0.23 mmol) in MeOH (4 cm^3) was then added and the mixture stirred for 2 h. The resulting homogeneous solution was refluxed for 36 h. Slow evaporation of the solvent at 5 °C resulted in the formation of 0.047 g of analytically pure yellow crystals which were filtered off, washed with cold MeOH and air dried. An additional portion of the compound was isolated from the mother-liquor to give a total yield of **1a** of 51% (Found: C, 26.65; H, 3.07; Pt, 43.71. Calc. for $C_{10}H_{14}ClNO_2PtS$: C, 27.12; H, 3.07; Pt, 44.05%). ^{1}H NMR ($CDCl_3$): δ 2.39 (s, CCH_3, J_{PtH} 6.3), 3.54 (s, SCH_3, J_{PtH} 23.8), 7.1–7.15 (m, H^3–H^5), 8.03 (dd, J_{PtH} 51, H^6) and 10.15 (s, J_{PtH} 6.6 Hz, OH). M.p. 155–157 °C (decomp.).

Complex 4a: cycloplatination of ferrocenyl methyl ketone oxime. The complex *cis*-[$PtCl_2$(dmso)$_2$] (0.127 g, 0.30 mmol) was added to a solution of the oxime (0.078 g, 0.32 mmol) in MeOH (15 cm^3). The mixture was refluxed for 12 h and the reaction course was analysed by TLC. The solution changed from orange to bright red. The crystals that formed on cooling were collected, washed with cold methanol, and air dried to give 0.035 g (21%) of **4a** (Found: C, 30.66; H, 3.62. Calc. for $C_{14}H_{18}ClFeNO_2PtS$: C, 30.53; H, 3.29%). ^{1}H NMR ($CDCl_3$): δ 2.27 (s, CCH_3, J_{PtH} 5.8), 3.55 (s, SCH_3, J_{PtH} 24.8), 3.60 (s, SCH_3, J_{PtH} 24.8), 4.38 (s, C_5H_5, 5 H), 4.39 (m, H^3), 4.45 (t, H^4), 4.89 (dd, H^5) and 9.51 (s, OH, J_{PtH} 6.4 Hz). M.p. 153–155 °C (decomp.).

Complex 2a: cycloplatination of benzamide oxime. The complex *cis*-[$PtCl_2$(dmso)$_2$] (1 g, 2.3 mmol) in MeOH (60 cm^3) was refluxed with stirring by a magnetic bar until complete dissolution of the complex (*ca.* 1 h). Then oxime **II** (310 mg, 2.3 mmol) dissolved in MeOH (25 cm^3) was added and the mixture refluxed for 12 h with stirring. The reaction course was followed by TLC (Silufol, benzene–acetone 7 : 3 v/v). The solution was filtered and concentrated by a factor of 3 on a vacuum evaporator. A pale yellow precipitate (200 mg) was filtered off and not analysed further due to its instability. The filtrate was evaporated to dryness to afford an orange oil. Acetone (20 cm^3) was added to the oil and a white precipitate formed (100 mg). The solvent of the second filtrate was removed in vacuum to afford a major portion of the product as a pale yellow oil-like product (550 mg). This material was purified by preparative thin-layer chromatography on silica gel (40 × 100 mesh) with the same eluent as above. The major bright yellow band was collected ($R_f \approx 0.75$) and washed with MeOH. The methanol was then evaporated to afford 250 mg (25%) of **2a**. Analytically pure material (160 mg) was isolated after recrystallization from $CHCl_3$–hexane (1 : 1 v/v) (Found: C, 24.68; H, 3.08; Pt, 44.13. Calc. for $C_9H_{13}ClN_2O_2PtS$: C, 24.36; H, 2.95; Pt, 43.96%). ^{1}H NMR ($CDCl_3$): δ 3.54 (s, CH_3, J_{PtH} 23), 6.88 (dd, H^3), 7.1–7.2 (m, H^4, H^5), 8.09 (dd, J_{PtH} 52, H^6), 8.83 (s, J_{PtH} 7 Hz, OH) and 5.4 (br s, NH_2). *m/z* 444. M.p. 182 °C.

Complex 5a: interaction of ferrocenecarboxamide oxime V with *cis*-[$PtCl_2$(dmso)$_2$]. The complex *cis*-[$PtCl_2$(dmso)$_2$] (0.44 g, 1.04 mmol) was added to a solution of **V** (250 mg, 1.02 mmol) in dry MeOH (37 cm^3) and the mixture was refluxed with stirring for 16 h. The reaction progress was monitored by TLC using benzene–acetone mixtures as eluents. The crimson solution that formed was filtered, concentrated by 66% using a rotary evaporator, filtered again, and finally evaporated to dryness. The crude mixture was separated by preparative TLC on silica gel with benzene–acetone (7 : 3 v/v) as an eluent. The bands with R_f 0.7 and 0.5 were separated, washed with MeOH, the solvent removed in vacuum and the residues were recrystallized from chloroform–hexane (1 : 1 v/v). A work-up of the first band gave light crimson crystals of the cycloplatinated compound **5a** (100 mg, 18%) (Found: C, 25.78; H, 2.76. Calc. for $C_{13}H_{17}ClFeN_2O_2PtS{\cdot}CHCl_3$: C, 25.06; H, 2.70%). ^{1}H NMR ($CDCl_3$): δ 3.52 (s, SCH_3, J_{PtH} 24.8), 3.58 (s, SCH_3, J_{PtH} 24.8), 4.24 (s, C_5H_5, 5 H), 4.32 (m, H^3 and H^4), 4.79 (br s, H^5, J_{PtH} 11.7), 5.14 (br s, NH_2) and 8.24 (s, OH, J_{PtH} 7.8 Hz). M.p. 153–154 °C. From the second band N-bound complex **5b** was isolated as a brownish yellow material (27.3 mg, 5%) (Found: C, 29.74; H, 3.25. Calc. for $C_{13}H_{18}Cl_2FeN_2O_2PtS{\cdot}0.5C_6H_{14}$: C, 30.44; H, 3.99%). ^{1}H NMR (CD_3OD): δ 3.53 (s, SCH_3, J_{PtH} 22.7 Hz), 4.26 (s, C_5H_5, 5 H), 4.39 (t, 2 H), 4.64 (t, 2 H) and 4.89 (s, NH_2, OH). M.p. 222 °C (decomp.).

Complex 7: reaction of 2-methyl-1-phenylbutan-1-one oxime with *cis*-[$PtCl_2$(dmso)$_2$]. The complex (0.422 g, 1 mmol) and the oxime (0.196 g, 1.1 mmol) were placed in absolute MeOH (50 cm^3) and refluxed for 5 h. The poorly soluble starting complex dissolved completely to afford a pale yellow solution. The solution was then kept for 12 h at room temperature. The light yellow needle-like crystals of **7** formed (0.104 g, 29%) were separated and dried. They are poorly soluble in chloroform at ambient temperature but the solubility increases on heating. The compound is better soluble in MeCN and dmso (Found: C, 28.97; H, 3.70; Cl, 19.70; N, 2.65. Calc. for $C_{13}H_{20}Cl_3NOPtS$: C, 28.93; H, 3.73; Cl, 19.70; N, 2.59%). ^1H NMR (50 °C, $CDCl_3$): δ 0.98 and 0.99 (t, CH_2CH_3, J_{HH} 7.5), 1.47 (d, $CHCH_3$, J_{HH} 7.1), 1.53 (br s, $CHCH_3$), 1.82–1.90 (m, $CHHCH_3$), 2.01–2.11 (m, $CHHCH_3$), 2.19 (s, SCH_3, J_{PtH} 20.1), 2.24 (s, SCH_3, J_{PtH} 19.7), 2.57 (s, SCH_3, J_{PtH} 18.0), 2.61 (s, SCH_3, J_{PtH} 17.8), 3.40 (br m, $CHCH_3$), 7.26–7.47 (m, H^3–H^5), 7.88 and 7.91 (m, J_{PtH} 24 Hz, H^6), 11.27 and 11.28 (br s, NOH). M.p. 185–187 °C.

Crystallography

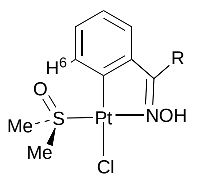
Details of the X-ray experiments and crystallographic parameters are given in Table 1. Experimental reflections were measured at 293 K on an Enraf-Nonius CAD4 diffractometer (Mo-Kα radiation, λ 0.710 73 Å, and graphite monochromator). The structure was solved by the direct method and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions and included in the least-squares refinement according to the riding scheme. Isotropic thermal parameters for H atoms were taken as much as 1.5 times the equivalent isotropic thermal parameters of their carbon atoms. The structures **4a** and **7** were refined using full-matrix least squares with anisotropic displacement parameters. In complex **7** three carbon atoms of the *sec*-butyl substituent [C(8)–C(10)] manifested rather high thermal displacement parameters and the terminal carbon C(11) was disordered between two positions with site occupation factors of 0.61 and 0.39. These facts resulted in poor geometrical parameters for the fragment. Rather high values of residual electron-density holes and peaks are, probably, due to the relatively poor quality of the single crystal used. In **7** it is also caused by the disorder and a small contribution of a foreign twin phase in the single crystal used. The inclusion of the twin phase is believed to be non-systematic based on the following facts: (*i*) a list of the most disagreeable reflections contains a comparatively large number of reflections with $F_o^2 \gg F_c^2$; (*ii*) no systematic dependence between these reflections was found however; (*iii*) an examination of the unit-cell parameters failed to reveal any matrix correlation that would suggest regularity in probable systematic twinning. All residual peaks were located in the vicinity of the heavy atoms. All calculations were performed using SHELX 76[13] and SHELXL 93[14] software. Table 2 gives selected bond lengths and angles.

CCDC reference number 186/715.

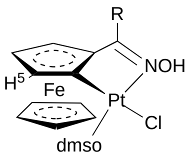
Results

Synthesis of platinum(II) metallacycles

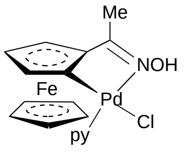
The complex *cis*-[$PtCl_2(dmso)_2$] proved to be a reasonable metallating agent with respect to the sterically unhindered oximes **I**, **II**, **IV** and **V**. Following the work of Ranatunge-Bandarage *et al.*,[7] the reactions were carried out in refluxing methanol, *viz.* under moderately mild conditions, to afford the expected platinum(II) metallacycles **1a**, **2a**, **4a** and **5a**, respectively. The yields were dependent on the nature of the oxime, the highest (51%) being observed for acetophenone derivative **1a**. The yield is noticeably higher than that obtained in the case of $K_2[PtCl_4]$ as a metallating agent.[6] An advantage of using *cis*-[$PtCl_2(dmso)_2$] is that the platination proceeds more cleanly than in the case of $K_2[PtCl_4]$ and the isolation of **1a** and **4a** requires neither column nor preparative thin-layer chromatography. It should probably be mentioned that cyclopalladation of benzamide[15] and ferrocenyl methyl ketone oxime[16] has been reported, but this is the first example of their cycloplatination. It should also be mentioned that complexes **2a** and **5a**, *viz.* with the C(NH_2)=NOH chelate arm, possess enhanced solubility in alcohols compared with other oxime platinacycles. This fact can be very advantageous from the point of view of using these compounds in cancer therapy.



R = Me (**1a**), NH_2 (**2a**), CHMeEt (**3a**)



R = Me (**4a**), NH_2 (**5a**)



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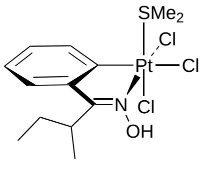

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The composition of the platinacycles was established on the basis of the analytical and diagnostic ^1H NMR data. The structure of ferrocene derivative **4a** was additionally confirmed by a crystal structural study (see below). The central atom in arene complexes **1a** and **2a** has basically a square-planar environment and the metal plane is the plane of symmetry. This is suggested by the appearance of the methyl resonance of the co-ordinated dmso at δ *ca.* 3.5 as one singlet for **1a** and **2a** with J_{PtH} *ca.* 23 Hz. The resonance from the proton H^6 of the orthoplatinated aromatic ring at lowest field compared to the remaining ring hydrogens is indicative of the fact that the dmso sulfur and the phenyl carbon are mutually *cis*. The origin of deshielding is a through-space interaction between the dmso oxygen and the aromatic proton H^6. As could be anticipated, H^6 is strongly coupled with platinum, the corresponding value of J_{PtH} being *ca.* 50 Hz. The ^1H NMR spectra of the ferrocene complexes **4a** and **5a** show two dmso methyl singlets because the platinum plane is not a plane of symmetry. The resonances from three hydrogen atoms of the cyclometallated cyclopentadienyl ring follow the same pattern as in the case of complexes **1a** or **2a** and H^5 is at lowest field. Interestingly, the Pt–H^5 coupling constant for ferrocene complexes **4a** and **5a** is significantly lower, *ca.* 11 Hz.

A study of the interaction between complex **4a** and pyridine (py) by ^1H NMR spectroscopy demonstrates that the dmso S-donor ligand can be replaced by the N-donor py to afford **4b**. This substitution markedly affects the chemical shifts of protons of the platinated C_5H_3 ring because the ring current of py causes a shielding effect as opposed to the deshielding effect of the dmso ligand. The chemical shifts show that the substitution does not affect the geometry of the complex. In particular, the resonance from the proton H^5 shifts upfield and is observed at δ 3.91 with J_{PtH} *ca.* 8 Hz, as expected for the hydrogen affected by the py ring current. The α-protons of py in **4b** appear as a doublet of doublets at δ 9.16 with J_{PtH} 43 Hz.

Crystal structure of complex 4a

The molecule and atom numbering are shown in Fig. 1. The platinum atom has a square-planar co-ordination. Dimethyl sulfoxide is *trans* to the oxime nitrogen and chloride is *trans* to the cyclopentadienyl carbon. The Pt–S bond length 2.186(2) Å is virtually equal to the values of 2.19–2.22 Å observed in other (dimethyl sulfoxide) platinum(II) compounds involving the S–Pt–N linear fragment.[17] The Pt–N bond length 2.042(6) Å is somewhat shorter than the Pt–N (py) bond distances of 2.07–

Table 1 Crystal data and structure refinement for complexes **4a** and **7** *

	4a	**7**
Empirical formula	$C_{14}H_{18}ClFeNO_2PtS$	$C_{13}H_{20}Cl_3NOPtS$
M	550.74	539.79
Crystal color, habit	Bright red, block	Bright yellow, block
Crystal size/mm	0.08 × 0.10 × 0.14	0.36 × 0.25 × 0.18
a/Å	9.291(4)	7.179(8)
b/Å	9.699(3)	8.361(5)
c/Å	9.920(3)	15.855(7)
α/°	82.50(2)	76.68(3)
β/°	64.52(3)	85.99(4)
γ/°	85.80(3)	74.49(3)
U/Å^3	799.9(5)	892.3(12)
D_c/g cm^{-3}	2.287	2.005
μ(Mo-Kα)/mm^{-1}	9.940	8.423
F(000)	524	514
θ Range for data collection/°	2.12–29.96	5.59–26.00
Index ranges	$-11 \leqslant h \leqslant 9, -13 \leqslant k \leqslant 13, -9 \leqslant l \leqslant 13$	$-9 \leqslant h \leqslant 8, -10 \leqslant k \leqslant 11, 0 \leqslant l \leqslant 20$
Reflections collected	4524	3290
Independent reflections (R_{int})	3949 (0.0803)	3201 (0.2133)
Minimum, maximum transmission	0.6653, 0.9785	0.7632, 0.9234
Data, restraints, parameters	3935, 0, 191	3182, 2, 18
Goodness of fit on F^2	1.080	1.027
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0458, 0.1206	0.0774, 0.2040
(all data)	0.0514, 0.1255	0.0921, 0.2289
Extinction coefficient	0.0067(11)	0.000(2)
Largest difference peak and hole/e Å^{-3}	3.521, −3.539	4.223, −2.927

* Details in common: triclinic, space group $P\bar{1}$; $Z = 2$; scan mode ω; scan speed 8.0° min^{-1}; scan range 1.0 + 0.35 tan θ; empirical absorption correction (ψ scan).

Table 2 Selected bond lengths (Å) and angles (°) of complexes **4a** and **7**

Complex **4a**			
Pt–C(1)	1.976(7)	S–C(13)	1.752(8)
Pt–N	2.042(6)	S–C(14)	1.767(9)
Pt–S	2.186(2)	O(2)–N	1.366(7)
Pt–Cl	2.395(2)	N–C(11)	1.312(10)
S–O(1)	1.465(6)		
C(1)–Pt–N	80.2(2)	O(1)–S–Pt	120.7(2)
C(1)–Pt–S	97.0(2)	C(13)–S–Pt	109.7(3)
N–Pt–S	176.2(2)	C(14)–S–Pt	108.4(3)
C(1)–Pt–Cl	170.3(2)	C(11)–N–O(2)	116.3(6)
N–Pt–Cl	90.1(2)	C(11)–N–Pt	118.4(4)
S–Pt–Cl	92.73(7)	O(2)–N–Pt	125.2(5)
O(1)–S–C(13)	106.8(4)	C(5)–C(1)–Pt	141.1(5)
O(1)–S–C(14)	108.8(5)	C(2)–C(1)–Pt	112.5(5)
C(13)–S–C(14)	100.7(5)	N–C(11)–C(2)	111.8(5)
Complex **7**			
Pt–C(1)	1.99(2)	S–C(13)	1.80(2)
Pt–N	2.00(2)	O–N	1.38(2)
Pt–Cl(2)	2.306(4)	N–C(7)	1.29(2)
Pt–Cl(3)	2.323(4)	C(1)–C(6)	1.40(3)
Pt–S	2.334(4)	C(10)–C(11)	1.52(3)
Pt–Cl(1)	2.464(4)	C(10)–C(11′)	1.54(3)
S–C(12)	1.79(2)		
C(1)–Pt–N	79.3(7)	C(13)–S–Pt	107.5(8)
C(1)–Pt–Cl(2)	96.3(5)	C(7)–N–O	119(2)
N–Pt–Cl(2)	175.5(4)	C(7)–N–Pt	121.0(13)
C(1)–Pt–Cl(3)	86.6(4)	O–N–Pt	119.6(13)
N–Pt–Cl(3)	89.5(5)	C(6)–C(1)–Pt	128.4(13)
Cl(2)–Pt–Cl(3)	91.1(2)	C(2)–C(1)–Pt	112.8(12)
C(1)–Pt–S	93.3(4)	C(3)–C(2)–C(7)	126(2)
N–Pt–S	87.4(5)	C(1)–C(2)–C(7)	115.8(13)
Cl(2)–Pt–S	92.1(2)	N–C(7)–C(2)	111.1(14)
Cl(3)–Pt–S	176.8(2)	N–C(7)–C(8)	123(2)
C(1)–Pt–Cl(1)	169.9(5)	C(10)–C(8)–C(7)	113(2)
N–Pt–Cl(1)	90.7(5)	C(10)–C(8)–C(9)	125(3)
Cl(2)–Pt–Cl(1)	93.7(2)	C(8)–C(10)–C(11)	127(4)
Cl(3)–Pt–Cl(1)	91.6(2)	C(8)–C(10)–C(11′)	130(5)
S–Pt–Cl(1)	87.9(2)	C(11)–C(10)–C(11′)	44(5)
C(12)–S–C(13)	97.6(12)	C(11′)–C(11)–C(10)	69(3)
C(12)–S–Pt	109.3(7)	C(11)–C(11′)–C(10)	67(3)

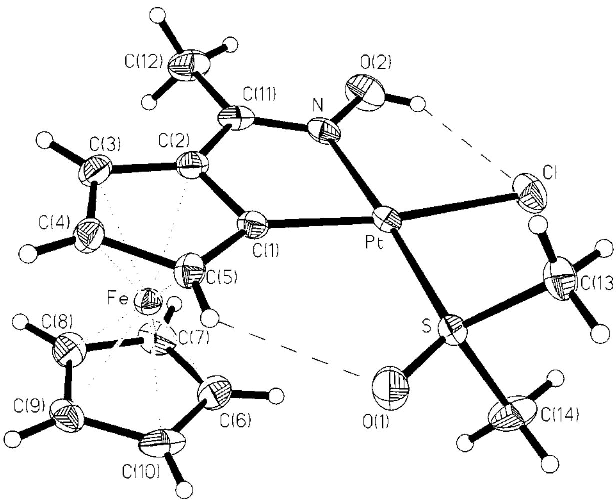


Fig. 1 Crystal structure of complex **4a**. Thermal ellipsoids are drawn at the 30% probability level

2.06 Å in the complexes containing the S (dmso)–Pt–N (py) fragment.[7,17a,f–i] However, for orthopalladated oximes, we have found that the Pd–N (oxime) bond is shorter than the Pd–N (py) bond (1.99–2.00 compared to 2.03–2.04 Å).[18] Apparently, such a feature is typical of platinum complexes as well. The Pt–C and Pt–Cl bond lengths equal 1.976(7) and 2.395(2) Å, respectively, and are very close to those observed in the structurally similar cycloplatinated dimethylaminomethylferrocene derivative in which the mutually *trans* Pt–C and Pt–Cl bond distances are 2.00–2.01 and 2.412–2.422 Å, respectively.[7] The sulfur atom of dmso has the expected tetrahedral co-ordination. The Pt–S–O(1) angle is somewhat increased (120.7°) compared to the ideal tetrahedral value typical of all metal complexes with co-ordinated dimethyl sulfoxide.[19] At the oxime center the hydroxyl hydrogen is oriented toward the chloride. The Cl···O(2) and Cl···H distances (3.11 and 2.44 Å, respectively) and Cl···H–O(2) bond angle (140°) are consistent with an intramolecular hydrogen bond. Similar hydrogen

Table 3 Electrochemical properties of ferrocenyl methyl ketone oxime **IV** and its cyclometallated derivatives of Pt^{II} (**4a**) and Pd^{II} (**6**). For conditions see legend to Fig. 2

Compound	E_a/mV	E_c/mV	ΔE/mV
IV	387	310	77
4a	198	100	98
6	211	110	101

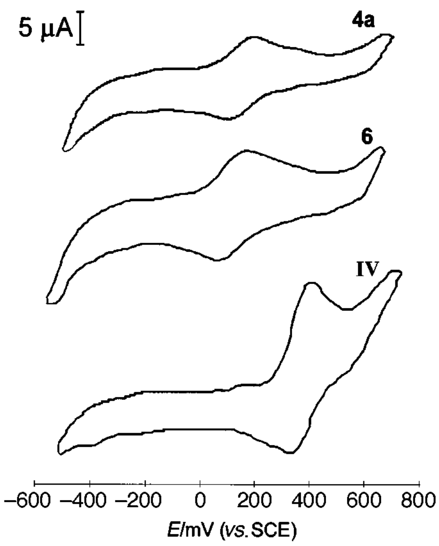


Fig. 2 Cyclic voltammograms of oxime IV and its cyclometallated derivatives of Pt^{II} (**4a**) and Pd^{II} (**6**) recorded in an acetonitrile–water mixture, pH 8 (0.01 M phosphate), at 25 °C, scan rate 20 mV s^{-1}

bonds were previously found in orthometallated complexes of Pd^{II}[18] and Pt^{II}[20] of aryl oximes. In complex **4a** a second hydrogen bond involves the ring hydrogen H^5 and the dmso oxygen O(1). The atom separation is 2.49 Å [O(1)···C(5) 3.09 Å and O(1)···H(5)–C(5) 122.6°]. This contact, which might be even more pronounced in the arene complexes **1a** and **2a**, accounts for the origin of the upfield shift of the resonances of protons H^6 and H^5 in the arene and ferrocene complexes, respectively, on the one hand, and the chemical equivalence of the dmso methyl groups in **1a** and **2a** on the other. It seems to stabilize the dmso geometry such as to preserve the platinum(II) plane as a plane of symmetry.

Effect of cyclometallation of compound IV on $E^{\circ\prime}$

Since the electrochemical properties of pallada-[21] and platinacycles[17b,22] appear to be a subject of current interest, we have characterized ferrocenyl methyl ketone oxime **IV**, its cycloplatinated **4a** and cyclopalladated derivative **6** (the latter for the sake of comparison) by cyclic voltammetry in aqueous solution in the presence of 12% MeCN, Fig. 2 and Table 3. The choice of the medium was dictated by our long-term interest in various ferrocene derivatives as possible substrates of oxidoreductases, horseradish peroxidase and glucose oxidase, in particular.[23] As seen in Fig. 2, the 'ferrocene'-centered redox transition shifts cathodically by *ca.* 200 mV (Table 3) on cyclometallation. Similar effects were noticed by Headford *et al.*[17b] and Bosque *et al.*[21] in the case of ferrocene platina- and pallada-cycles, respectively. Since the peak separation for the cyclometallated species is 90–100 mV, this is a quasi-reversible behavior at a glassy carbon electrode. The significant cathodic drift seemed at first rather surprising, since an opposite trend could be expected considering Pt^{II} and Pd^{II} to be Lewis acids. However, if one takes into account that both cations are σ bound to the ferrocene cyclopentadienyl ring and at least the platinum(II) group might be viewed as an electron-donating center in terms of the resonance Hammett σ_R constant [−0.26 for *trans*-$Pt(PEt_3)_2Cl$],[24] the trend observed is better understood. Therefore, it seems very likely that similar cathodic shifts for ferrocene derivatives σ bound to late transition-metal centers will be found.

Mechanism of formation of platina(II)cycles

A careful separation of the products formed on the reaction between *cis*-$[PtCl_2(dmso)_2]$ and oxime **V** allowed us to isolate, together with the main cycloplatinated complex **5a**, the additional *N*-co-ordinated oxime compound $[PtCl_2\{N(OH)=C(NH_2)C_5H_4FeC_5H_5\}(dmso)]$ **5b** which has no metallacyclic fragment and is very similar to the reported product formed in the case of 1,1′-bis(dimethylaminomethyl)ferrocene[17b] and $[PhN=C(Me)C_5H_4FeC_5H_5]$.[8b] Its formulation was made according to the analytical and ^1H NMR data. In particular, the ferrocenyl protons displayed the same pattern as for the free oxime **V**. The dmso methyls were not diastereotopic and appeared as one singlet with the platinum satellites (J_{PtH} 24.8 Hz). Interestingly, the amount of **5b** formed relative to **5a** was strongly time-dependent; as the reaction time increased the yield of **5b** became lower. This observation and the fact that **5b** transforms slowly into **5a** in refluxing MeOH suggests that **5b** might be an intermediate from starting material **V** to reaction product **5a**. Taking into account the fact that N-donor ligands can readily substitute dmso in the co-ordination sphere of Pt^{II}, the substitution of dmso by **V** in methanol solvent [equation (1)] seems reasonable. The intimate nature of step (2)

$$[PtCl_2(dmso)_2] + \mathbf{V} \longrightarrow \mathbf{5b} + dmso \qquad (1)$$

$$\mathbf{5b} \longrightarrow \mathbf{5a} + HCl \qquad (2)$$

is, however, difficult to specify. It could be either electrophilic substitution or a two-step oxidative addition–reductive elimination process. Both seem to fit the mechanism of cycloplatination.[4]

Formation of platinum(IV) metallacycle: coupled oxidative cyclometallation–sulfur deoxygenation

The primary goal of performing the interaction between oxime **III** and *cis*-$[PtCl_2(dmso)_2]$ was to work out an approach to an oxime platina(II)cycle with a chiral carbon in a ligand side chain. Compound **III** as prepared was a mixture of *E* and *Z* isomers according to the ^1H NMR data with two sets of signals of approximately equal intensity. The most significant difference in chemical shifts was observed for sextets from the MeC*H* proton seen at δ 2.62 and 3.55. We assume that these refer to *Z* and *E* isomers, respectively, because the MeC*H* proton at δ 3.55 should be strongly deshielded by the hydroxy group in the case of *E*-2-methyl-1-phenylbutan-1-one oxime. Since the *E* isomer seemed to be a better ligand for cycloplatination, the isomers were separated by preparative TLC.

The reaction between *E*-2-methyl-1-phenylbutan-1-one oxime and *cis*-$[PtCl_2(dmso)_2]$ was carried out as for all other compounds used in this study and resulted in the formation of needle-like light yellow crystals. The material appeared to be sparingly soluble in warm chloroform, reasonably soluble in acetonitrile, and much better in dmso. From the mother-liquor we isolated a small amount of pale yellow material which was much more soluble in chloroform. According to the ^1H NMR data it was formulated as **3a** because of an intense dmso singlet at δ 3.52 with platinum satellites (J_{PtH} 24 Hz) and a doublet from H^6 at δ 8.04 with J_{PtH} *ca.* 50 Hz, *i.e.* the compound had resonances similar to those observed for the fully characterized platinum(II) complexes **1a** and **2a**. The ^1H NMR spectrum of the needle-like crystals formed became interpretable only after we carried out a crystal structural investigation.

Crystal structure of complex 7

Fig. 3 shows that the compound is an octahedral ortho-

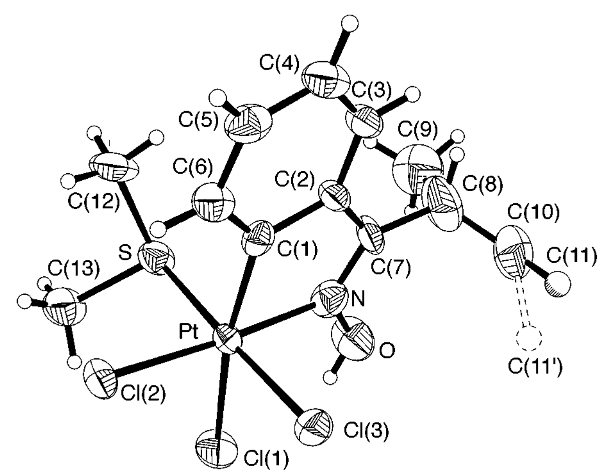


Fig. 3 Crystal structure of complex **7**. Thermal ellipsoids are drawn at the 30% probability level

metallated platinum(IV) derivative with co-ordinated dimethyl sulfide instead of dmso and three facial chloro ligands which have nitrogen, sulfur and carbon in *trans* positions. As could be expected, the three Pt–Cl bond distances are markedly different, 2.306(4), 2.323(4) and 2.464(4) Å where the atoms *trans* are N, S and C, respectively. Thus, the ground-state *trans* influence holds! The Pt–Cl bond distance *trans* to the phenyl carbon is substantially longer than that of 2.370 Å *trans* to the sulfur of *N,N,N′,N′*-tetramethylthiourea (tmtu) in the recently reported related platinum(IV) complex [$PtCl_4$(tmtu)(NH_3)][25] and corresponds to that of 2.446 Å found in the pincer compound *mer*-[2,6-bis(dimethylaminomethyl)phenyl]trichloroplatinum(IV).[26] In *cis*-tetrachloro(3-trifluoromethyl-2,5-dithiahexane)platinum(IV),[27] where two linear S–Pt^{IV}–Cl fragments occur, the two Pt–Cl bond distances are different, 2.318 and 2.338 Å. Their mean value of 2.328 Å is in agreement with the SPt^{IV}–Cl distance observed in complex **7**. The Pt–Cl bond *trans* to nitrogen [2.306(4) Å] is close to the range 2.310–2.322 Å typical of the linear Cl–Pt^{IV}–N fragment in [$PtCl_3$(L-*C,N,S*)] {HL = 1-(4-methylphenyl)-2-[2-(methylsulfanyl)phenyl]diaz-1-ene}[28] and tetrachloro(1,4-diaminocyclohexane)platinum(IV).[29] The Pt–C and Pt–N bond lengths in **7** of 1.99(2) and 2.00(2) Å are close to those of 1.948 and 1.999–2.082 Å reported in refs. 26, 28 and 29, respectively. The Pt–S bond distance of 2.334(4) Å is a little longer than those found for chelated $MeSCHCF_3CH_2SMe$ (2.319 and 2.317 Å).[27] A slightly longer Pt–S distance (2.354 Å) was reported for the above-mentioned complex [$PtCl_4$(tmtu)(NH_3)].[25]

The oxime OH group is involved in intramolecular hydrogen bonding with the Cl(1) atom. The corresponding Cl···O and Cl···H distances (2.99 and 2.39 Å, respectively) are comparable with those in complex **4a**.

Infrared and ^1H NMR spectral features of complex 7: solution behavior

Infrared spectroscopy confirmed the reduction of dmso to SMe_2. The starting compound *cis*-[$PtCl_2$(dmso)$_2$] is characterized by a strong band at 1155 cm^{-1} and a weaker one at 1135 cm^{-1} due to S-co-ordinated dmso.[30] Complex **7**, by contrast, has no strong bands in the 1400–1050 cm^{-1} spectral region. The ^1H NMR spectrum appeared to be rather complex for such a simple compound. Sources of complication were (*i*) the absence of strong resonances from co-ordinated dmso around δ 3.5 and (*ii*) the stereochemistry of the metal center because dimethyl sulfide occupies an axial position with respect to the ortho-metallated C,N-chelate and there is no rapid SMe_2 migration within the co-ordination sphere of Pt^{IV} in chloroform, acetonitrile or dmso solvents. Since there is a chiral center in the ligand, *i.e.* the sp^3 asymmetric carbon C(8), the compound could be a pair of diastereomers. In accord with this proposal there are two sets of signals in the ^1H NMR spectrum. In particular, the diastereotopic SMe_2 methyls appear as four singlets each coupled to Pt and there are two CH_2CH_3 triplets and $CHCH_3$ doublets. Thus, the spectral data are also indicative of the fact that the interaction of *cis*-[$PtCl_2$(dmso)$_2$] with 2-methyl-1-phenylbutan-1-one oxime involves oxidative cyclometallation coupled with sulfur deoxygenation. This is the first example of such a transformation.

The recent investigation of [$PtCl_4$(tmtu)(NH_3)] in aqueous solution[25] revealed that the compound displays a pronounced acidity due to a considerable Pt–Cl bond labilization by the sulfur atom of thiourea. The large bond distances in **7** indicate that even higher hydrolytic lability could be expected in the present case. Our experiments consisting of dissolving the platinum complex in ethanol or acetonitrile, addition of the resulting solution to water followed by pH measurements showed that this is the case. In particular, when a 1.4×10^{-3} M solution of **7** in EtOH was mixed with an equal volume of water the pH of the mixture dropped to 2.80 within the mixing time and there were no further changes. When a similar experiment was carried out with the platinum(II) complex [$PtCl_2$(MeCN)$_2$] it took 6 h to achieve a constant pH of 3.4. Apparently, the major contribution to the pH drop in the case of **7** comes from the hydrolysis of chloride which is *trans* to carbon, equation (3). (C–N stands

$$\mathbf{7} + H_2O \rightleftharpoons cis\text{-}[Pt(C\text{–}N)Cl_2(OH)(SMe_2)] + HCl \quad (3)$$

for the cycloplatinated oxime). However, it should be mentioned that chloride *trans* to sulfur might undergo solvolysis as well. These preliminary observations suggest a potentially interesting co-ordination chemistry of the newly prepared complex of Pt^{IV}.

Discussion

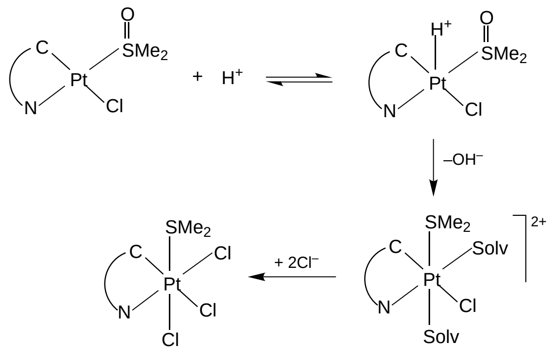
The cycloplatination of acetophenone, benzamide, acetylferrocene and aminocarbonylferrocene oximes by *cis*-[$PtCl_2$(dmso)$_2$] to form the platinum(II) species **1a**, **2a**, **4a** and **5a**, respectively, confirmed that this metallating agent is superior compared to $K_2[PtCl_4]$, but the yield was acceptable only in the case of acetophenone oxime. The most interesting aspect of the present work is the formation of platinum(IV) derivative **7**. The key issues here are the generation of Pt^{IV} when platinum(II) derivatives are the expected products (which are actually formed in the case of **I**, **II**, **IV** and **V**) and the deoxygenation of dimethyl sulfoxide within the co-ordination sphere of platinum. Separately, both processes have precedent in the literature. For instance, even water is capable of oxidizing certain platinum(II) complexes to platinum(IV) derivatives,[31] and there are several examples of the metal-ion mediated deoxygenation of sulfoxides.[32] The latter process which follows equation (4) is the most

$$Me_2S{=}O + 2\,H^+ + 2e \rightleftharpoons Me_2S + H_2O; \qquad pH\ 7, E = +0.16\ V \quad (4)$$

common in the presence of platinum(II) species. However, the reactions normally occur under rather severe conditions, *i.e.* in the presence of strong acids and at elevated temperatures. In our case the formation of **7** takes place under much milder conditions and equation (4) suggests that the two electrons could be supplied by the starting platinum(II) complex. The acid catalyst is produced during the primary cycloplatination step (5).

$$N\text{–}C\text{–}H + Pt^{II} \rightleftharpoons Pt(C\text{–}N)^+ + H^+ \quad (5)$$

The crucial importance of the proton release as a mechanism of launching platinum(II) reactions has recently been documented.[2] The isolation of traces of the platinum(II) complex **3a**



Scheme 1

suggests a pathway for the formation of the platinum(IV) complex **7**. The complex **3a** forms first *via* steps 1 and 2 discussed above. A tentative mechanism is shown in Scheme 1. The 'normal' cycloplatination of **III** affords the expected complex **3a** and hydrochloric acid. The latter might be a true catalyst of the deoxygenation of dmso. Thus, the subsequent step is likely to be the intramolecular oxidation–deoxygenation sequence leading to **7** and oxygen dissociation in the form of water.

It should be mentioned however that the formation of complexes of type **7** does not take place in the case of sterically unhindered oximes. For instance, we have not yet been able to convert **1a** into anything similar to **7**. A working hypothesis is that the bulky alkyl radical of **III** protects the co-ordination sphere of Pt^{II} from ligands from the bulk, thus opening a channel for the intramolecular redox transformation involving the coupled platinum oxidation and dmso deoxygenation. However, intriguing questions associated with the intimate mechanisms, the steric control and the effects of other, possibly chiral, sulfoxides in the reported transformation are the subject of further investigations.

In conclusion, the formation of dimethyl sulfide from dmso which takes place within the co-ordination sphere of a platinum complex suggests an analogy with a biological process, namely deoxygenation of dimethyl sulfoxide catalysed by the molybdenum-dependent enzyme dimethyl sulfoxide reductase.[33] Further studies will show how widespread is this analogy and whether the formation of complex **7** can mimic the enzyme action.

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