Targeting of Pallada- and Platinacycles to the *N*-((*tert*-Butyloxy)carbonyl)-L-methionine *p*-Nitrophenyl Ester for Promotion of the Ester Cleavage

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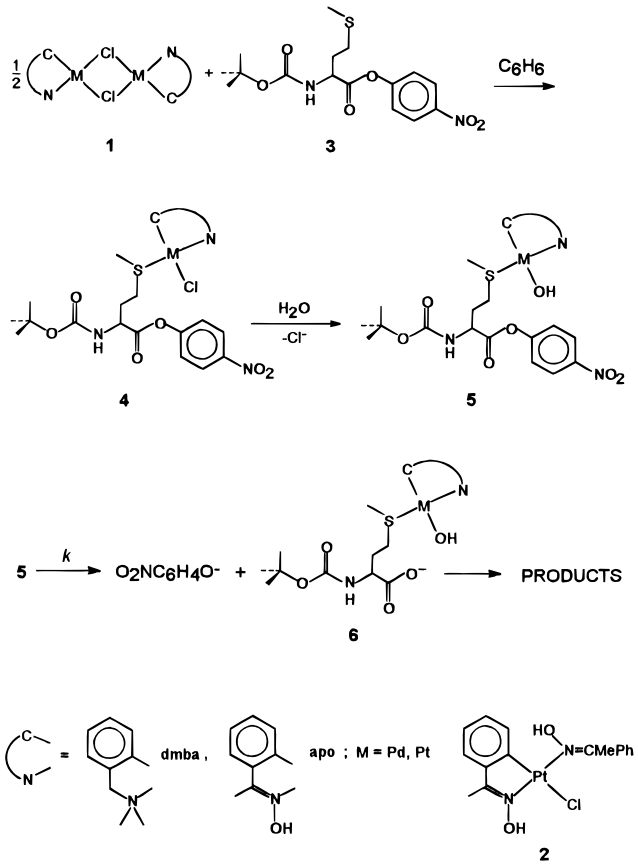
Ribozymes, abzymes, synzymes, and dendrizymes are now becoming customary terms,[1] illustrating the strong insistence of the scientific community to elaborate novel catalysts competitive with the native enzymes. The progress in mimetics of metalloenzymes[2,3] as a branch of biomimetic chemistry[4] suggests that probably other *zymes*, such as metallozymes, are at a threshold. In fact, lanthanide complexes appear to be extremely efficient in the hydrolysis of phosphate mono- and diesters.[5] Illustrative evidence was also provided by Kostić and coworkers,[6] who showed that methionine sulfur residues of peptides and proteins linked to rather simple aqua complexes of Pd(II) and Pt(II), which in some cases were formed from amine complexes as precursors, are efficient promoters of the hydrolysis of the adjacent nonactivated amide bonds at 40 °C and pH 1−2. An important question is the magnitude of the catalytic effect that can be achieved in such systems. A correct answer can be obtained by operating with a substitutionally inert metal complex, bound to the methionine sulfur of a corresponding substrate, with an aqua/hydroxo ligand at the proximity of the amide or ester bond to be cleaved. Our previous experience in the aqueous chemistry of cyclopalladated and cycloplatinated compounds[7] prompts an attractive model system for mechanistic investigations, the general features of which are illustrated in Scheme 1.

Scheme 1



Complex	M	C,N
1a	Pd	dmba
1b	Pt	dmba
1c	Pd	apo
4a	Pd	dmba
4b	Pt	dmba
4c	Pd	apo
4d	Pt	apo

The chloro-bridged cyclometalated Pd(II) or Pt(II) dimer **1** reacts with a methionine substrate, e.g. the *N*-((*tert*-butyloxy)-carbonyl)-L-methionine *p*-nitrophenyl ester **3**, in nonaqueous organic solvent to give the monomeric compound **4**. This must have an S,N-trans geometry in order for the chloride to be trans to the σ-bound carbon. Aquation of **4** will result in the substitution of an aqua/hydroxo ligand for chloride,[7] the coordinated nucleophile being in the vicinity of the ester function, and the departure of *p*-nitrophenolate ion can easily be followed by UV−vis spectrophotometry. In this paper, we will demonstrate that compounds **4** can be synthesized as depicted in Scheme 1 and the rate enhancement may reach a factor of 535.

Dimeric chloro-bridged Pd(II)[8] and Pt(II)[9] derivatives of *N*,*N*-dimethylbenzylamine **1a** and **1b** were prepared as described

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previously. The related palladium acetophenone oxime complex **1c** was obtained via a ligand exchange routine.[7a] These dimers (0.05 mmol) were dissolved in a minimum amount of benzene and reacted with a 10% excess of **3**. Addition of *n*-pentane with vigorous stirring induced crystallization of **4a**−**c**, which were separated by filtration, washed with *n*-pentane, and air-dried. The platinum analog of **4c**, complex **4d**, was synthesized in a similar way from monomer **2**.[10] The stoichiometry of these species was established on the basis of analytical data and is in accord with the ^{1}H and ^{13}C NMR measurements carried out in $CDCl_3$ and CD_3CN as solvents.[11] The values of the *J*(PtH) coupling constant for the S-bound methionine methyl group equal 55.9 and 53.0 Hz in complexes **4b** and **4d**, respectively, giving direct evidence for the sulfur donor being trans to nitrogen rather than to the *σ*-bound phenyl carbon.[12] The same geometry should be expected for complexes **4a** and **4c**, since the bridge cleavage in Pd(II) dimers **1** leads exclusively to the compounds in which a nitrogen chelate donor is *trans* to the incoming nucleophile.[7a] Although the formation of the Pt−S bond brings about a new chiral center,[13] only the platinum derivative **4d** is a mixture of two stereoisomers at ambient temperature according to the ^{1}H NMR data. It is well documented[13b,c] that the monodentate binding between the methionine sulfur and the $PtCl_3^-$ fragment is insufficient for the manifestation of diastereomerism in the ^{1}H and ^{13}C NMR spectra. In case of complexes **4**, however, the coordination of sulfur affords an additional pair of diastereomers, provided the rotation around the M−S bond is frozen[14] and the *S*-methyl group is above or below the Pd(II) or Pt(II) plane. Since at ambient temperatures diastereomerism is only seen for **4d** in $CDCl_3$, i.e. for the Pt(II) compound in which the apo and Cl^- ligands are basically in the metal plane,[15] the *S*-methyl group may anchor axially to the metal via an agostic C−H···Pt interaction similar to those observed in numerous square-planar metal complexes.[16] There is less space for an agostic contact in the related dmba complex **4b** because, according to the X-ray structural data, the dmba *N*-methyl groups are nearly perpendicular to the platinum plane.[15] Consequently, the diastereomerism in **4b** is observed on cooling the $CDCl_3$ solution, the coalescence temperature (T_c) being 300 K ($\Delta G^{\ddagger} = 68.5$ kJ mol^{-1}). Remarkably, the C$^{\alpha}$H, NH, *S*-CH_3, *N*-CH_3, and *N*-CH_2 groups of **4b** become anisochronous below 300 K. The net dynamic behavior shown for the *S*-CH_3 and *N*-CH_3 resonances in Figure 1 may result from either rotation around the Pt−S bond or inversion at sulfur. It is difficult to discriminate between the two processes because the "rotamer" and the "invertomer" are enantiomers with respect to each other. However, the literature comparisons suggest inversion rather than rotation.[17] In particular, the value of $\Delta G^{\ddagger} = 68.5$ kJ mol^{-1} is very close to those of 69.0 ($CDCl_3$), 69.0 (CD_2Cl_2), and 66.0 ($CDCl_3$) kJ mol^{-1} for sulfur inversion in the *cis* complexes $[PtCl_2\{S(CH_2Ph)_2\}_2]$,[17a] $[PtCl_2(MeSCH_2Ph)_2]$,[17b] and $[PtCl_2\{S(CH_2CHMe)_2\}_2]$.[17c] Dynamic behavior for the palladium complex **4a** is observed at much lower temperatures in

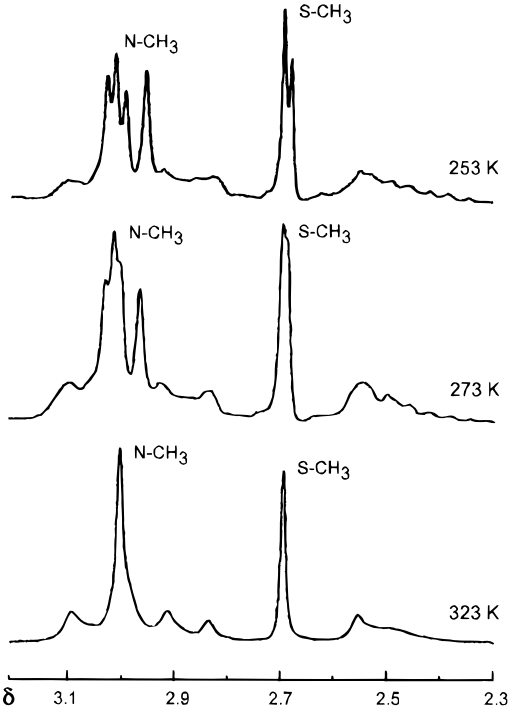

Figure 1. Temperature-dependent ^{1}H NMR spectra of **4b** recorded in $CDCl_3$.

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(11) Satisfactory C, H, N analyses were obtained for new complexes **4a**−**d**; NMR spectra were run on a CXP-200 Bruker instrument (200 MHz for ^{1}H, 50.3 MHz for ^{13}C). **3** (Sigma): ^{1}H NMR ($CDCl_3$; 303 K, *J* in Hz throughout) *δ* 1.46 (s, $C(CH_3)_3$), 2.13 (s, SCH_3), 2.13 (m, *β*-CH_2), 2.66 (dd, *γ*-CH_2), 4.64 (dd, α-CH), 5.14 (d, NH, *J*(HH) 8.0), 7.30 (d, H2,6), 8.26 (d, H3,5), ^{13}C NMR ($CDCl_3$) *δ* 15.55 (SCH_3), 28.26 ($C(CH_3)_3$), 30.07 (*β*-C), 31.34 (*γ*-C), 53.10 (α-C), 80.64 (CMe_3), 122.25 (C2, C6), 125.28 (C3, C5), 145.62 (C4), 155.16 (COO), 170.34 (CONH). **4a** (70% yield): ^{1}H NMR ($CDCl_3$) *δ* 1.45 (s, $C(CH_3)_3$), 2.50 (br m, *β*-CH_2), 2.63 (s, SCH_3), 2.86 (s, NCH_3), 3.19 (br m, *γ*-CH_2), 3.97 (s, CH_2), 4.73 (br m, α-CH), 5.60 (d, NH), 6.74−7.40 (m, H3′−H6′), 7.28 (d, H2,6), 8.24 (d, H3,5); ^{13}C NMR ($CDCl_3$) *δ* 21.77 (SCH_3), 28.12 ($C(CH_3)_3$), 30.17 (*β*-C), 34.73 (*γ*-C), 51.99 (NCH_3), 53.04 (α-C), 73.48 (NCH_2), 80.51 (CMe_3), 122.27 (C2, C6), 125.06 (C3, C5), 125.59 (C3′, C4′), 132.36 (C5′, C6′), 145.46 (C4), 146.70 (C2′), 148.05 (C1′), 155.00 (C1), 155.32 (COO), 169.64 (CONH). **4b** (87%): ^{1}H NMR ($CDCl_3$) *δ* 1.45 (s, $C(CH_3)_3$), 2.49 (br m, *β*-CH_2), 2.69 (s, SCH_3, *J*(PtH) 55.9), 3.00 (s, NCH_3, *J*(PtH) 35.9), 3.60 (br m, *γ*-CH_2), 3.94 (s, NCH_2, *J*(PtH) 42.3), 4.64 (br m, α-CH), 5.48 (br d, NH), 6.80−7.40 (m, H3′−H6′), 7.32 (d, H2,6), 8.22 (d, H3,5); ^{13}C NMR ($CDCl_3$) *δ* 22.37 (SCH_3), 28.33 ($C(CH_3)_3$), 30.04 (*β*-C), 34.58 (*γ*-C), 52.60 (NCH_3), 53.18 (α-C), 75.40 (NCH_2), 80.72 (CMe_3), 121.80 (C4′), 122.42 (C2, C6), 124.24 (C5′), 125.20 (C3, C5), 125.7 (C3′), 134.40 (C6′), 145.80 (C4), 147.40 (C2′), 151.8 (C1′), 155.34 (COO), 169.70 (CONH); **4c** (77%): ^{1}H NMR ($CDCl_3$) *δ* 1.45 (s, $C(CH_3)_3$), 2.27 (s, N=CCH_3), 2.48 (m, *β*-CH_2), 2.62 (br s, SCH_3), 3.15 (br m, *γ*-CH_2), 4.64 (m, α-CH), 5.33 (d, NH), 6.94−7.40 (m, H3′−H6′), 7.28 (d, H2,6), 8.22 (d, H3,5), 10.09 (s, NOH). **4d** (81%): ^{1}H NMR ($CDCl_3$; a 2:1 mixture of two stereoisomers) *δ* 1.46 (s, $C(CH_3)_3$), 2.29(2) and 2.32(1) (2s, N=CCH_3), 2.39 (m, *β*-CH_2), 2.73(2) and 2.76(1) (2s, SCH_3, *J*(PtH) 53.0), 3.49 (br m, *γ*-CH_2), 4.69 (br m, α-CH), 5.26 (br d, NH), 6.89 (d, H3′), 7.08 (m, H4′, H5′), 7.34 (2d, H2,6), 7.68 (dd, H6′, *J*(HH) 8.0), 8.13(2) and 8.22(1) (2d, H3,5), 10.26(1) and 10.30(2) (br s, NOH).

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Table 1. Rate Constants for Hydrolysis of Pd(II) and Pt(II) Complexes **4a**−**d** and Free Ligand **3** at pH 8.0 (0.01 M Phosphate) and 23 °C

complex or ligand	k,[a] s^{-1}
free ligand, **3**	$(1.12 \pm 0.03) \times 10^{-4}$
apo-Pd(II), **4c**	$(3.1 \pm 0.1) \times 10^{-4}$
dmba-Pd(II), **4a**	$(1.21 \pm 0.05) \times 10^{-3}$
dmba-Pt(II), **4b**	$(7.2 \pm 0.2) \times 10^{-3}$
apo-Pt(II), **4d**	$(6.0 \pm 0.6) \times 10^{-2}$

[a] Mean value of at least three measurements.

$CDCl_3$, and T_c equals 243 K. The spectral pattern differs from that for **4b**. The *N*-methyl and *N*-methylene protons give two singlets and a broadened quartet, respectively, while a single singlet is still observed for *S*-CH_3. The absence of ^{195}Pt satellites allows us to apply a full line-shape analysis to **4a**.[18] The corresponding rate constants equal 82, 177, 450, 1440, and 2220 s^{-1} at 213, 233, 253, 283, and 313 K, respectively; $\Delta H^{\ddagger} = 17.1 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = -125 \pm 8$ J K^{-1} mol^{-1}. $\Delta G^{\ddagger}$ is 54.6 kJ mol^{-1} at 300 K, and this value can be compared with that derived for platinum derivative **4b**. In terms of the rate difference, the dynamic process at the Pd(II) center occurs 260 times faster than at Pt(II), in accord with the higher lability of Pd(II) complexes compared to Pt(II) ones, thus supporting the inversion.[19] Its mechanism is intramolecular because the coupling to ^{195}Pt in **4b** persists at higher temperatures.[17] On the basis of the structural and dynamic data reported, one may thus conclude that the methionine sulfur of this particular amino acid derivative, as well as of peptides and, probably, small proteins, could serve as an appropriate donor center for dinuclear pallada- and platinacycles to provide the precatalytic complexes **4**, which will transform into reactive species after the substitution of the aqua/hydroxo for the chloro ligand.

The aquation occurs immediately when chloro species **4** are in contact with water.[7a,c] The complexes were first dissolved in acetonitrile, and these stock solutions were than added to a 0.01 M phosphate buffer (pH 8). Even in acetonitrile the halide is no longer bound to Pt(II) because of a pronounced trans influence of the in-plane σ-bound phenyl group.[20] There is previous evidence of this, for in water the aqua ligand is trans to the σ-bound phenyl group in similar Pd(II) and Pt(II) complexes.[7] The corresponding aqueous pK_a values are normally around 5;[7] thus, the hydroxo species **5** with the coordinated nucleophilic center should dominate at pH 8. Consequently, an accelerated, inhibited by Cl^- release of *p*-nitrophenolate in complexes **4**, as compared to free **3**, can be expected.

The values of rate constants k,[21] which are summarized in Table 1, show a rate increase in all cases. The 2.4-fold rate retardation from added 0.05 M NaCl was demonstrated by the example of **4b**. The magnitude of the catalytic effect is dependent on the nature of both the metal center and the cyclometalated ligand. The rates are appreciably higher for Pt(II) derivatives compared to the corresponding Pd(II) ones. We see the reason for this, the possibility of which is suggested by the preliminary X-ray structural data,[22] in the enhanced potency of Pt(II) to be involved in through-space interactions via axial coordination sites. If the ester carbonyl oxygen is capable of approaching such a site, an increase in the effective positive charge at the carbonyl carbon should be expected, resulting in acceleration of its attack by hydroxide. The highest acceleration, of a factor of 535, was achieved in the case of Pt(II) complex **4d**, for which axial interactions might be favorable on steric grounds. The Pd(II) compound **4c** with the same cyclometalated ligand brings about a 2.8-fold acceleration presumably because the axial interactions are less pronounced for the palladium species. *N*,*N*-Dimethylbenzylamine complexes of Pd(II) and Pt(II) also show different reactivities and hydrolysis within the latter occurs 6 times faster. The higher activity of Pt(II) species seems to be worthy of attention in light of the fact that palladium(II) complexes are usually more reactive because of faster substitution within their coordination spheres.[23] Unfortunately, attempts to isolate Pd- or Pt-containing products such as **6** failed. The final reaction mixtures always contained several species which were difficult to separate. We assume that these are all secondary products formed after the clean, first-order departure of *p*-nitrophenolate, viz. a model reaction widely used in biochemically relevant studies.[24] Presumably, the secondary reactions involve the transformation of the *N*-(*tert*-butyloxy)carbonyl moiety, which is rather labile in the presence of Pd(II) and Pt(II) complexes.[25]

In conclusion, we have shown an approach to substitutionally inert metal complexes with a cyclometalated backbone bound to the methionine sulfur. It is based on the bridge-cleavage reaction involving parent dimeric species. Similar complexes could, however, be obtained on reaction of monomeric cyclometalated species such as **2** with a good leaving ligand. A 535-fold rate acceleration of the 4-nitrophenolate departure was achieved in the case of Pt(II) acetophenone oxime complex **4c**. The binding of di- and polynuclear halo-bridged organometallics to methionine residues of peptides, proteins, and enzymes may find different applications in various aspects of organometallic biochemistry,[26] including the creation of artificial metallopeptidases.

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(21) The departure of *p*-nitrophenolate was followed spectrophotometrically (Hitachi 150−20) at 395 nm after addition of 0.1 mL of a 3.0×10^{-3} M solution of **4** in acetonitrile with 3.0 mL of buffer (0.01-0.02 M phosphate). First-order rate constants (k) were evaluated by fitting the absorbance (A) versus time (t) data to the equation $A(t) = A_\infty + (A_0 - A_\infty)e^{-kt}$ using nonlinear regression.
(22) In the solid state, the carbonyl oxygen of the ortho-platinated *O*-acetyl acetophenone oxime complex $[Pt(o\text{-}C_6H_4CMe{=}NOCOMe)Cl]_2$, the composition of which is exactly as for **1c** but with the $-OCOCH_3$ group instead of $-OH$, is localized above platinum(II), the Pt−O contact being 3.5−3.6 Å (Kazankov, G. M.; D'yachenko, O. G.; Ryabov, A. D. To be submitted for publication).
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