were refined with the site-occupation factor of 0.667 per position. The number of variable parameters was 748, affording a data-to-parameter ratio of 8.3. The refinement converged (maximum shift/esd of 0.093) to $R = 0.0530$, $R_w = 0.0672$, and GOF = 1.20, with the largest difference peak of 0.78 e Å^{-3} near the metal atoms. Atomic coordinates and isotropic thermal parameters are tabulated in Table V.

Acknowledgment. Crystallography was done at the National Single Crystal Diffractometer Facility, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science. Financial support received from the Department of Science and Technology, New Delhi, India, and the Council of Scientific and Industrial Research, New Delhi, India, is acknowledged.

Registry No. $Ru(Qc)(tap)_2$, 137495-83-1; $Ru(BuQc)(tap)_2$, 137495-84-2; $Ru(Bu_2Qc)(tap)_2$, 137495-85-3; $Ru(Cl_4Qc)(tap)_2$, 137495-86-4; $[Ru(Qc)(tap)_2]ClO_4$, 137495-88-6; $[Ru(BuQs)(tap)_2]ClO_4$, 137495-90-0; $[Ru(Bu_2Qs)(tap)_2]ClO_4$, 137495-92-2; $[Ru(Cl_4Qs)(tap)_2]ClO_4$, 137495-94-4; $[\{Ru(Qc)(tap)_2\}_2H_2O]\cdot CH_2Cl_2$, 137495-95-5; *tc*-$[Ru(OH_2)_2(tap)_2](ClO_4)_2$, 84027-73-6.

Supplementary Material Available: Full listings of bond distances (Table VI), bond angles (Table VII), anisotropic thermal parameters (Table VIII), and hydrogen atom coordinates (Table IX) and a summary listing of structure determination data (Table X) (9 pages); a listing of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

Contribution from the Centro di Studio sulla Stabilitá e Reattivitá dei Composti di Coordinazione, CNR, c/o Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Via Marzolo 1, 35131 Padova, Italy, and Dipartimento di Scienze Farmaceutiche, Via Marzolo 5, 35131 Padova, Italy

cis-Bis(phosphine)platinum(II) Complexes with Pyrimidyl Nucleobases. Synthesis, Characterization, and Crystal Structures of *cis*-(1-Methylthyminato-N^3)(N,N-dimethylformamide-O)(1,1′-bis(diphenylphosphino)-ferrocene)platinum(II) Tetrafluoroborate–Dichloromethane, $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(DMF)]BF_4\cdot CH_2Cl_2$, and *cis*-(1-Methylthyminato-N^3)(1-methylcytosine-N^3)(1,1′-bis(diphenylphosphino)-ferrocene)platinum(II) Tetrafluoroborate, $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(1\text{-}MeCy)]BF_4$

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Received March 14, 1991

The dinuclear complex $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$, where dppf is 1,1′-bis(diphenylphosphino)ferrocene, reacts with 1-methylthymine (1-MeTy), in dimethylformamide, dimethyl sulfoxide, or acetonitrile, to give the mononuclear complex $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(S)]^+$. The dimethylformamide adduct (S = DMF), $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(DMF)]BF_4\cdot CH_2Cl_2$ (**1**), has been characterized by single-crystal X-ray analysis. The complex crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 13.492$ (3) Å, $b = 14.063$ (3) Å, $c = 23.906$ (4) Å, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares techniques to $R = 0.078$ for 2949 unique data ($I > 3\sigma(I)$). In the cationic unit, the ligand geometry around Pt is distorted square planar, the chelating bis(phosphine) dppf, the N(3)-bonded 1-methylthyminate and the O-bonded DMF ligands defining the coordination sphere of the metal ion. The 1-MeTy(-H) ring forms an angle of 104.8° with the ligand square plane, while the DMF mean plane is at 73.0° to the same plane. Addition of 1-methylcytosine (1-MeCy) to **1** affords the corresponding adduct $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(1\text{-}MeCy)]^+$ (**2**) as a mixture of two isomeric forms (**2a**,**b**). In solution at room temperature **2a** extensively converts in **2b** (90% in DMF) in several hours. Crystals of **2** are obtained from a chloroform solution of the two isomers and have been characterized by single-crystal X-ray analysis. They crystallize in the monoclinic system, space group $C2/c$, with $a = 17.821$ (5) Å, $b = 21.718$ (7) Å, $c = 13.814$ (3) Å, $\beta = 113.6$ (2)°, and $Z = 4$. The structure was solved by heavy-atom methods and refined by least-squares techniques to $R = 0.060$ for 2657 unique data ($I > 3\sigma(I)$). In the cationic complex $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(1\text{-}MeCy)]^+$ the platinum atom is coordinated by the chelated bis(phosphine), by the deprotonated 1-MeTy, and by the neutral 1-MeCy ligands. In **2** both the nucleobases are platinated at the N(3) site with their rings being perpendicular to the PtP_2 plane. The structures in solution of the two isomers **2a** and **2b** are discussed on the basis of their ^1H and ^{31}P NMR spectra. Isomer **2b** contains the neutral cytosine ligand coordinated to the platinum through the monodeprotonated exocyclic amino group, with the proton switched to the N(3) position. The conversion of **2a** into **2b** is consistent with the migration of the platinum from the N(3) to N(4) site of 1-MeCy indicating that the thermodynamically favored adduct of this neutral ligand is its imino oxo tautomeric form. In addition, the characterization of the species $[(dppf)Pt(1\text{-}MeCy(\text{-}H))]^+$, obtained from $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$ and 1-MeCy in acetonitrile, is described. On the basis of ^1H and ^{31}P NMR spectra, the complex appears to contain the deprotonated 1-MeCy chelated to the $(dppf)Pt^{2+}$ moiety through its N(3) and N(4) donor atoms.

Introduction

Platinum nucleobase chemistry has been extensively studied in the last two decades, in particular the complexes of Pt^{II} and Pt^{IV} stabilized by amine ligands.[1] We have been investigating in recent years the solution chemistry of bis(phosphino) complexes of platinum(II)[2] and their interactions with nucleic acid components.[3] It has been shown that the complex $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) reacts with 3′,5′-diacetylthymidine, $Ac_2(dT)$, and deoxycytidine, dC, in dimethyl sulfoxide (DMSO) or dimethylformamide (DMF), to give the two isomeric species A and B of Chart I, depending on the sequence of the addition of the biomolecules.[4] Isomer A appears

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(1) (a) Lippert, B. *Prog. Inorg. Chem.* **1989**, *37*, 1. (b) Lippert, B. *Gazz. Chim. Ital.* **1989**, *118*, 153 and references therein.
(2) Longato, B.; Pilloni, G.; Valle, G.; Corain, B. *Inorg. Chem.* **1988**, *27*, 956.
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(4) Longato, B.; Corain, B.; Bonora, G. M.; Valle, G.; Pilloni, G. In *Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*; Nicolini, M., Ed.; Martinus Nijhoff: Boston, MA, 1988; p 705.

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Chart I

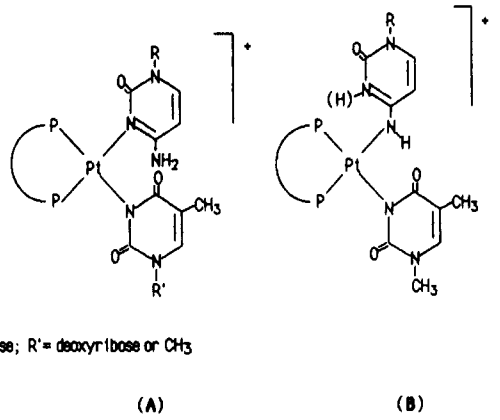

Table I. $^{31}P\{^1H\}$ NMR Data for the Complex $[(dppf)Pt(1\text{-}MeTy(\text{-}H))]^+$ in Various Solvents at 27 °C

solvent	δ_P, ppm	J_{Pt-P}, Hz	J_{P-P}, Hz
DMSO-d_6	8.34	3427	19.5
	6.57	4418	
DMF-d_7	7.99	3375	18.9
	6.13	4419	
CD_3CN	9.18	4303	17.1
	4.92	3165	
CD_2Cl_2[a]	8.66	3383	18.3
	6.57	4430	

[a] $[(dppf)Pt(1\text{-}MeTy(\text{-}H))](BF_4)\cdot 2DMF$.

thermodynamically unstable with respect to isomer B in solution of chlorinated solvents.

The binding modes of the nucleosides in the two isomers A and B were proposed on the basis of the ^1H and ^{31}P NMR data of the isolated complexes. Attempts to obtain good crystals for a single-crystal X-ray diffraction study were unsuccessful. The replacement of the thymidine with the corresponding 1-methyl-substituted nucleobase (1-MeTy) allowed us to isolate the mixed nucleoside/nucleobase complex $[(dppf)Pt(dC)(1\text{-}MeTy(\text{-}H))]^+$ and to undertake a single-crystal X-ray investigation. Preliminary data of the diffractometric analysis showed that the nucleobase was coordinated as a deprotonated species through the N(3)-donor atom and the nucleoside deoxycytidine through the deprotonated exocyclic amino group (isomer B of Chart I). This binding mode of the cytosine moiety as neutral ligand suggested that the observed isomerization of $[(dppf)Pt(dC)(1\text{-}MeTy(\text{-}H))]^+$ was due to a migration of the platinum from the N(3) to N(4) site of the nucleobase.[4] Subsequent efforts devoted to refine this structure for a precise determination of the bond distances and angles were unsuccessful. In addition, several attempts were made for improving the crystal quality by changing the crystallization solvents or the anionic group by synthesizing the nitrato derivative $[(dppf)Pt(dC)(1\text{-}MeTy(\text{-}H))]NO_3$. The failure of these efforts prompted us to study the reaction of $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$ with simple nucleobases, i.e. by replacing the nucleoside dC with methylcytosine (1-MeCy). In this paper we report on the reactivity of the dinuclear hydroxo complex with 1-methylthymine and 1-methylcytosine.

Results

Reaction of $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$ with 1-Methylthymine. The interaction of the dinuclear complex $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ with 1-MeTy has been followed by ^1H and ^{31}P NMR spectroscopy. Addition of 1 equiv of 1-MeTy to a solution of $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$ in DMSO causes a slow reaction, which is complete in ca. 14 h at room temperature and characterized in the ^{31}P NMR spectrum by the replacement of the singlet at δ 8.24 due to the reacting hydroxo complex with an AB multiplet, symmetrically flanked by the ^{195}Pt satellites. The pertinent spectroscopic data are collected in Table I. In the ^1H NMR spectrum, the deprotonation of the nucleobase is evidenced by the disappearance of the thymine-NH resonance at δ 11.18 and by the shift to higher field of the H(6) (δ 6.77, quartet), CH_3 (δ 1.45, doublet with J_{HH} ca. 1 Hz) and N–CH_3 (δ 2.91, singlet) resonances. Moreover, the coordination of the nucleobase determines a drastic modification of the Cp (Cp = cyclopentadienyl) protons of dppf. In the free ligand, as well as in many of its complexes, these protons exhibit two equally intense multiplets in the range δ 3.9–4.6. In the present complex they occur as four well-separated resonances (singlets), with the same relative intensities, in the range δ 3.3–5.3.

Table II. ^{31}P NMR data for the Complex $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(1\text{-}MeCy)]^+$ in Various Solvents at 27 °C

solvent	isomer	δ_P, ppm	J_{Pt-P}, Hz	J_{P-P}, Hz
DMF-d_7	**2a**	3.84	3505	18.3
		−1.48	3723	
	2b	10.85	3554	17.7
		3.09	3322	
CD_2Cl_2	**2a**	3.74	3508	17.1
		−0.91	3718	
	2b	11.47	3604	17.7
		4.69	3340	
DMSO-d_6	**2a**	3.85	3505	19.5
		−1.26	3717	
	2b	11.0	3536	18.3
		3.28	3332	
CD_3CN	**2a**	10.70	3600	17.1
		3.49	3320	

Similar results are obtained when $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ reacts with 1-MeTy in DMF and acetonitrile (MeCN). A list of the pertinent ^{31}P NMR parameters of the reaction product obtained in these solvents is reported in Table I. It can be seen that both resonances of the AB multiplet exhibit an evident solvent effect, particularly in CD_3CN solution. In this solvent the chemical shift difference in the AB multiplet becomes more than twice the value observed in the other ones and the higher field resonance experiences the lower platinum–phosphorus coupling constant. This remarkable solvent effect, together with the absence of any long-range platinum–phosphorus coupling effects, as found in related dimeric complexes,[5] agrees with the formation of mononuclear species in which the deprotonated nucleobase acts as a monodentate ligand and a solvent molecule is directly involved in the coordination to the platinum ion. This conclusion is supported by the characterization of the solvento complex $[(dppf)Pt(1\text{-}MeTy(\text{-}H))](BF_4)\cdot 2DMF$, which can be isolated when the reaction of $[(dppf)Pt(\mu\text{-}OH)]_2(BF_4)_2$ with 1-MeTy is carried out in DMF. In fact, the ^1H NMR spectrum of the isolated solid, dissolved in $CDCl_3$, exhibits two sets of resonances, in 1:1 intensity ratio, attributable to the methyl protons of coordinated (δ 2.93, 2.74) and free (δ 2.91, 2.81) DMF. The resonances attributable to 1-MeTy(-H) and to the phosphine Cp protons, as well as the ^{31}P NMR parameters (Table I), are very similar to those observed when the isolated solid is dissolved in DMF-d_7. In this solvent the phosphine Cp protons exhibit even a more complex pattern than in DMSO, in that one of the four groups of resonances occurs as a couple of broad singlets at 27 °C centered at δ 5.53 and 5.41, respectively. These resonances merge into a singlet at δ 5.47 when the temperature is increased to 80 °C. The other three resonances are temperature-independent.

The whole of the data are consistent with the occurrence in solution of the solvento complexes $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(S)]^+$, where S is DMF, DMSO, or MeCN. The coordination of a solvent molecule has been confirmed in the solid state by a single-crystal X-ray determination of the dimethylformamide adduct.

Reaction of $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(S)]^+$ with 1-Methylcytosine. Addition of 1 equiv of 1-MeCy to a DMSO solution of $[(dppf)Pt(1\text{-}MeTy(\text{-}H))(S)]^+$ causes the facile substitution of the solvent molecules. In the ^{31}P NMR spectrum this reaction is evidenced by the gradual replacement of the original AB multiplet by a new one, for which the chemical shift difference of the two phosphorus nuclei (δ 3.85 (J_{PtP} = 3505 Hz) and −1.26

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(J_{PtP} = 3717 Hz), respectively) is large enough to approach an AX system (isomer **2a** in Table II). Moreover, the platinum–phosphorus coupling constants become quite similar, their difference being only one-fifth of the value observed in the initial complex. In the ^{1}H NMR spectrum the reaction is characterized by a complex modification of the spectrum in the Cp proton region and by the development of two broad singlets, with a 1:1 relative intensity, at δ 8.54 and 8.25, respectively, attributable to the NH_2 protons of the N(3)-coordinated 1-MeCy.[6] The expected H(5) and H(6) multiplets cannot be assigned, as they overlap with the phenyl and/or Cp resonances of the bis(phosphine) ligand. On the other hand, the 1-MeTy proton resonances appear only weakly shifted (e.g. CH_3(5) shifts upfield of 0.05 ppm and H(6) appears virtually unchanged), indicating that the nucleobase is still coordinated to the platinum atom. After 12 h, when the substitution reaction has proceeded more than 50%, the reaction product is seen to evolve as shown by the appearance of a new AB multiplet centered at δ 11.0 (J_{PtP} = 3536 Hz) and 3.28 (J_{PtP} = 3332 Hz), respectively, with $J_{P(A)P(B)}$ of 18.3 Hz (isomer **2b**, Table II).

In a few days, at room temperature, the resonances due to the species [(dppf)Pt(1-MeTy(-H))(S)]$^+$ are completely replaced by those due to [(dppf)Pt(1-MeTy(-H))(1-MeCy)]$^+$, which exists therefore in the two isomeric forms **2a,b**, with a relative intensity of 1:9, respectively. In addition, a number of very weak absorptions, in the same spectral region, are detectable, indicating that minor additional species are formed. In the ^{1}H NMR spectrum, the conversion of isomer **2a** into **2b** is characterized by the disappearance of the NH_2 cytosine resonances at δ 8.54 and 8.25 with the concomitant development of a new broad absorption at δ 10.9, whose relative intensity accounts for a single proton. Moreover, the cytosine H(5) and H(6) resonances, not attributed for the isomer **2a**, appear well resolved in the case of the isomer **2b**. In particular the H(5) proton, in addition to the coupling with H(6), appears to be coupled with a phosphorus nucleus (J_{PH} ca. 2 Hz). No coupling with the ^{195}Pt nuclei is observed. The same reactivity pattern is observed in the reaction of [(dppf)Pt(1-MeTy)(-H))(DMF)]$^+$ with 1-MeCy in DMF. The product isolated from the DMF solution by addition of diethyl ether can be formulated as a chelated ferrocenylbis(phosphine)platinum(II) complex containing the deprotonated 1-MeTy and the neutral cytosine ligand, [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF_4 (**2**).

Reaction of [(dppf)Pt(μ-OH)]$_2$(BF$_4$)$_2$ with 1-Methylcytosine. The reaction of the [(dppf)Pt(μ-OH)]$_2^{2+}$ with 1-MeCy in DMSO-d_6 is not easily interpretable. The ^{31}P NMR spectrum of the reaction mixture appears to be very complex, and no direct information on the nature of the resulting products can be obtained. However, when MeCN-d_3 is used as reaction medium, a clean reaction occurs. In fact, by the warming of a solution of [(dppf)Pt(μ-OH)]$_2$(BF_4)$_2$ in the presence of stoichiometric amounts of 1-MeCy for a few hours at 50 °C, the complete dissolution of the nucleobase is observed. The ^{31}P NMR spectrum of the resulting solution exhibits an AB multiplet, flanked by the ^{195}Pt satellites, at δ 11.12 (J_{PtP} = 3557) and δ 7.64 (J_{PtP} = 3545 Hz) with a $J_{P(A)P(B)}$ value of 25 Hz. In the corresponding ^{1}H NMR spectrum the cytosine protons are seen as a sharp doublet at δ 6.87 for H(6), with $J_{H(5)H(6)}$ of 7.1 Hz, and as doublet of doublets at δ 5.75 for H(5). This proton is coupled, in addition to the phosphorous in the trans position ($^5J_{PH}$ = 1.7 Hz), also to platinum with $^4J_{PtH}$ of 12 Hz. A very broad singlet at δ 6.0, whose intensity accounts for a single proton, is attributable to a NH resonance. The Cp protons exhibit four resonances, as sharp unresolved multiplets, with the same relative intensity. These spectral data, in particular the almost identical values of the platinum–phosphorus coupling constants, are best explained by the formation of the species [(dppf)Pt(1-MeCy(-H))]$^+$ (**3**), in which the deprotonated nucleobase is coordinated to the platinum atom through its N(3) and N(4) atoms (see below).

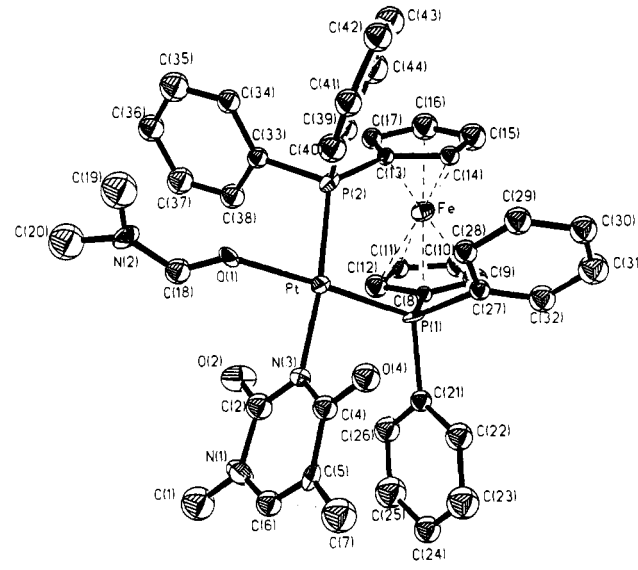

Figure 1. Perspective view of the [(dppf)Pt(1-MeTy(-H))(DMF)]$^+$ cation in **1**. The atom-numbering scheme is shown. The counteranion BF_4^- and the CH_2Cl_2 molecule are omitted for clarity.

The reaction product, which was not further characterized, is reactive toward 1-MeTy. The added nucleobase, which is slightly soluble in acetonitrile, reacts slowly at room temperature (ca. 50% in 24 h). The ^{31}P NMR spectrum of the reaction mixture, in addition to the original multiplet due to [(dppf)Pt(1-MeCy(-H))]$^+$, contains two almost first-order doublets at δ 3.49 (J_{PtP} = 3320 Hz) and δ 10.70 (J_{PtP} = 3600 Hz). Yellow-orange crystals precipitated spontaneously, after 2 days. Their elemental analysis was in fairly good agreement with the complex **2**. Moreover, the ^{31}P NMR spectrum of the isolated solid obtained in DMF-d_7 indicates that the isomer **2b** is the predominant form of the complex [(dppf)Pt(1-MeTy(-H))(1-MeCy)]$^+$.

Crystals of **1** and **2** were examined by X-ray diffractometry.

Solid-State Structures of [(dppf)Pt(1-MeTy(-H))(DMF)]BF$_4$·CH$_2$Cl$_2$ (1) and [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF$_4$ (2). The overall high thermal motion, the severe disorder of the anion, the difficulty in the space group choice for **2**, and the slight deterioration of the crystals during the data collection, as shown by the intensity decay (ca. 10% and 8% for **1** and **2**, respectively) of three standard reflections monitored at 2-h intervals, did not allow an accurate structural analysis of **1** and **2**; however, the models provide an adequate answer to the binding/stereochemistry question. In **1** the Pt coordination sphere is completed by the two *cis*-phosphorus donor atoms of the dppf ligand, the N(3)-bonded 1-MeTy(-H), and by O(1) of the DMF molecule (Figure 1). The ligand geometry around the Pt atom is distorted square planar, as shown by the larger P(1)–Pt–P(2) angle (99.1°), by the smaller P(1)–Pt–O(1) and P(2)–Pt–N(3) ones (174.0 and 172.3°, respectively), and by the significant deviations (±0.04 Å) of the donor atoms from the best P_2NO mean plane, with Pt out of the plane by 0.05 Å.

The monoanionic 1-MeTy(-H) ring is roughly orthogonal (104.8°) to the P_2NO mean plane, as well as to the mean plane of the DMF ligand (73.0°), while the two cyclopentadienyl rings, in the staggered configuration and at 6° to each other, are at 66.9 and 61.1° with respect to the P_2NO mean plane.

The centroids of the Cp rings are at 3.28 Å, and they are displaced by +2.22 and +0.78 Å from the P_2NO plane. The cation and the BF_4^- counteranion are well separated, and the dichloromethane molecule is trapped inside the lattice without any significant interaction with the complex, the shortest interaction being between Cl(2) and F(2) (at 1 + x, y, z) (3.02 Å).

In the cation [(dppf)Pt(1-MeTy(-H))(1-MeCy)]$^+$ of **2**, the platinum ion has a distorted square-planar coordination with cis-disposed phosphine and monodentate base ligands (Figure 2).

Both the nucleobases are coordinated to the methyl through the endocyclic N(3) atom, one from the monoanionic 1-MeTy(-H)

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(7) Clemente, D. A.; Pilloni, G.; Corain, B.; Longato, B.; Tiripicchio-Camellini, M. *Inorg. Chim. Acta* **1986**, *L9*, 115.

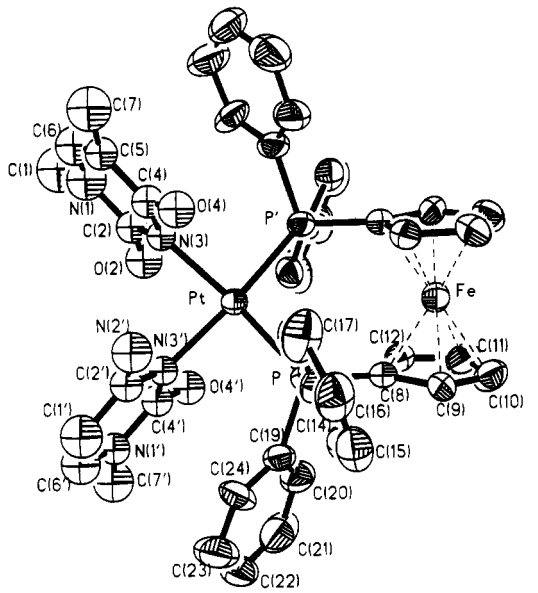


Figure 2. Perspective view of the $[(dppf)Pt(1\text{-}MeTy(-H))(1\text{-}MeCy)]^+$ cation in **2**. The atom-numbering scheme is shown. The anionic BF_4^- counterion is omitted for clarity. The Pt---Fe line is coincident with the binary axis, and symmetry-related atoms (at $-x, y, {}^1/_2 - z$) are primed.

ring and the other from the neutral 1-MeCy, although the rings cannot be unambiguously differentiated by X-ray analysis and this "crystallographic ambiguity" of the base ligands comes from the C_2 symmetry of the complex (see Experimental Section). The N and P atoms are above and below the N_2P_2 plane (±0.02 Å), with Pt and Fe lying on this plane. The tilting between the PtN_2P_2 plane and base ligand plane is 82.6°. The Cp rings are strictly planar, in a staggered configuration, and their centroids are equally placed far from the P_2N_2 coordination plane (+0.76 and −0.76 Å).

The $(dppf)Pt^{2+}$ portion of the complex closely parallels that of $[(dppf)PtCl_2]\cdot{}^1/_2Me_2CO$ (Pt–P = 2.27 vs 2.26 Å; Pt---Fe = 4.31 vs 4.28 Å; P–Pt–P = 99.8 vs 99.3°),[7] while comments on the distance/angle values in the remaining portion of the complex are not meaningful. In fact, the differences with related Pt^{II} complexes containing "pyrimidine" bases, as neutral or anionic ligands,[8] should not be regarded as being chemically significant because of the low accuracy of the structure determination (large estimated standard deviations for the bonds, up to 0.06 Å for N(1)–C(1) and 3.6° for the angles at N(1)) in **1** and **2**. Intermolecular contacts are not unusually short, and the cationic and anionic entities are well separated.

A superimposition[9] of the cations **1** and **2**, the fitted portion being PtP_2FeCp_2, shows a weighted root-mean-square deviation of only 0.20 Å but a severe difference in the configuration of the phenyl groups.

Discussion

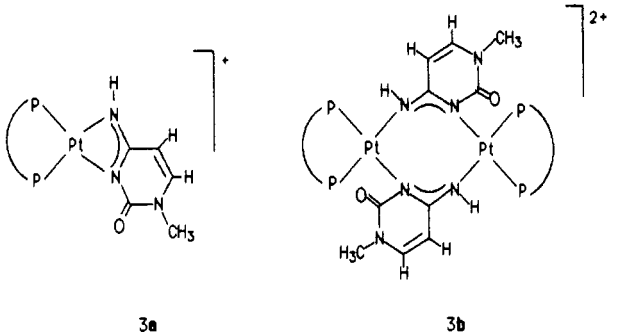
The bridging hydroxo complex $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ reacts with the weakly acidic NH proton of the 1-methylthymine in a solution of DMF or DMSO, under very mild conditions, to give the thyminate complex as the result of the neutralization reaction (eq 1).

$$^1/_2cis\text{-}[(dppf)Pt(\mu\text{-}OH)]_2^{2+} + 1\text{-}MeTy \rightarrow [(dppf)Pt(1\text{-}MeTy(-H))(S)]^+ + H_2O \quad (1)$$

S = DMF, DMSO, MeCN

As it was observed with the nucleoside 3′,5′-diacetylthymidine,[3] the deprotonation of the nucleobase occurs quantitatively at room temperature in a few hours. In MeCN, since the solubility of the nucleobase is quite low at the ordinary temperature, the reaction can be observed only upon moderate heating. The characterization of the solvento complex $[(dppf)Pt(1\text{-}MeTy(-H))(DMF)]^+$ clearly indicates that the nucleobase acts as monodentate ligand and the dimethylformamide molecule competes successfully for the fourth coordination site of the metal center. The solvent dependence of the ^{31}P NMR parameters of Table I seems to indicate a similar coordination for the other solvents, even though the trends on the phosphorus chemical shift and J_{PtP} as function of the solvent are not clearly rationalizable. As an example, the resonance of the phosphorus trans to the anionic ligand, for which the lower J_{PtP} value is expected,[10] is observed at lower field in DMSO and DMF but it shifts to higher field in MeCN solution.

Chart II



It is known that deprotonated 1-methylthymine in aqueous solution forms with *cis*-diammineplatinum(II) moieties very stable mononuclear adducts in which the nucleobase acts as a monodentate ligand[11] or dinuclear complexes in which two bridging deprotonated nucleobases bind the metal centers (through N(3) and O(4)) in a symmetric (head–tail)[12] or asymmetric (head–head) fashion.[13] In the coordination of the $\{cis\text{-}(dppf)Pt^{2+}\}$ unit, the thyminate ion binds the platinum atom exclusively through the N(3) atom giving mononuclear complexes, since no effects attributable to long-range platinum–phosphorus coupling are detectable in the ^{31}P NMR spectra for the adduct. Moreover, the analysis of the ^{31}P NMR spectra obtained in the course of reaction 1 does not allow the identification of any intermediate of the type $[L_2Pt(\mu\text{-}OH)(\mu\text{-}1\text{-}MeTy(-H))PtL_2]^{2+}$, which has been reported when L is NH_3.[14]

If the facile deprotonation of 1-MeTy by $[(dppf)Pt(\mu\text{-}OH)]_2^{2+}$ is expected in view of the relatively high acidity of its N(3) hydrogen atom,[15] the reaction of the same complex with neutral 1-MeCy (eq 2) is quite remarkable.

$$^1/_2cis\text{-}[(dppf)Pt(\mu\text{-}OH)]_2^{2+} + 1\text{-}MeCy \rightarrow [(dppf)Pt(1\text{-}MeCy(-H))]^+ + H_2O \quad (2)$$

In fact, the spectroscopic ^1H and ^{31}P NMR data are more consistent with the formation of a mononuclear adduct in which the anionic base acts as bidentate ligand with the simultaneous binding of the N(3) and the N(4) donor atoms (**3a** of Chart II).

Although the four-atom ring in **3a** is expected to be strained, this coordination mode of the cytosinate ligand is not unprecedented and it is known in platinum(IV) amine complexes.[16] On the other hand, the dinuclear structure with the bridging nucleobase (**3b** of Chart II) would give rise to a more complex ^{31}P pattern, owing to the effect of long-range ^{195}Pt–^{31}P coupling. A

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Table III. Crystallographic Data for [(dppf)Pt(1-MeTy(-H))(DMF)]BF_4·CH_2Cl_2 (**1**) and [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF_4 (**2**)

	1	**2**
empirical formula	$C_{44}H_{44}N_3O_3BCl_2F_4FeP_2Pt$	$C_{45}H_{42}N_5O_3BF_4FeP_2Pt$
fw	1133.2	1100.5
cryst syst	orthorhombic	monoclinic
space group	$P2_12_12_1$	$C2/c$
a, Å	13.492 (3)	17.821 (5)
b, Å	14.062 (3)	21.718 (7)
c, Å	23.906 (4)	13.814 (3)
β, deg		113.6 (2)
V, Å^3	4535.5 (1.2)	4898.7 (1.3)
Z	4	4
D_{calcd}, g/cm^3	1.659	1.492
D_{measd}, g/cm^3	1.6	1.5
μ, cm^{-1} (Mo Kα)	36.9	31.0
I(max)/I(min)	1.0/0.45	1.0/0.60
T, °C	23	23
residuals, %: R; R_w	7.8; 8.2	6.0; 6.0

trimethylphosphine complex $[(PMe_3)_2Pt(\mu\text{-}1\text{-}MeCy(-H))]_2^{2+}$, containing the symmetrically bonded cytosinate-$N(3),N(4)$ ligand, has been recently reported by us.[5] This dimeric complex proved to be quite inert toward the bridge splitting, as shown by the fact that the monomeric adduct is formed only by warming its solution for several hours at 80 °C. In the case of the ferrocenyl bis(phosphine) derivative, the dinuclear complex of Chart II is likely to be an intermediate of reaction 2, and the preferred formation of the mononuclear adduct can be due to the steric effects due to the presence of the bulky substituents on the phosphine ligand.

The results herein described show that the reactivities of the 1-methyl-substituted nucleobases are similar to those of the corresponding nucleosides, 3′,5′-diacethylthymidine (Ac_2dT) and deoxycytidine (dC).[3] In the case of the thymidine derivative, $[(dppf)Pt(Ac_2dT(-H))(S)]^+$, it has been shown that the solvent molecule can be easily replaced by a chloride ligand with formation of the neutral complex $[(dppf)Pt(Ac_2dT(-H))Cl]$ or by another nucleoside to give bis(nucleoside) adducts. In fact, the interaction of $[(dppf)Pt(Ac_2dT(-H))(S)]^+$ with deoxycytidine gave the adduct $[(dppf)Pt(Ac_2dT(-H))(dC)]^+$ in two isomeric forms (A and B of Chart I). Complex A is thermodynamically unstable with respect to B, and it isomerizes quantitatively in a few hours at ambient temperature in chlorinated solvents. The same result was obtained by replacing Ac_2dT with 1-MeTy. The structure of isomer B was proposed on the basis of the X-ray analysis of the mixed nucleoside/nucleobase complex [(dppf)Pt(1-MeTy(-H))(dC)]BF_4. Preliminary data showed that the thyminate ion was N(3) bonded, whereas the nucleoside that resulted coordinated to the platinum through the deprotonated exocyclic group.[4] The location of the transferred proton was not established, since the refinement of the structure did not allow a precise determination of bond distances and angles. However, the broad resonance at δ 10.8 (in DMSO-d_6) observed in the ^{1}H NMR spectrum of complexes $[(dppf)Pt(1\text{-}MeTy(-H))(dC)]^+$ and $[(dppf)Pt(Ac_2dT(-H))(dC)]^+$ suggested the presence of a proton on the N(3) atom of the cytosine (or cytidine) molecule as a result of the migration of platinum from the N(3) to N(4) sites of the nucleobase (or nucleoside). Subsequent efforts for improving the structural data of complex $[(dppf)Pt(1\text{-}MeTy(-H))(dC)]^+$ (the residual R factor was 0.112) were unsuccessful.

We have now shown that the thyminato complex $[(dppf)Pt(1\text{-}MeTy(-H))(S)]^+$ reacts with 1-MeCy similarly to the corresponding nucleoside, to give the adduct $[(dppf)Pt(1\text{-}MeTy(-H))(1\text{-}MeCy)]^+$ in a kinetically controlled process followed by the isomerization of the initial product (isomer **2a**) in the more stable form (isomer **2b**). On the basis of the ^{1}H NMR data the cytosine molecule in **2b** appears coordinated to the platinum center in its imino oxo tautomeric form (for B of Chart I).[17] However, the single-crystal X-ray analysis of the solid **2**, separated from a solution of $[(dppf)Pt(1\text{-}MeTy(-H))(1\text{-}MeCy)]^+$, in spite of the large excess of the isomer **2b** at the equilibrium, shows a structure in which both the nucleobases are platinated at the N(3) site, i.e. the coordination mode of isomer A of Chart I.

In conclusion, although we are giving further convincing spectrometric proof about the bonding ability of the cytosine molecule as the imino oxo tautomeric form, the isolation and X-ray single-crystal analysis of the relevant metal adduct turns out to be still an unattained goal.

Table IV. Fractional Coordinates and Thermal Parameters for [(dppf)Pt(1-MeTy(-H))(DMF)]BF_4·CH_2Cl_2 (**1**)

	x/a	y/b	z/c	U_{eq}, Å^2
Pt	0.8658 (1)	−0.0019 (1)	0.8478 (1)	0.032
Fe	0.8731 (3)	−0.2447 (2)	0.9502 (2)	0.040
P(1)	0.8818 (5)	−0.0059 (7)	0.9409 (2)	0.041
P(2)	0.9347 (5)	−0.1445 (5)	0.8269 (3)	0.033
N(1)	0.6509 (19)	0.2244 (17)	0.8490 (13)	0.073
C(1)	0.5369 (29)	0.2271 (27)	0.8415 (18)	0.091
C(2)	0.6993 (22)	0.1311 (21)	0.8475 (14)	0.056
O(2)	0.6527 (14)	0.0577 (14)	0.8365 (10)	0.071
N(3)	0.8021 (13)	0.1302 (13)	0.8555 (8)	0.026
C(4)	0.8520 (21)	0.2066 (19)	0.8668 (11)	0.043
O(4)	0.9437 (15)	0.2010 (15)	0.8744 (9)	0.055
C(5)	0.8046 (21)	0.2972 (18)	0.8734 (10)	0.037
C(6)	0.7073 (22)	0.2982 (20)	0.8641 (12)	0.048
C(7)	0.8608 (30)	0.3827 (24)	0.8840 (14)	0.080
C(8)	0.8268 (13)	−0.1154 (10)	0.9714 (8)	0.023
C(9)	0.8546	−0.1674	1.0198	0.059
C(10)	0.7923	−0.2486	1.0235	0.053
C(11)	0.7260	−0.2467	0.9774	0.041
C(12)	0.7473	−0.1644	0.9452	0.048
C(13)	0.9496 (13)	−0.2407 (11)	0.8790 (6)	0.025
C(14)	1.0140	−0.2383	0.9260	0.033
C(15)	1.0003	−0.3238	0.9566	0.065
C(16)	0.9275	−0.3790	0.9286	0.064
C(17)	0.8962	−0.3276	0.8806	0.038
O(1)	0.8573 (15)	0.0163 (15)	0.7592 (6)	0.064
C(18)	0.7796 (20)	0.0145 (24)	0.7317 (11)	0.049
N(2)	0.7903 (16)	0.0043 (26)	0.6765 (10)	0.069
C(19)	0.8851 (25)	0.0121 (31)	0.6436 (14)	0.094
C(20)	0.6987 (29)	−0.0190 (31)	0.6412 (16)	0.100
C(21)	0.8101 (14)	0.0843 (11)	0.9782 (8)	0.036
C(22)	0.8590	0.1619	1.0019	0.057
C(23)	0.8047	0.2345	1.0272	0.082
C(24)	0.7015	0.2295	1.0289	0.058
C(25)	0.6526	0.1519	1.0053	0.083
C(26)	0.7068	0.0793	0.9800	0.056
C(27)	1.0081 (8)	0.0054 (17)	0.9630 (6)	0.032
C(28)	1.0781	0.0159	0.9205	0.039
C(29)	1.1789	0.0155	0.9333	0.051
C(30)	1.2098	0.0046	0.9886	0.052
C(31)	1.1398	−0.0059	1.0311	0.069
C(32)	1.0390	−0.0055	1.0183	0.054
C(33)	0.8610 (12)	−0.2016 (12)	0.7723 (6)	0.036
C(34)	0.9037	−0.2422	0.7249	0.043
C(35)	0.8437	−0.2828	0.6838	0.070
C(36)	0.7409	−0.2827	0.6902	0.059
C(37)	0.6982	−0.2420	0.7376	0.063
C(38)	0.7583	−0.2015	0.7787	0.052
C(39)	1.0612 (11)	−0.1298 (13)	0.7991 (8)	0.043
C(40)	1.0942	−0.0429	0.7779	0.055
C(41)	1.1915	−0.0336	0.7591	0.046
C(42)	1.2559	−0.1111	0.7615	0.052
C(43)	1.2230	−0.1979	0.7827	0.059
C(44)	1.1256	−0.2073	0.8015	0.069
B	0.0698	0.9470	0.1751	0.232
F(1)	0.1660	0.9288	0.1658	0.145
F(2)	0.0187	0.8781	0.1371	0.148
F(3)	0.0547	0.9258	0.2309	0.172
F(4)	0.0424	1.0310	0.1606	0.137
Cl(1)	0.9504 (8)	0.5027 (13)	0.0748 (5)	0.127
Cl(2)	0.9879 (11)	0.6660 (10)	0.1437 (6)	0.143
C(45)	0.9609 (34)	0.5369 (32)	0.1492 (20)	0.127

Experimental Section

All chemicals used were reagent grade. The solvents were dried over molecular sieves. The nucleobases 1-methylthymine and 1-methylcytosine were from Sigma. Literature methods were used for the prep-

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Table V. Fractional Coordinates and Thermal Parameters for [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF_4 (**2**)

atom	x/a	y/b	z/c	U_{eq},[a] Å^2
Pt[b]	0.0000	0.0922 (0)	0.2500	0.040
Fe[b]	0.0000	0.2907 (2)	0.2500	0.055
P	−0.1001 (2)	0.1597 (2)	0.1553 (3)	0.048
N(3), N(3)′	0.0877 (8)	0.0215 (6)	0.3054 (10)	0.050
C(2), C(2)′	0.1014 (11)	−0.0109 (8)	0.3963 (14)	0.063
O(2), N(2)′	0.0576 (9)	−0.0021 (6)	0.4446 (11)	0.089
N(1), C(1)′	0.1660 (12)	−0.0558 (9)	0.4228 (16)	0.103
C(1)[b]	0.1839 (36)	−0.0882 (32)	0.5094 (48)	0.141
C(6), C(6)′	0.2081 (14)	−0.0620 (11)	0.3626 (18)	0.094
C(5), N(1)′	0.1940 (10)	−0.0321 (8)	0.2815 (14)	0.062
C(7), C(7)′	0.2458 (16)	−0.0383 (12)	0.2217 (20)	0.110
C(4), C(4)′	0.1312 (11)	0.0120 (8)	0.2461 (14)	0.061
O(4), O(4)′	0.1187 (8)	0.0415 (6)	0.1673 (10)	0.074
C(8)	−0.1002 (9)	0.2375 (7)	0.1965 (13)	0.052
C(9)	−0.1141 (10)	0.2920 (8)	0.1339 (14)	0.064
C(10)	−0.1045 (10)	0.3438 (8)	0.2010 (16)	0.070
C(11)	−0.0850 (11)	0.3228 (9)	0.3042 (16)	0.079
C(12)	−0.0817 (10)	0.2580 (8)	0.3045 (13)	0.060
C(13)	−0.1030 (9)	0.1670 (7)	0.0246 (11)	0.049
C(14)	−0.1707 (10)	0.1925 (8)	−0.0578 (13)	0.063
C(15)	−0.1707 (13)	0.1999 (9)	−0.1591 (14)	0.074
C(16)	−0.1057 (16)	0.1821 (10)	−0.1781 (15)	0.088
C(17)	−0.0359 (14)	0.1553 (11)	−0.0970 (15)	0.088
C(18)	−0.0355 (12)	0.1483 (8)	0.0049 (13)	0.068
C(19)	−0.2038 (9)	0.1337 (8)	0.1334 (15)	0.065
C(20)	−0.2374 (12)	0.1517 (10)	0.2049 (20)	0.089
C(21)	−0.3146 (17)	0.1320 (13)	0.1959 (29)	0.128
C(22)	−0.3573 (16)	0.0911 (17)	0.1076 (35)	0.154
C(23)	−0.3213 (17)	0.0706 (14)	0.0370 (24)	0.128
C(24)	−0.2464 (10)	0.0925 (11)	0.0513 (14)	0.084
B[b]	1.000	0.543	0.250	0.16
F(1)	1.059	0.506	0.318	0.16
F(2)	1.032	0.579	0.195	0.16

[a] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$. [b] Occupancy factor of 0.5.

aration of complexes (dppf)$PtCl_2$[7] and [(dppf)Pt(μ-OH)]$_2(BF_4)_2$.[2] The NMR spectra were obtained with a Jeol FX 90Q spectrometer at 27 °C with the residual solvent peak as an internal reference for the proton spectra. The $^{31}P\{^1H\}$ NMR spectra in DMF were obtained by using a coaxial capillary containing DMSO-d_6 for a deuterium lock. H_3PO_4 (85% v/v) was used as the external standard, and the chemical shifts are reported positive to lower shielding.

Preparation of [(dppf)Pt(1-MeTy(-H))(DMF)]$(BF_4)\cdot CH_2Cl_2$ (1). To a solution of [(dppf)Pt(μ-OH)]$_2(BF_4)_2$ (164 mg, 0.096 mmol) in 4 mL of DMF was added 27 mg (0.19 mmol) of 1-MeTy. The suspension was stirred at room temperature for 24 h. Addition of 20 mL of Et_2O to the resulting solution afforded a yellow precipitate, which was collected by filtration, washed with Et_2O, and dried under vacuo overnight. The yield of the isolated solid, calculated for the formulation [(dppf)Pt(1-MeTy-(-H))]$BF_4\cdot$2DMF was 199 mg, 92.2%. Anal. Calcd for $C_{46}H_{49}N_4O_4P_2PtFeBF_4$: C, 49.25; H, 4.40; N, 4.99. Found: C, 49.11; H, 4.95; N, 4.97. ^1H NMR in $CDCl_3$ at 27 °C (δ): 1-MeTy resonances, 6.35 (quartet, J_{HH} = 1 Hz, H(6)), 2.16 (singlet, NCH_3), 1.51 (doublet, J_{HH} = 0.9 Hz, CH_3); dppf resonances, 8.0–7.2 (complex multiplet, C_6H_5), 5.3 (broad singlet, 1 H), 5.2 (b s, 1 H), 4.75 (b s, 2 H), 4.32 (unresolved multiplet, 2 H), 3.57 (u m, 2 H, cyclopentadiene protons); DMF, 2.93 (3 H), 2.91 (3 H), 2.81 (3 H), 2.74 (3 H). Crystallization of the crude product from CH_2Cl_2 affords the dichloromethane solvate (**1**). Anal. Calcd for $C_{44}C_{44}N_3O_3P_2FeB_4Cl_2Pt$: C, 46.6; H, 3.91; N, 3.71. Found: C, 47.16; H, 4.22; N, 3.87.

Preparation of [(dppf)Pt(1-MeTy(-H))(1-MeCy)](BF_4) (2). To a solution of [(dppf)Pt(μ-OH)]$_2(BF_4)_2$ (257 mg, 0.15 mmol) in 4 mL of DMF was added 42 mg (0.3 mmol) of 1-MeTy. The suspension was stirred at room temperature for 3 days. To the resulting solution was added 38.2 mg (0.3 mmol) of 1-MeCy. The suspension was stirred at room temperature for 4 days. The reaction mixture was filtered, and then Et_2O (10 mL) was added. The oil initially formed gradually converted to a powdered brown solid upon stirring for 1 h. The solid recovered by filtration weighed 270 mg. Anal. Calcd for $C_{45}H_{42}N_5O_3F_4P_2BFePt$: C, 49.11; H, 3.85; N, 6.36. Found: C, 48.16; H, 3.75; N, 6.23. ^1H NMR in DMF-d_7 (δ): 1-MeTy(-H) resonances, 6.81 (quartet, J_{HH} = 1.2 Hz, H(6)), 1.46 (doublet, J_{HH} = 1 Hz, CH_3), 2.99 (singlet, NCH_3); 1-MeCy resonances, 10.93 (broad singlet, NH), 7.10 (doublet, J_{HH} = 7.8 Hz, H(6)), 5.58 (doublet of doublets, J_{HH} = 7.8 Hz, J_{PH} = 2.05 Hz, H(5)), 3.24 (singlet, NCH_3); dppf resonances, 7.4–8.0 (complex multiplet, C_6H_5), 5.38 (1 H), 5.24 (1 H), 4.98 (1 H), 4.92 (1 H), 4.49 (2 H), 3.85 (1 H), 3.68 (1 H) (broad singlets, C_5H_4P).

Table VI. Selected Interatomic Distances (Å) and Angles (deg) for [(dppf)Pt(1-MeTy(-H))(DMF)]$BF_4\cdot CH_2Cl_2$ (**1**) and for [(dppf)Pt(1-MeTy(-H))(1-MeCy)]BF_4 (**2**)

Distances for 1			
Pt–P(1)	2.237 (6)	N(1)–C(2)	1.55 (5)
Pt–P(2)	2.265 (7)	C(2)–N(3)	1.40 (3)
Pt–O(1)	2.14 (1)	N(3)–C(4)	1.30 (3)
Pt–N(3)	2.06 (2)	C(4)–C(5)	1.43 (4)
Pt---Fe	4.202 (3)	C(5)–C(6)	1.33 (4)
Fe–C(av)	2.04 (2)	C(6)–N(1)	1.34 (4)
P–C(av)	1.83 (2)	N(1)–C(1)	1.40 (3)
O(1)–C(18)	1.24 (3)	C(2)–O(2)	1.24 (4)
C(18)–N(2)	1.34 (3)	C(4)–O(4)	1.25 (3)
N(2)–C(19)	1.50 (4)	C(5)–C(7)	1.44 (4)
N(2)–C(20)	1.53 (5)		
Angles for 1			
P(1)–Pt–P(2)	99.1 (3)	Pt–P(2)–C(33)	108.9 (6)
P(1)–Pt–O(1)	174.0 (6)	Pt–P(2)–C(39)	111.1 (7)
P(1)–Pt–N(3)	88.5 (6)	Pt–O(1)–C(18)	124.7 (1.7)
P(2)–Pt–O(1)	84.8 (6)	O(1)–C(18)–N(2)	115.7 (2.3)
P(2)–Pt–N(3)	172.3 (5)	C(18)–N(2)–C(19)	126.9 (2.4)
O(1)–Pt–N(3)	87.5 (8)	C(18)–N(2)–C(20)	118.6 (2.4)
Pt–P(1)–C(8)	111.8 (7)	C(19)–N(2)–C(20)	114.5 (2.4)
Pt–P(1)–C(21)	114.7 (7)	Pt–N(3)–C(2)	114.2 (1.6)
Pt–P(1)–C(27)	112.5 (5)	Pt–N(3)–C(4)	123.4 (1.7)
Pt–P(2)–C(13)	122.9 (6)	C(2)–N(3)–C(4)	122.4 (2.2)
Distances for 2			
Pt–P	2.274 (4)	C(2)–O(2), C(2)′–N(2)′	1.23 (2)
Pt–N(3)	2.10 (1)	C(2)–N(1), C(2)′–C(1)′	1.44 (3)
Pt---Fe	4.310 (2)	N(1)–C(1)	1.31 (6)
Fe–C(av)	2.03 (1)	N(1)–C(6), C(1)′–C(6)′	1.33 (4)
P–C(8)	1.78 (2)	C(6)–C(5), C(6)′–N(1)′	1.23 (3)
P–C(13)	1.79 (1)	C(5)–C(7), N(1)′–C(7)′	1.47 (3)
P–C(19)	1.84 (2)	C(5)–C(4), N(1)′–C(4)′	1.40 (2)
C_{Ph}–C_{Ph}(av)	1.40 (2)	C(4)–O(4), C(4)′–O(4)′	1.21 (2)
C_{Cp}–C_{Cp}(av)	1.42 (2)	C(4)–N(3), C(4)′–N(3)′	1.35 (3)
N(3)–C(2), N(3)′–C(2)′	1.37 (2)		
Angles for 2			
P–Pt–N(3)	167.6 (4)	Pt–N(3)–C(2)	122.8 (1.2)
P–Pt–P′	99.8 (2)	Pt–N(3)–C(4)	114.5 (1.1)
N(3)–Pt–N(3)′	86.3 (7)	C(8)–P–C(13)	103.5 (7)
Pt–P–C(8)	121.8 (6)	C(8)–P–C(19)	102.4 (8)
Pt–P–C(13)	109.6 (6)	C(13)–P–C(19)	103.9 (8)
Pt–P–C(19)	113.7 (6)		

Crystallography. Single crystals suitable for X-ray analysis were grown from CH_2Cl_2 for **1** and from a mixture of CH_2Cl_2/Me_2CO for **2** upon slow evaporation. Crystallographic data are reported in Table III, while other numbers related to data collection and refinement procedure have been deposited as supplementary material. For the calculation of the structure factors, corrections of the Lorentz–polarization effects and absorption, using an empirical method based on ψ scans of three reflections at $\chi \sim 90°$, were made. Pt atom parameters were found from Patterson synthesis, and all non-H atoms of the cation were located in subsequent difference Fourier syntheses. The structure of **2** was refined in the centrosymmetric space group $C2/c$ although systematic extinctions were consistent also with Cc. At the beginning, refinement in Cc space group was performed but unsuccessfully; in fact, it led to a rather low value of R (0.058) but with some chemically unrealistic bond distances (Å) (for example, Pt–P = 2.21, Pt–P′ = 2.33, C(5)–C(6) = 0.09, C(1)′–C(6)′ = 0.95, N(3)′–C(2)′ = 1.61, and N(1)′–C(6)′ = 1.87 Å) (see Figure 2 for the atomic labeling scheme), along with large correlation matrix elements (0.90 between P and P′; 0.85 between N(3) and N(3)′; 0.80 between O(2) and N(2)′). Thus, a resonable structure could only be deduced with the use of $C2/c$, and the choice of this space group yielded crystallographically equivalent the 1-MeTy(-H) and 1-MeCy ligands and it forced the Pt and Fe atoms to reside on a special position (2-fold axis). Moreover, the whole molecule seems to suffer from considerable thermal motion; in particular, the BF_4 fluorines are disordered and the final difference Fourier syntheses showed at least six peaks of comparable height around B (which lies on the 2-fold axis), but any attempt to refine their positions and occupancies failed. On the other hand, these difficulties arise when trying to refine a noncentrosymmetric structure, containing heavy atoms, which is pseudocentrosymmetric. For **1** to ensure a good observation/variable ratio and to achieve convergence, the phenyl and cyclopentadienyl rings were treated as regular hexagons (C–C = 1.395 Å) and pentagons (C–C = 1.42 Å) to be fitted to groups of atoms and then refined as rigid groups in the refinement procedure.

Fractional atomic coordinates and thermal parameters for **1** and **2** are listed in Tables IV and V, while some relevant interatomic distances and angles are reported in Table VI. Additional details, including a full presentation of data collection parameters and refinement information, nonessential bond distances and angles, least-squares planes, and tables of structure factors, are available as supplementary material. The SHELXTL-PLUS package of computer programs was employed for the solution and refinement of the structures.[18]

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Acknowledgment. Parke-Davis is gratefully acknowledged for a research grant to G.T. We thank the Progetto Finalizzato Chimica Fine II, CNR, for partial support.

Supplementary Material Available: For **1** and **2**, Table A, containing a full presentation of data collection parameters and refinement information, Tables B-D, listing bond distances and angles, least-squares planes, deviations of the relevant atoms, and dihedral angles, Figure A, showing another perspective view of **1**, Figure B, showing a packing diagram of **2**, and Figure C, showing superimposition of the cations of **1** and **2** (8 pages); Tables E and F, listing observed and calculated structure factors for both compounds (19 pages). Ordering information is given on any current masthead page.

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Electron-Transfer Reactions of Bis(dipeptide)nickel(III) Complexes

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Received May 22, 1991

The kinetics and mechanism of the oxidation of $[Co(edta)]^{2-}$ ($edta^{4-}$ = 1,2-diaminoethane-*N*,*N*,*N*′,*N*′-tetraacetate(4−)) by four bis(dipeptide)nickel(III) complexes, $[Ni(H_{-1}GG)_2]^-$, $[Ni(H_{-1}GA)_2]^-$, $[Ni(H_{-1}AG)_2]^-$, and $[Ni(H_{-1}AA)_2]^-$ (GH = glycine, AH = (*S*)-alanine), have been investigated at 25.0 °C and in 0.10 M perchlorate media. The reactions are first order in each reagent and have a complex dependence on pH. The dominant pathway over the pH range 4–10 involves the acid-catalyzed formation of a precursor complex through which electron transfer takes place. Structural information on the intermediate has been obtained from ^1H NMR relaxation studies of the diamagnetic analogue $[Co(H_{-1}AA)_2]^-$ in the presence of the paramagnetic probe $[Cr(edta)]^-$. There is indirect evidence for a strong hydrogen-bonding interaction between the N-terminal amine hydrogen atoms of a coordinated dipeptide ligand and the carboxylate oxygen atoms of the probe complex. The bis(dipeptide) ligands are arranged meridionally around the nickel(III) to produce a chiral center, and the complexes with optically active dipeptides exist as diastereomers which are readily separated by chromatography. Spectroscopic properties are reported. Stereoselectivity in the reaction with $[Co(edta)]^{2-}$ has been investigated with these complexes, and the results are interpreted in light of the structure of the proposed intermediate.

Introduction

Over the past decade there have been a number of reports of stereoselectivity in electron-transfer reactions between chiral metal complexes.[1-5] In general, stereoselectivities are not large but have proved useful in suggesting structures for intermediates in the electron-transfer process, an important component of mechanism which complements kinetic information. Despite the availability of chiral structures in biological systems, few studies of electron-transfer stereoselectivity involving complexes with biological ligands have been published. The unusually long-lived complexes[6,7] of nickel(III) $[Ni(H_{-1}GG)_2]^-$ (GGH = glycylglycine) and related analogues with optically active dipeptides $[Ni(H_{-1}GA)_2]^-$, $[Ni(H_{-1}AG)_2]^-$, and $[Ni(H_{-1}AA)_2]^-$ (AH = (*S*)-alanine) are of particular interest as chiral oxidants. Structural data are available for the corresponding nickel(II) complexes[8,9] and reveal that the dipeptide ligands are tridentate chelates coordinated meridionally in the high-spin d^8 complexes and are related by a C_2 axis. EPR evidence for the low-spin d^7 nickel(III) analogues indicates a similar coordination geometry.[6] The complex $[Ni(H_{-1}GG)_2]^-$ is chiral (Figure 1), and the enantiomers are designated P(C_2) and M(C_2), where P and M refer to plus (clockwise) and minus (anticlockwise) helicity around the C_2 axis, respectively. For the complexes with optically active dipeptides, the isomers are diastereomers.

The reduction potential[6] of $[Ni(H_{-1}GG)_2]^-$ is sufficiently large to oxidize $[Co(edta)]^{2-}$, a useful probe[1,3,5] for electron-transfer stereoselectivity, and preliminary studies of stereoselectivity in the reaction between the optically active complex $[Ni(H_{-1}AA)_2]^-$ and $[Co(edta)]^{2-}$ were sufficiently encouraging to merit a more complete investigation. Stereoselectivity in this reaction is of particular interest since it involves electron transfer between two anionic complexes which experience electrostatic repulsions.

Experimental Details

(a) Materials. Metal perchlorate salts, $Ni(ClO_4)_2$, $Co(ClO_4)_2$, and $NaClO_4$, were obtained from commercial sources (Alfa and Baker "Analyzed") or were prepared from the corresponding metal carbonate and perchloric acid and were recrystallized before use. The dipeptide ligands glycylglycine, (*S*)-glycylalanine, (*S*)-alanylglycine, and (*S*,*S*)-alanylalanine (all Sigma) were used without further purification. Solutions of $[Ni(H_{-1}GG)_2]^{2-}$ ($\approx 10^{-3}$ M) were prepared by the slow addition of NaOH to a solution of $Ni(ClO_4)_2$ containing a 5-fold excess of the GGH to pH 11. The resulting pale blue solution of $[Ni(H_{-1}GG)_2]^{2-}$ was filtered and oxidized to the deep violet $[Ni(H_{-1}GG)_2]^-$ by controlled-potential electrolysis at 850 mV with use of a flow cell comprising a charcoal working electrode packed in a 70 × 7 mm Vycor glass column, a platinum-wire counter electrode, and a Ag/AgCl reference with 0.10 M $NaClO_4$ as electrolyte.[10] A PAR Model 173 potentiostat was used to supply the voltage which was measured relative to the reference

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