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Cyclometalated Analogues of Platinum Terpyridine Complexes: Kinetic Study of the Strong σ-Donor Cis and Trans Effects of Carbon in the Presence of a π-Acceptor Ligand Backbone

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The substitution kinetics of the complexes [Pt(N–N–C)Cl] (N–N–CH = 6-phenyl-2,2′-bipyridine), [Pt(N–C–N)Cl] (N–CH–N = 1,3-di(2-pyridyl)benzene), and [Pt(N–N–N)Cl]Cl (N–N–N = 2,2′:6′,2″-terpyridine) with the nucleophiles Br^-, I^-, and, for the first two complexes, also thiourea, *N*,*N*-dimethylthiourea, and *N*,*N*,*N*′,*N*′-tetramethylthiourea, have been studied in methanol as solvent. In case of the thioureas, the activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ were also determined from the temperature and pressure dependence of the reactions. Two crystal structures of [Pt(N–N–C)Cl] were determined (yellow and red polymorphs); the intense red color of the latter polymorph results from Pt–Pt interactions (Pt–Pt distance = 3.366 Å). The data enable an analysis of the cis and trans effects and the influence of the strong σ-donor carbon in the presence of an electron withdrawing π-acceptor ligand backbone. The results indicate that the intrinsic reactivity is enhanced greatly by the labilizing effect of the trans carbon donor, but the nucleophilic discrimination is dramatically reduced due to the decrease in electrophilicity on the metal center. However, although the electron withdrawing π-acceptor effect is partly counteracted by the σ-donor effect, the complex still benefits from a higher nucleophilic discrimination than in the comparable Pt(II) trans carbon donor complexes, where no or fewer π-acceptors are present. In the case of the cis carbon donor complex, the intrinsic reactivity remains unchanged, but the nucleophilic discrimination is reduced and leads to a reduced reactivity of the [Pt(N–N–C)Cl] complex in comparison to [Pt(N–N–N)Cl]Cl. On the basis of these results, a more detailed treatment of the nature of the cis effect is offered.

1. Introduction

In recent years, much attention has been given to the substitution behavior of Pt(II) complexes that contain one or more Pt−C bonds.[1−16] A reason for this is that two cis Pt−C bonds can induce a mechanistic changeover from the usual associative substitution route[1,2] to a dissociative mechanism.[3−8] It could be shown that, in the case of complexes of the type *cis*-$[Pt(L)_2(R)_2]$ (L = Me, Ph; R = thioethers or DMSO), the 14 valence electron intermediate participating in a dissociative substitution mechanism is

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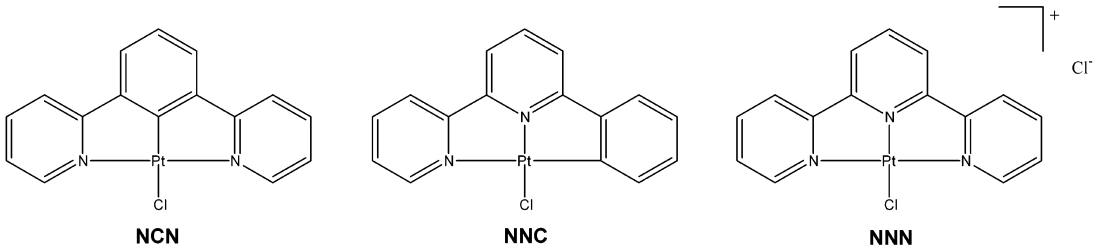

Figure 1. Schematic structures of the investigated complexes.

stabilized by the two strong σ-donor carbon atoms. If one of the thioethers is displaced by CO, the mechanism changes again from a dissociative to an associative one. This can be accounted for by the strong π-acceptor ability of CO which removes the high electron density from the metal center and favors a five-coordinate 18 valence electron intermediate encountered in an associative substitution mechanism.[9] Astonishingly, a comparison of the substitution reactions of the complexes *cis*-[Pt(Ph)$_2$(SMe$_2$)$_2$] and [Pt(2,2′-biphenyl)-(SMe$_2$)$_2$] showed that the latter reacts 10^2 times faster and still dissociatively despite its presumed π-acceptor ability. It was concluded from these findings that in-plane disposition of single aryl ligands does not increase the electrophilicity of the platinum center through π-back-bonding.[10]

This leads to another reason for the significant interest in this area. Over the past decade, the role of cyclometalation in controlling the reactivity of platinum complexes has been studied extensively.[10−16] For example, it was discussed whether the remarkable enhancement in rate observed for the substitution of water in the complexes [Pt(N−C)(N)-(H$_2$O)] (N−CH = *N*,*N*-dimethylbenzylamine, N = pyridine-3-sulfonic acid)[11,12] and [Pt(N−C−N)(H$_2$O)]$^+$ (N−CH−N = 2,6-bis((dimethylamino)methyl)phenyl))[13] is due to π-back-donation into the empty anti- or nonbonding π-orbitals of the in-plane aryl ligand,[12,13] or due to the strong trans labilizing effect of the Pt−C bond,[14,15] as also suggested by the investigations already mentioned.[9] Further kinetic studies on the role of cyclometalation have shown that the importance of cyclometalation for aliphatic carbon donors is minute, but in the case of phenyl as carbon donor, the in-plane configuration of the phenyl ring as induced by cyclometalation enables effective π-back-bonding comparable to that of an in-plane pyridine ring and, therefore, enhances the reaction rate ([Pt(N−N−C)Cl], N−N−CH = 6-phenyl-2,2′-bipyridine, and reacts 10^2 times faster than [Pt-(2,2′bipyridine)(phenyl)Cl]) due to an enhanced electrophilicity of the metal center.[16] In this case, only Pt−C bonds cis to the leaving ligand were investigated, whereas the previously mentioned studies focused on substitution reactions trans to the Pt−C bond. At least for the cis position, it could be shown that the electrophilicity of the metal center benefits from the π-back-bonding to the in-plane phenyl ring, whereas the importance of π-back-bonding of an in-plane phenyl ring in the trans position still remains uncertain.

In a recent study[17,18] on the π-acceptor effects of in-plane pyridine donors, we could show that π-back-bonding in the cis position seems to enhance the electrophilicity of the metal center slightly more than in the trans position. Nevertheless, there is still a thermodynamically and kinetically measurable increase in the electrophilicity if a trans amine is substituted by a trans in-plane pyridine ligand.[18] We have therefore now investigated the effect of a strong σ-donor Pt−C bond in the cis or trans position to the leaving group on the reactivity of the complex in the presence of a strong π-acceptor ligand backbone. We systematically studied the ligand substitution reactions of the complexes [Pt(N−C−N)Cl] (N−CH−N = 1,3-di(2-pyridyl)benzene) and [Pt(N−N−C)Cl] (N−N−CH = 6-phenyl-2,2′-bipyridine) in comparison to [Pt(N−N−N)-Cl]Cl (N−N−N = 2,2′:6′,2″-terpyridine) (see Figure 1). In the remaining text, these complexes are referred to as **NCN**, **NNC**, and **NNN**, respectively. In these complexes, the in-plane phenyl/pyridine rings act as π-acceptors, delocalize negative charge away from the reaction center, and thereby increase the electrophilicity of the Pt(II) center.[16−21] In addition, we successfully solved the crystal structure of the **NNC** complex, which enables us to discuss the cis influence of the Pt−C bond in comparison to the known structures of **NCN**,[22] [Pt(terpy)Cl]ClO$_4$,[23] and [Pt(terpy)Cl]SO$_3$CF$_3$.[24]

It was also our objective to gain more insight into the relationship between σ-donor and π-acceptor effects in Pt-(II) chemistry. Are these effects cumulative, do they counteract each other, or are they independent effects in which their importance is defined by the underlying reaction mechanism? Dissociative substitution reactions are expected to benefit mostly from σ-donor properties, whereas associative reactions are expected to be mainly enhanced by π-acceptor effects. Another question concerns the position of the σ-donor (cis or trans) to the leaving group. Furthermore, the investigated complexes allow us to analyze the trans and cis σ-donor effects and influence of the phenyl group, without affecting the steric or π-acceptor properties[16] of the trans or cis position, which often camouflage the relatively small cis σ-donor effect.

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2. Experimental Section

Chemicals and Ligands. The ligand 2,2′:6′,2″-terpyridine and all other chemicals were obtained in p.a. quality from Aldrich or Lancaster. In the case of 2-tri-*n*-butylstannylpyridine for the synthesis of 6-phenyl-2,2′-bipyridine, the technical grade product was used. Methanol p.a. obtained from Fluka was used as solvent in the kinetic and spectroscopic investigations.

6-Phenyl-2,2′-bipyridine (N−N−CH) was prepared according to the published procedure,[25] but the product was recrystallized from hexane instead of using column chromatography as suggested in the literature.

1,3-Di(2-pyridyl)benzene (N−CH−N) was synthesized as described in the literature,[22,26] but the crude product was chromatographed on silica gel with a diethyl ether/hexane (2:1) mixture instead of the suggested ratio of 1:4.

Synthesis of Complexes. [Pt(N−C−N)Cl] **(NCN)**[22,27] and [Pt(N−N−N)Cl]Cl (**NNN**)[28] were prepared according to published procedures.

[Pt(N−N−C)Cl] (NNC). All synthetic steps were performed under an atmosphere of argon. A mixture of 6-phenyl-2,2′-bipyridine (98 mg, 0.42 mmol) and K_2PtCl_4 (160 mg, 0.39 mg) in 100 mL of glacial acetic acid was stirred at 100 °C for 20 h until the red platinum salt disappeared completely. Cooling the orange solution to 4 °C (refrigerator) resulted in the formation of an orange precipitate, which was filtered off and washed with water, ethanol, and ether. The crude product was recrystallized from ethanol. Yield: 88 mg (0.19 mmol, 50%). Anal. Calcd for $C_{16}H_{11}ClN_2Pt$: H, 2.40; C, 41.61; N, 6.07. Found: H, 2.20; C, 41.36; N, 5.79. The recorded ^{1}H NMR spectrum is in perfect agreement with literature data.[29,30] Suitable crystals for the determination of the crystal structure were grown from CH_2Cl_2 by slow evaporation of the solvent in the refrigerator, resulting in yellow and red crystals.

X-ray Structure Determinations. Single crystals of **NNC** were obtained by slow evaporation of a CH_2Cl_2 solution, resulting in the deposition of red and yellow specimens. Diffraction measurements were made at 20 ± 2 °C on an Enraf-Nonius CAD-4 MACH 3 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å); collection of the diffraction intensities was by ω scans, with data corrected for absorption by ψ scans[31] (red polymorph, **NNC**(r), $T_{min} = 0.070$, $T_{max} = 0.185$; yellow polymorph, **NNC**(y), $T_{min} = 0.035$, $T_{max} = 0.727$). The structures were solved by direct methods and subsequently refined by full-matrix least-squares procedures on F^2 with allowance for anisotropic thermal motion of all non-hydrogen atoms employing the WinGX package[32] with the relevant programs (SIR-97,[33] SHELXL-97,[34] ORTEP-3[35]) implemented therein. **NNC**(r): $C_{16}H_{11}ClN_2Pt$ (461.81); triclinic $P\bar{1}$, $a = 8.880(5)$ Å, $b = 12.336(5)$ Å, $c = 13.624(3)$ Å, $\alpha = 102.10(3)°$, $\beta = 102.13(3)°$, $\gamma = 104.07(4)°$, $V = 1361(1)$ Å^3, $Z = 4$, $D_c = 2.254$ g cm^{-3}, μ(Mo Kα) = 10.496 mm^{-1}; 8296 reflections collected ($2.46° \le \theta \le 30.07°$; $-12 \le h \le +12$, $-17 \le k \le +16$, $0 \le l \le +19$), 7986 unique ($R_{int} = 0.0459$); wR2 = 0.1335 for all data and 361 parameters, R1 = 0.0494 for 6232 structure factors $F_o > 4\sigma(F_o)$. **NNC**(y): $C_{16}H_{11}ClN_2Pt$ (461.81); monoclinic $P2_1/c$, $a = 9.267(1)$ Å, $b = 7.541(1)$ Å, $c = 19.638(2)$ Å, $\beta = 99.84(1)°$, $V = 1352.2(3)$ Å^3, $Z = 4$, $D_c = 2.269$ g cm^{-3}, μ(Mo Kα) = 10.563 mm^{-1}; 3513 reflections collected ($2.11° \le \theta \le 28.17°$; $0 \le h \le +12$, $0 \le k \le +10$, $-26 \le l \le +25$), 3317 unique ($R_{int} = 0.0254$); wR2 = 0.1244 for all data and 181 parameters, R1 = 0.0421 for 2603 structure factors $F_o > 4\sigma(F_o)$.

Instrumentation and Measurements. NMR spectroscopy (Bruker Avance DPX 300) and a Carlo Erba elemental analyzer 1106 were used for complex characterization and chemical analysis, respectively.

Stock solutions of the complexes and nucleophiles were prepared by dissolving the required amounts in methanol and adding $LiSO_3CF_3$ to adjust the ionic strength to 0.1 M. The resulting complex concentrations were approximately 0.2 mmol/L (**NNC**), 0.05 mmol/L (**NCN**), and 0.02 mmol/L (**NNN**) before mixing with nucleophile solutions, respectively. A total of five, neutral and anionic, nucleophiles, viz. thiourea (TU), *N*,*N*-dimethylthiourea (DMTU), *N*,*N*,*N*′,*N*′-tetramethylthiourea (TMTU), bromide, and iodide, which have different nucleophilicities and steric hindrance,[18,36] were used as entering nucleophiles. The kinetics of the substitution of coordinated chloride was studied spectrophotometrically by following the change in absorbance as a function of time at suitable wavelengths. The selected wavelengths employed for each reaction are listed in Table S1 (see Supporting Information). The total absorbance changes were at least 0.1 absorbance units, except in the case of bromide as nucleophile where the spectral changes were smaller for all the complexes. Kinetic measurements were performed on an Applied Photophysics SX 18MV stopped-flow instrument coupled to an online data acquisition system, except for the slow reactions of **NNC** with Br^- and I^-, and of **NNN** with Br^-, which were investigated by the use of tandem cuvettes on a Varian Cary 5G spectrophotometer equipped with a thermostated cell holder. Experiments at elevated pressure (1−130 MPa) were performed on a laboratory-made high-pressure stopped-flow instrument.[37] Concentration and pressure dependences were performed at 25.0 °C, except for the pressure dependence of **NCN** which was investigated at 5.3 °C due to the longer dead-time of the high-pressure stopped-flow instrument. The temperatures of all instruments were controlled to an accuracy of ±0.1 °C. The ligand substitution reactions were studied under pseudo-first-order conditions by using at least a 10-fold excess of the entering nucleophile. All the reported rate constants represent an average value of at least seven kinetic runs for the fast reactions and at least three kinetic runs for the slow reactions for each selected experimental condition. All measured rate constants are summarized in Tables S2−S8 (see Supporting Information).

3. Results

In order to investigate the cis and trans σ-donor effect of a Pt(II)−carbon bond in the presence of the strong π-ac-

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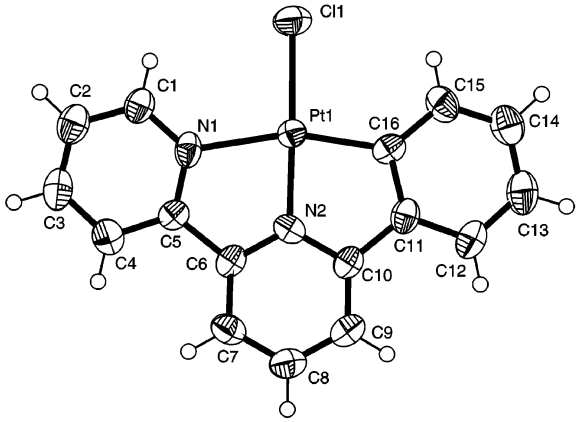

Figure 2. Molecular structure of **NNC**(y) showing the numbering scheme adopted. Thermal ellipsoids are shown at the 50% probability level.

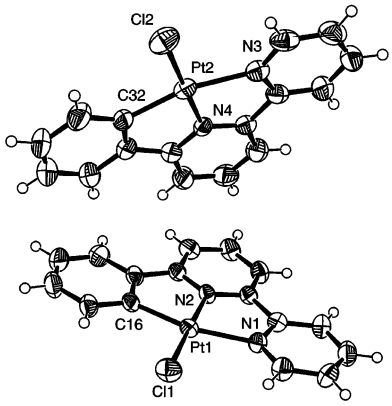

Figure 3. Molecular structure of the two crystallographically independent molecules of **NNC**(r) showing the numbering scheme adopted. Atom numbers which are not mentioned in the table have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

cepting terpyridine type of ligand backbone, three Pt(II) derivates were synthesized and characterized and their ligand substitution reactions studied kinetically. For the reactions of TU, DMTU, and TMTU with **NNC** and **NCN**, the corresponding activation parameters ($\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$) were also determined. In case of the **NNC** complex, the crystal structures of the red and yellow polymorphs were determined.

X-ray Structures. The X-ray crystal structures for **NNC** are shown in Figures 2 (yellow polymorph, **NNC**(y)) and 3 (red polymorph, **NNC**(r) containing two crystallographic independent molecules (**NNC**(r1) and **NNC**(r2)), and selected bond lengths and angles are listed in Table 1. The observed metal−ligand bonds and angles are in good agreement with those observed in related complexes.[38−42] The structures of both polymorphs exhibit a distorted square planar coordination geometry since the bite angle of the N−N−C ligand deviates substantially from 180° (viz. 161.6(3)°, 162.0(3)°, and 161.1(3)° for **NNC**(y), **NNC**(r1), and **NNC**(r2), respectively). This is comparable to the bite angles in the **NCN** complex (161.1(2)°)[22] and in [Pt(terpy)Cl]SO_3CF_3 (161.8(2)°).[24] The Pt−N bond length trans to the phenyl group (2.131(7), 2.116(6), and 2.124(8) Å for **NNC**(y), **NNC**(r1), and **NNC**(r2), respectively) is noticeably longer than the corresponding bond lengths in [Pt(terpy)Cl]SO_3CF_3 (2.018(5) and 2.030(5) Å)[24] due to the stronger trans influence exerted by the phenyl substituent. The average Pt−Cl bond length in the **NNC** complexes is slightly longer (2.312(2), 2.307(2), and 2.316(2) Å for **NNC**(y), **NNC**(r1), and **NNC**(r2), respectively) than in [Pt(terpy)Cl]SO_3CF_3 (2.307(1) Å)[24] or [Pt(terpy)Cl]ClO_4 (2.301(6) Å).[23] Whether this is due to a cis labilization effect of the phenyl group will be discussed later. In the crystal packing diagram of **NNC**(y) (Figure 4), the complexes are orientated in a head-to-tail style and form a continuous stack with alternating short/long Pt−Pt distances (4.466 and 6.660 Å, respectively). These Pt−Pt

Table 1. Selected Crystallographic Bond Distances and Angles for **NNC** (Red and Yellow Polymorph)

Yellow Polymorph Bond Distances (Å)			
Pt(1)−N(1)	2.131(7)	Pt(1)−C(16)	1.994(9)
Pt(1)−N(2)	1.942(7)	Pt(1)−Cl(1)	2.312(2)
Yellow Polymorph Bond Angles (deg)			
N(2)−Pt(1)−N(1)	79.5(3)	N(1)−Pt(1)−Cl(1)	99.3(2)
N(2)−Pt(1)−C(16)	82.4(3)	C(16)−Pt(1)−Cl(1)	99.0(3)
C(16)−Pt(1)−N(1)	161.6(3)	N(2)−Pt(1)−Cl(1)	176.1(2)
Red Polymorph Bond Distances (Å)			
Pt(1)−N(1)	2.116(6)	Pt(2)−N(3)	2.124(8)
Pt(1)−N(2)	1.950(6)	Pt(2)−N(4)	1.946(6)
Pt(1)−C(16)	1.995(8)	Pt(2)−C(32)	2.014(9)
Pt(1)−Cl(1)	2.307(2)	Pt(2)−Cl(2)	2.316(2)
Red Polymorph Bond Angles (deg)			
N(2)−Pt(1)−N(1)	79.6(2)	N(4)−Pt(2)−N(3)	79.5(3)
N(2)−Pt(1)−C(16)	82.4(3)	N(4)−Pt(2)−C(32)	81.7(3)
C(16)−Pt(1)−N(1)	162.0(3)	C(32)−Pt(2)−N(3)	161.1(3)
N(1)−Pt(1)−Cl(1)	98.9(2)	N(3)−Pt(2)−Cl(2)	99.5(2)
C(16)−Pt(1)−Cl(1)	99.0(2)	C(32)−Pt(2)−Cl(2)	99.4(3)
N(2)−Pt(1)−Cl(1)	177.7(2)	N(4)−Pt(2)−Cl(2)	178.7(2)

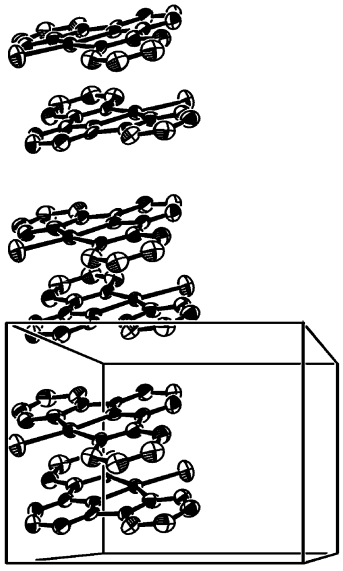

Figure 4. Crystal packing of **NNC**(y), viewed normal to 001. Hydrogen atoms have been omitted for clarity.

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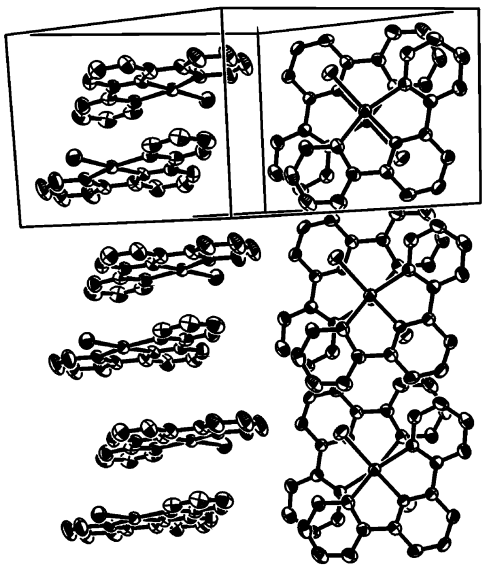

Figure 5. Crystal packing of **NNC**(r). Hydrogen atoms have been omitted for clarity. On the left side, the endless chain of Pt2 complexes can be seen; on the right side, three "dimeric" Pt1 complex units are displayed.

distances (>4 Å) indicate that there are no metal−metal interactions. The interplanar separations of ca. 3.5 Å between the N−N−C ligands are sufficiently close for $\pi-\pi$ interactions as already observed in similar structures.[38−42] In the case of **NNC**(r), crystal packing is a little bit different (see Figure 5). The Pt(2) complex from the asymmetric unit behaves very similarly, showing the same endless head-to-tail stacking with alternating short/long Pt−Pt distances (4.610 and 7.210 Å, respectively) without any metal−metal interaction, but with a $\pi-\pi$ interaction of the ligand due to the small interplanar separation of ca. 3.5 Å. Although the head-to-tail stacking can also be observed for the Pt(1) complex of **NNC**(r1), only "dimeric" units instead of endless chains are formed. However, these are closer together, the interplanar distance is ca. 3.3 Å, and the Pt−Pt distance is only 3.366 Å (the Pt−Pt distance between two dimeric units is 8.880 Å). The two metal atoms are directly on top of each other, indicating not only a $\pi-\pi$ interaction of the ligands, but also a metal−metal interaction. We believe that the weak repulsion between the filled d-orbitals of the two platinum atoms is responsible for the intense red color of this polymorph, since it is suggested that the intense color observed for the Magnus type salts is due to mutual disturbances between the d-electron clouds above and below the platinum centers as a result of the close Pt−Pt proximity.[43−45]

Kinetic Measurements. Kinetic traces gave excellent fits to single exponentials. There was no indication of a ring-opening (dechelation) reaction within the studied time range as observed for the strong nucleophile phosphine in similar investigations.[16] The obtained pseudo-first-order rate constants, k_{obsd}'s, were plotted against the concentration of the

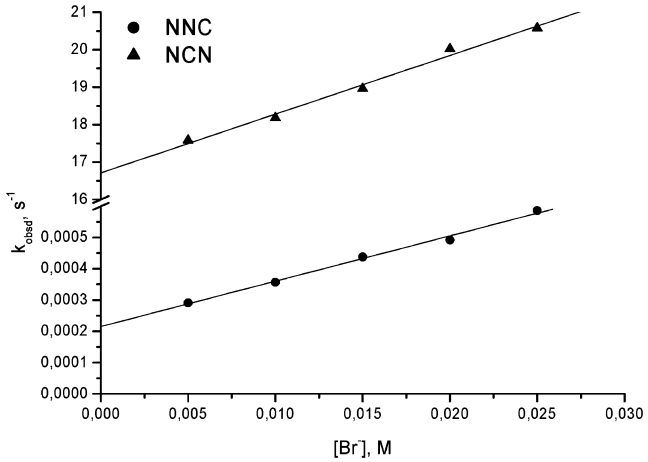

Figure 6. Plots of k_{obsd} versus Br^- concentration for the reactions with **NCN** and **NNC**. $I = 0.1$ M ($LiSO_3CF_3$); $T = 25.0$ °C.

entering nucleophile. A linear dependence on the nucleophile concentration was observed for all reactions. An intercept was observed for all reactions with **NCN**. Since the error in the intercept (k_S) was considerably higher for the reactions with TU ($k_S = 12 \pm 6$ s^{-1}, at 25.0 °C), these values were not used in further calculations (i.e., temperature dependence). In the case of the weakest investigated nucleophile Br^-, an intercept could also be observed in the concentration dependence of **NNN** and **NNC**. Representative results for **NCN** and **NNC** are shown in Figure 6. In experiments performed at the lowest employed nucleophile concentration for the weakest nucleophile bromide, the presence of a 10-fold excess (in comparison to the complex concentration) of chloride indicated that a possible contribution of a back reaction with chloride to the intercept can be neglected in the case of **NCN** and **NNC**. Only in the reaction with **NNN**, where very small nucleophile concentrations had to be used to obtain the intercept accurately, was the back reaction found to contribute significantly to the intercept. Therefore, the concentration dependence for the reaction of **NNN** with Br^- was performed in the presence of a 10-fold excess of chloride in order to guarantee pseudo-first-order conditions for both the forward and backward reactions. By measuring the chloride concentration dependence of the backward reaction in the presence of a 10-fold excess of bromide, we could subtract the rate constant for the back reaction (k_{-2}) from the intercept. The remaining intercept and the intercept observed for reactions with **NNC** and **NCN** can be ascribed to a parallel solvolysis reaction pathway, well-known in Pt(II) chemistry.[46] In the case of **NNN**, however, the solvolysis reaction of the bromo complex also contributes to the observed back reaction as shown in Scheme 1. Since it is impossible to separate k_S and k_{-S} experimentally in this particular case, the relative values of k_S and k_{-S} had to be predicted. It is known from the literature that the solvolysis rate constants for the complexes $[Pt(dien)(Br)]^+$ and $[Pt(dien)(Cl)]^+$ are within ±30% almost the same.[47−49] There-

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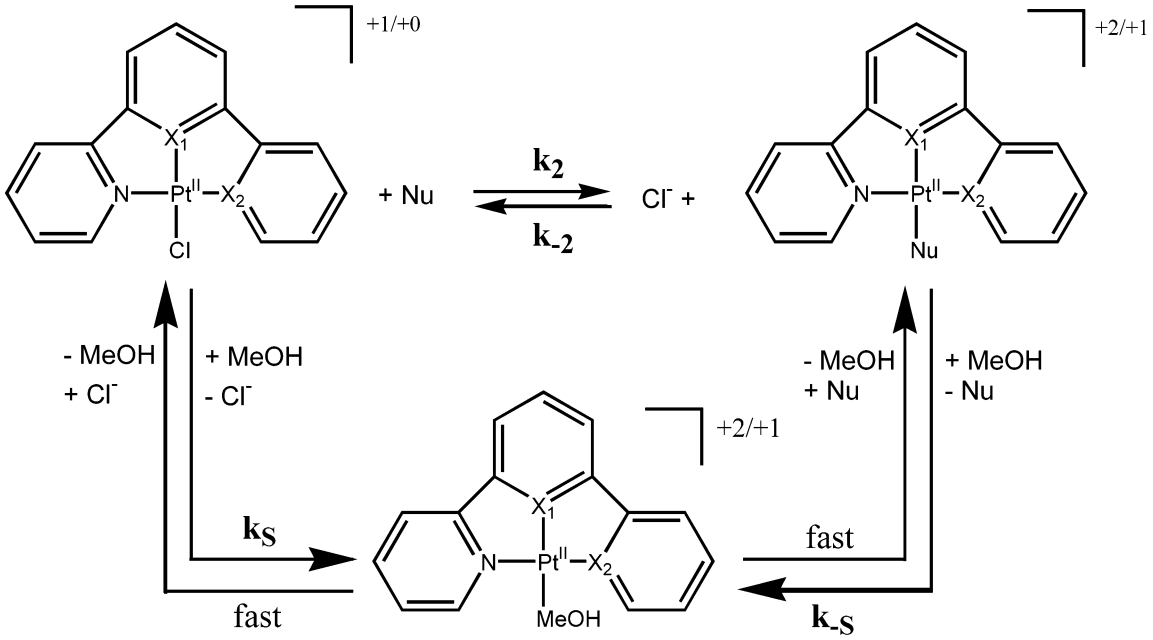
(44) Atoij, M.; Richardson, J. W.; Rundle, R. E. *J. Am. Chem. Soc.* **1957**, *79*, 3017.
(45) Yamada, S. *J. Am. Chem. Soc.* **1951**, *73*, 1579.
(46) Gray, H. B.; Olcott, R. J. *Inorg. Chem.* **1962**, *1*, 481.
(47) Belluco, U.; Ettorre, R.; Basolo, F.; Pearson, R. G.; Turco, A. *Inorg. Chem.* **1966**, *5*, 591.

Scheme 1



$X_1, X_2 = N, N / N, C^- / C^-, N$

$Nu = TU, DMTU, TMTU, Br^-, I^-$

fore, it is reasonable to assume that k_S and k_{-S} contribute equally to the observed intercept. In fact, it is more the order of magnitude of k_S and k_{-S} that is important for the subsequent treatment of the data. The overall substitution process can therefore be represented by the mechanism outlined in Scheme 1, and the corresponding expression for k_{obsd} is given by eq 1.

$$k_{obsd} = k_S + k_2[Nu] \; (+k_{-2}[Cl^-] + k_{-S} \text{ in the case of } \mathbf{NNN}) \quad (1)$$

Note that the solvolysis pathway occurs for all investigated reactions, but since its contribution to k_{obsd} in the reaction with the stronger nucleophiles is rather small, the observed intercept is smaller than the experimental error. Therefore, for the reactions of **NNC** and **NNN** with the nucleophiles I^-, TU, DMTU, and TMTU, the corresponding plot for the concentration dependence of k_{obsd} was taken through zero. The resulting rate constants are summarized in Table 2. The obtained rate constants for the substitution of chloride by bromide (6.5 ± 0.1 M^{-1} s^{-1}; lit., 8.1 ± 0.5 M^{-1} s^{-1}) and iodide (267 ± 1 M^{-1} s^{-1}; lit., 303 ± 11 M^{-1} s^{-1}), and the corresponding nucleophilic discrimination factor s (1.39 ± 0.02, obtained by a linear fit through 3 points; lit., 1.23 obtained from a fit through 2 points), are in good agreement with the quoted literature values.[19]

The activation parameters for the reactions of **NCN** and **NNC** with TU, DMTU, and TMTU were determined from a systematic variation of temperature and pressure. Since k_{obsd} consists of two independent rate constants k_S and k_2 in the case of the reactions with **NCN** (see eq 1), a concentration dependence at different temperatures was performed (see Figure 7 for a typical example), whereas the temperature dependence for **NNC** was studied at only one nucleophile concentration. The thermal activation parameters for k_S and k_2 ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) were calculated from the Eyring equation using a weighted error linear fit as shown in Figure 8. For the effect of pressure on the reaction rates of **NCN**, a pressure dependence study at different TMTU concentrations was performed (see Figure S1, Supporting Information). The obtained pressure dependent values of k_S were subtracted from the corresponding k_{obsd} values observed for the reactions of **NCN** with TU and DMTU, which were performed at one nucleophile concentration only. This enabled us to calculate the activation volume for k_2 independently of k_S. In the case of **NNC**, the pressure dependence was studied at a single

Table 2. Summary of Rate Constants for the Displacement of Chloride by a Range of Nucleophiles in Methanol at 25.0 °C and 0.1 M ($LiSO_3CF_3$) Ionic Strength

	complexes		
nucleophile	**NCN**	**NNC**	**NNN**
TU,[a] k_2 [M^{-1} s^{-1}]	44 500 ± 2000	98 ± 2	1500 ± 10[d]
DMTU,[b] k_2 [M^{-1} s^{-1}]	18 400 ± 500	42.5 ± 0.4	450 ± 10[d]
TMTU,[c] k_2 [M^{-1} s^{-1}]	7400 ± 300	32.3 ± 0.3	95 ± 4[d]
Br^-, k_2 [M^{-1} s^{-1}]	157 ± 9	0.0145 ± 0.0006	6.5 ± 0.1
I^-, k_2 [M^{-1} s^{-1}]	1464 ± 14	0.64 ± 0.02	267 ± 1
MeOH, k_S, [s^{-1}]	16.4 ± 0.9[e]	(2.2 ± 0.1) × 10^{-4} [f]	(2.1 ± 0.4) × 10^{-4} [f,g]

[a] Thiourea. [b] *N,N*-Dimethylthiourea. [c] *N,N,N′,N′*-Tetramethylthiourea. [d] Data taken from the literature.[72] [e] Average value for the reactions with DMTU, TMTU, Br^-, and I^-. [f] Obtained from the reaction with Br^-. [g] k_S was assumed to be equal to k_{-S} (see Results section).

(48) Rindermann, W.; Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1980**, *40*, 179.
(49) Palmer, D. A.; Kelm, H. *Inorg. Chim. Acta* **1976**, *19*, 117.

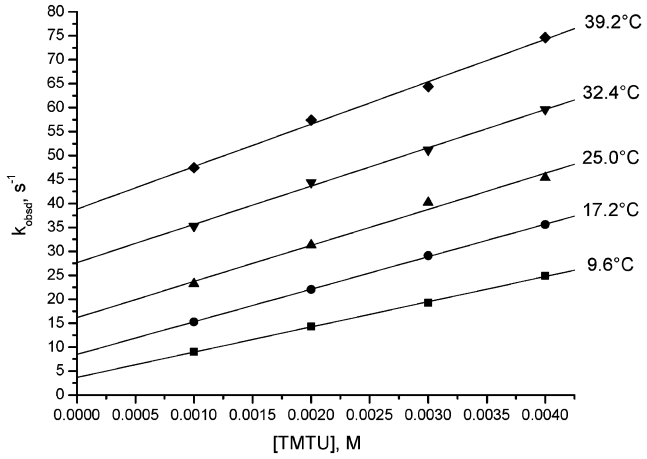


Figure 7. Plots of k_{obsd} versus TMTU concentration for the reaction with **NCN** at different temperatures. $I = 0.1$ M ($LiSO_3CF_3$).

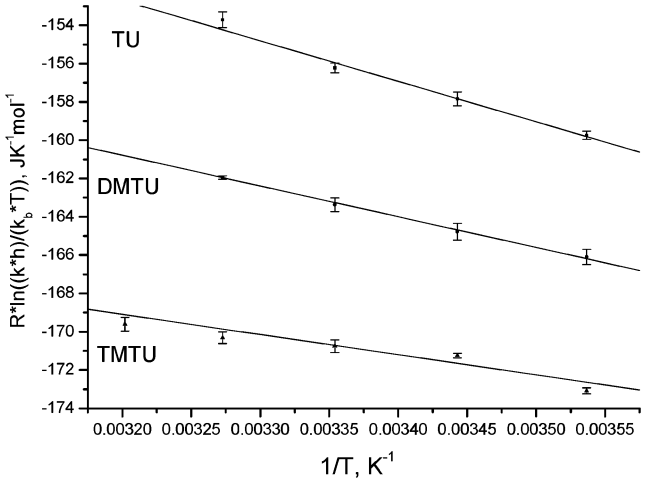


Figure 8. Eyring plots for the determination of the activation enthalpies and entropies for the reaction of the **NCN** complex with TU, DMTU, and TMTU.

Table 3. Activation Parameters for the Reactions of TU, DMTU, and TMTU with **NCN** and **NNC**

nucleophile	complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^{-3} mol^{-1}
TU	NNC	40.8 ± 1.5	-70 ± 5	-8.9 ± 0.4
	NCN	21.1 ± 1.4	-85 ± 5	-7.1 ± 0.4
DMTU	NNC	39.2 ± 0.8	-82 ± 3	-10.5 ± 0.6
	NCN	16.1 ± 1.3	-109 ± 4	-7.9 ± 0.3
TMTU	NNC	29.1 ± 1.6	-119 ± 5	-13.1 ± 0.7
	NCN	10.5 ± 0.9	-135 ± 3	-10.7 ± 1.7
MeOH	NCN	55.0 ± 1.0^a	-37 ± 3^a	-8.7 ± 2.2^b

[a] Average value of the temperature dependence of the intercept (k_S) from the reactions with DMTU and TMTU. [b] From the intercept of the reaction with TMTU.

nucleophile concentration. The values of k_{obsd} and k_S increase with increasing pressure, and the dependences of $\ln(k_{obsd/S})$ on the applied pressure were in all cases linear, as can be seen from the selected plots in Figure S2 (Supporting Information). The acceleration of the reaction by pressure is indicative of an associative substitution mechanism. This is also supported by the negative $\Delta S^{\ddagger}$ values calculated from the temperature dependence of the reactions. All activation parameters are summarized in Table 3.

In order to gain further information on the influence of a single Pt−C bond in the cis or trans position on the

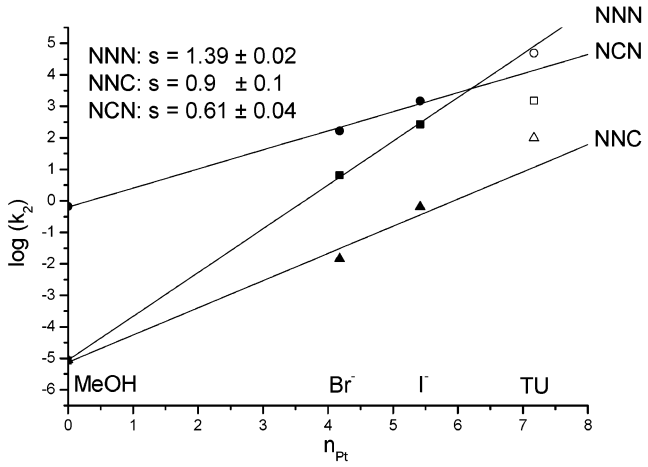


Figure 9. Plots of $\log(k_2)$ vs n_{Pt} for the determination of the nucleophilic discrimination factor *s*. Note that the empty points (TU) are not considered in the linear fit, due to the biphilic behavior of TU (see Discussion section).

nucleophilic discrimination ability of the complex, the rate constants for substitution of Cl^- by MeOH, Br^-, and I^- were measured, and the corresponding $\log(k_2)$ values plotted against their n_{Pt} values ($n_{Pt}(MeOH) = 0$, $n_{Pt}(Br^-) = 4.18$, $n_{Pt}(I^-) = 5.42$),[36,50] as shown in Figure 9. To obtain the k_2 value for substitution by MeOH, the rate constant for the solvolysis pathway (k_S) was divided by the concentration of methanol as solvent (24.7 M). Although the values for TU as entering nucleophile are also included in the plot, they were omitted from the fit since it is known that their behavior in determining the nucleophilic discrimination factor (s) is misleading due to their biphilic character.[51] The resulting values for *s* are 0.61 ± 0.04 (**NCN**), 0.9 ± 0.1 (**NNC**), and 1.39 ± 0.02 (**NNN**), respectively.

4. Discussion

A major part of the following discussion is based on the assumption that the π-acceptor effect of a phenyl ligand is comparable to that of a pyridine ligand, at least as far as the kinetic effects are concerned. Romeo et al. could demonstrate that the reactivity of the complex [Pt(2,2′bipyridine)(phenyl)-Cl] is enhanced by a factor of 191, as soon as the phenyl ring becomes part of the π-acceptor system due to its in-plane arrangement in **NNC**.[16] Nearly the same enhancement (factor 114 to 133) is achieved, when ammonia[52] in the complex [Pt(2,2′-bipyridine)(NH_3)OH_2] is displaced with an in-plane pyridine to give [Pt(2,2′:6′,2″-terpyridine)OH_2], due to the π-acceptor properties of the in-plane pyridine ring.[18] In both cases, the increased reactivity has its origin in the π-acceptor properties of the in-plane pyridine/phenyl ring,[16,18] showing clearly that these are indeed approximately the same. Therefore, the π-acceptor environment of **NNC** can be considered to be similar to that of **NNN**, as already suggested by Romeo et al.[16]

Cis and Trans Influence. The X-ray structure of **NNC** enables us to compare the trans influence of the phenyl group

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(51) Cattalini, L.; Orio, A.; Nicolini, M. *J. Am. Chem. Soc.* **1966**, *88*, 5734.
(52) Preliminary calculations have shown that the σ-donor strengths of ammonia and pyridine are very similar.

in the complex **NCN** with its cis influence, by a comparison of the lengthening of the Pt−Cl bond on displacing a trans or cis pyridine in **NNN** by a phenyl ligand. In the case of **NCN**, a Pt−Cl distance of 2.417(2) Å is reported,[22] which is in perfect agreement with other Pt−Cl bond lengths trans to the phenyl carbon donor.[15,53,54] The average Pt−Cl bond length for $[Pt(terpy)Cl]ClO_4$[23] and $[Pt(terpy)Cl]SO_3CF_3$[24] is 2.304 Å. This bond length is therefore increased by approximately 0.113 Å through the trans labilizing influence of the phenyl group. This rather large increase in bond length is not surprising, since it is known that the phenyl group is a very strong trans labilizing ligand (an approximate trans influence sequence is Cl < S < Sn, P < C, H < Si) due to its high σ-donor strength.[53,55] Perhaps more interesting is how this strong σ-donor affects the Pt−Cl bond in case of the **NNC** complex. It is known that the cis influence for a specific ligand is usually much smaller than its trans influence.[56,57] It is therefore not surprising that the average Pt−Cl bond length of **NNC** is 2.312 Å and only 0.008 Å longer than that in the $[Pt(terpy)Cl]^+$ complex. Considering three standard deviations, this difference in bond length is too small to allow a convincing interpretation. Nevertheless, two independent structures of **NNN** type complexes and two independent structures of **NNC** do show the same trend, viz. the Pt−Cl bond is always longer in the latter ligand arrangement. This may indicate a slight cis labilization via the σ-bond framework due to the higher σ-donor strength of the phenyl group as compared to the pyridine group. However, if there is such an effect, it is too small to be observed clearly in the available X-ray structures.

Reactivity of the Trans σ-Donor Complex. Despite the fact that the trans influence of the carbon σ-donor in the **NCN** complex is in perfect agreement with literature values (see preceding discussion), the observed reactivity of this complex is orders of magnitude higher than in comparable complexes. To our knowledge, the observed rate constants are the highest ever found for the substitution of chloride trans to a Pt(II)−carbon bond by the selected nucleophiles.[15,58] Since there is no evidence for a larger trans influence that would indicate a higher σ-donor strength of the trans phenyl group and therefore a higher ground state labilization,[1] other reasons must account for this unusually high reactivity. There are two possible explanations: First, the planar coordination sphere of the metal center, as induced by the in-plane pyridine/phenyl ligand system, offers only minute steric hindrance to the entering nucleophile, which leads to faster substitution reactions compared to complexes which are sterically more crowded in the cis positions.[53] Second, the in-plane arrangement of pyridine/phenyl rings at Pt(II) centers is known to accelerate associative substitution reactions by stabilizing the additional electron density in the transition state via their π-acceptor ability, thereby increasing the electrophilicity (and therefore the nucleophilic discrimination factor *s*) of the complex.[12,13,16−18] We believe that both effects contribute to the observed high reactivity. On one hand, the influence of steric crowding in the cis position on the substitution rate has been very well investigated for square planar Pt^{II}/Pd^{II} complexes,[1,59] and it is therefore known that reducing the steric crowding in the cis position accelerates the reaction. On the other hand, the nucleophilic discrimination factor *s* of **NCN** is about 0.61, whereas for the complexes $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OH_2)]^+$ and $[Pt\{C_6H_4(CH_2NMe_2)\text{-}2\}(NC_5H_4SO_3\text{-}3)(OH_2)]$ this factor is significantly smaller (0.40 and 0.43, respectively).[13] This indicates that transition state stabilization due to π-backbonding to the in-plane pyridine/phenyl groups also contributes to the observed high reactivity, at least for strong nucleophiles which benefit more from the nucleophilic discrimination ability of the metal center.[60]

On comparing the reactivity of **NCN** with **NNN**, it is seen that the substitution reaction is accelerated by 5 orders of magnitude in the case of the solvolysis reaction in methanol, but only by a factor of 5 in the case of the reaction with iodide, on displacing one nitrogen donor by a much stronger carbon donor. There is a simple explanation for this strange behavior. The high reactivity of **NCN** is mainly due to the *trans*-labilizing effect of the Pt−C bond which induces a high intrinsic reactivity, whereas the high reactivity of **NNN** is due to the increased electrophilicity of the metal center that causes a high nucleophilic discrimination. On displacing the trans pyridine of **NNN** by the strong phenyl σ-donor, the intrinsic reactivity goes up 5 orders of magnitude, but the nucleophilic discrimination factor drops from 1.39 (**NNN**) to 0.61 (**NCN**) because the electron withdrawing effect of the π-acceptor rings is partially canceled by the electron donating effect of the carbon atom.[61] Therefore, on comparing the reaction rates of **NNN** and **NCN**, the nucleophilicity

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(59) *Inorganic High Pressure Chemistry*; Kotowski, M., van Eldik, R., Eds.; Elsevier Science Publisher: New York, 1986; Vol 7, pp 219.
(60) A referee pointed out that the observed increase in nucleophilic discrimination (0.61 for **NCN** vs 0.40/0.43)[13] could also be due to a decrease in steric discrimination of **NCN** in comparison with the sterically more hindered reference complexes, and therefore not necessarily due to an electronic effect. If this is the case, a decrease in the ratio of the rate constants in going from unsubstituted to substituted thioureas would be expected since the complex is less sensitive towards steric hindrance on the entering nucleophile. Since such a decrease in comparison with the literature complexes[13] could not be observed, we conclude that the increased nucleophilic discrimination of **NCN** is mainly due to the electron withdrawing, electrophilicity enhancing π-acceptor effect of the pyridine/phenyl rings.
(61) Literature data suggest that the nucleophilic discrimination factor *s* depends strongly on the charge of the complex.[51] We do not believe that the decrease in nucleophilic discrimination from **NCN** (charge 0) to **NNN** (charge +1) is due to an overall charge effect of the complex, but rather that the electron density on the reacting platinum center is crucial. Since the formal charge of a complex does not necessarily reflect the charge at the platinum center (for example, the complex $[Pt(terpy)OH_2]^{2+}$ has a formal charge of +2 and a calculated NBO charge of +0.83 on the platinum center),[18] we discuss the change in the nucleophilic discrimination in terms of electron density on the platinum center due to electron donation by the better σ-donor phenyl and not in terms of a change in the overall charge on the complex.

of the incoming ligands is very important. Weak nucleophiles such as methanol will benefit most from the increased intrinsic reactivity of **NCN**, whereas strong nucleophiles will benefit more from the higher nucleophilic discrimination ability of **NNN**. For the reaction of a medium strong nucleophile like iodide with **NCN**, the gain in reactivity by the first factor is almost canceled by the reduced nucleophilic discrimination as compared to **NNN**.

Role of Biphilic Nucleophiles. Following these arguments, it is expected that the stronger nucleophiles TU, DMTU, and TMTU should react faster with **NNN** than with **NCN**. However, the opposite is true, and this must be due to the biphilic character of these nucleophiles. Their high nucleophilicity is partly due to their π-acceptor ability that assists the stabilization of the electron rich five-coordinate transition state.[51] This means that electron rich metal centers as in **NCN** (and **NNC**) will benefit much from this specific ability of the nucleophile, whereas the already very electrophilic metal center of **NNN** cannot take advantage of this effect. Therefore, the reactivity of biphilic nucleophiles depends on the electrophilicity of the reactant complexes.[62] If the electrophilicity of the investigated complex is higher than that of the reference complex for the calculation of the n_{Pt} value for a specific nucleophile (viz. *trans*-[Pt(pyridine)$_2$Cl$_2$]),[36] the reaction rate for a biphilic nucleophile will be smaller than that predicted by its n_{Pt} value and vice versa. This assumption only considers electronic effects, whereas steric effects which also affect nucleophilic discrimination are not considered. From the n_{Pt} versus log k_2 plots in Figure 9, it can clearly be seen that TU reacts faster with **NNC** and **NCN** and slower with **NNN** than predicted from the linear fit based on the other nucleophiles (MeOH, Br^-, and I^-) as expected from the already outlined arguments.

Reactivity of the Cis σ-Donor Complex. The cis effect has not been studied in much detail before, and the experimental findings are to some extent contradictory.[17,18,63−67] The obvious reason for these different results lies in the fact that changes in the σ-donor, π-acceptor, and steric properties of the cis ligand have opposite effects on the reactivity of the complex. In the present study, the steric and π-acceptor properties of the cis and trans ligands were not changed;[16] only the σ-donor ability was changed by displacing the weak σ-donor nitrogen by the strong σ-donor carbon.

From a comparison of the reactivity of **NNN** and **NNC**, it follows that the substitution reactions of the latter complex are up to 450 times slower (Nu = Br^-) for all nucleophiles, except for the solvolysis rate constants which are similar within the experimental error limits. This behavior emphasizes the general assumption that the cis effect is smaller and has the opposite trend than the trans effect.[63−65] Since only the σ-donor property of the chelating ligand was altered, we conclude that this finding only applies in cases where only the σ-donor properties of the cis and trans ligands are altered, meaning that stronger σ-donors in the cis position result in slower substitution reactions. Taking into account that π-acceptors behave in exactly the opposite way, viz., the reactivity is enhanced more if stronger π-acceptors are in the cis position than if they are in the trans position,[17,18] it seems clear why such different results are reported in the literature. If a ligand possesses both σ-donor and π-acceptor properties, its observed cis effect depends on whatever effect is stronger since the former decelerates and the latter accelerates the reaction.

Romeo et al. showed that the reactivity of a complex which benefits from a strong π-acceptor environment is decreased, if a strong σ-donor is placed in the cis position, because the electron donating effect of the σ-donor counteracts the electron withdrawing effect of the π-acceptors.[16] On the basis of our data, we believe that this deceleration of the substitution rate of **NNC** as compared to **NNN** is caused by the reduced nucleophilic discrimination of the **NNC** complex ($s = 0.9$ as compared to $s = 1.39$ for **NNN**). This means that cis σ-donor lowers the nucleophilic discrimination as its trans counterpart by reducing the electrophilicity of the platinum metal center due to their electron donating effect. However, the decrease in nucleophilic discrimination for **NNC** is smaller than for **NCN** ($s = 0.61$). It is important to note that the intrinsic reactivity of **NNC** is comparable with that of **NNN**, which indicates that the observed decrease in reactivity is mainly caused by the reduced nucleophilic discrimination and therefore depends on the nucleophilicity of the entering nucleophile.

Steric Influence of the Nucleophile. The substitution of chloride by the nucleophiles TU, DMTU, and TMTU shows a clear dependence on the steric hindrance of the nucleophile. With increasing steric hindrance, the substitution rate decreases for all the studied complexes. The observed rate constant for the substitution of chloride by TU is about 6 (**NCN**) to 16 (**NNN**) times larger than for the reaction with TMTU, which is in good agreement with literature values for the corresponding reactions in methanol.[68−70] However, in the case of the **NNC** complex, the difference in rate is much smaller; TU reacts only 3 times faster than the sterically demanding TMTU ligand. This cannot be due to the reduced nucleophilic discrimination of **NNC**, since **NCN** is even less able to discriminate between different nucleophiles. Therefore, the reduced influence of steric crowding on the nucleophile must be due to the reduced steric demand of the complex. The steric bulk of the investigated chelates themselves is comparable, but in the case of **NNC**, the overall N−Pt−C distance of the cis ligands is 4.145 Å due to the strong trans influence of the phenyl carbon donor, and therefore significantly longer than the corresponding N−Pt−N

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distance in the case of **NNN** or **NCN** (viz. 4.048 and 4.074 Å, respectively).[22,23] Since it is known that associative substitution reactions on Pd(II)/Pt(II) centers are very sensitive to steric hindrance in the cis position,[1,52] we believe that cis bond lengthening reduces the steric hindrance of the complex and therefore also reduces its ability to discriminate between nucleophiles with differing steric bulk. This can also account for the slightly reduced steric discrimination of **NCN** (TU/DMTU/TMTU = 6.0:2.4:1) as compared to **NNN** (TU/DMTU/TMTU = 15.8:3.3:1) since the N−Pt−N distance is 0.026 Å longer for **NCN** due to the cis influence of the trans carbon donor. This suggests that the ratio of the rate constants (TU/TMTU) is an indication of the steric discrimination ability of the complexes.[60]

Transition State Effects and Activation Parameters. The much higher reactivity of **NCN** as compared to **NNC** is also reflected by a large decrease in activation enthalpy $\Delta H^{\ddagger}$ (a difference of approximately 20 kJ mol^{-1}) for the substitution reactions of the **NCN** complex with the investigated thioureas. This can be ascribed to the trans influence of the phenyl group, which destabilizes the ground state, makes it easier to cleave the bond to the leaving group, and has a large influence on the observed reactivity.[71] It is interesting to compare the activation enthalpies for the reactions of TU, DMTU, and TMTU with a specific complex. In the case of **NNC**, the observed sequence for increasing $\Delta H^{\ddagger}$ is TMTU < DMTU ≈ TU, whereas for **NCN** it is TMTU < DMTU < TU, respectively. This is not in accordance with the observed reactivity sequence, where DMTU reacts faster than TMTU, and TU has the highest reaction rate of all investigated thioureas. Therefore, it can be concluded that the difference in the activation entropies must be responsible for the observed steric retardation.

Since it is known from the literature that not a single trans Pt−carbon bond nor a single cis Pt−carbon bond but only the combination of a trans and a cis Pt−carbon bond can induce a mechanistic changeover in the substitution behavior from associative to dissociative,[3−8] negative values for both the activation entropy $\Delta S^{\ddagger}$ and activation volume $\Delta V^{\ddagger}$ are expected for the investigated reactions. This is exactly what is observed for both **NNC** and **NCN**, and the reported values are in good agreement with literature values for related complexes.[13] The observed volume collapse in the transition state results from bond formation with the entering nucleophile, which is partially offset by a volume increase that results from a square planar to a trigonal bipyramidal change in geometry on forming the five-coordinate transition state. The latter volume increase is larger in the case where platinum−ligand bonds of the entering and leaving ligands are longer, as in the case of **NCN** due to the large trans influence. This explains why the observed activation volumes for the investigated nucleophiles are less negative for **NCN** than for **NNC**, where the bonds to the leaving and entering groups are significantly shorter.

The activation entropies behave in the opposite direction; they are more negative for the reactions of **NCN** than for **NNC**. This can be ascribed to an increase in solvent electrostriction in the transition state as a result of partial charge separation that accompanies the lengthening of the platinum chloride bond in the transition state and induces an increase in the dipole moment of the complex. Therefore, the dipole character of **NCN** in the transition state is larger than that of **NNC**, and there is a stronger influence on the reorganization of the polar solvent that leads to more negative $\Delta S^{\ddagger}$ values for the **NCN** complex. Both $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ become more negative on increasing the size of the entering thiourea nucleophile for a specific complex. This can be ascribed to a more effective overlap of the van der Waals radii on forming the five-coordinate transition state with larger entering nucleophiles.

5. Conclusions

We systematically investigated the trans and cis effect and influence of a phenyl carbon donor in the presence of a good π-acceptor ligand backbone. The crystal structures of the two polymorphs of **NNC** exhibit a strong trans influence of the phenyl donor, which leads to a longer N−Pt−C distance (as compared to N−Pt−N in **NCN** or **NNN**), reduces the steric hindrance in the cis positions to the leaving/entering group, and therefore also reduces the steric discrimination of incoming nucleophiles by the complex. Furthermore, a comparison of the yellow and red crystal polymorphs of the **NNC** complex suggests that the intense red color of the latter results from the short Pt−Pt distance of 3.366 Å, where such metal−metal interactions are proposed to result in more intense colors.

From a comparison with literature data, it could be shown that the electron withdrawing effect of in-plane aryl/phenyl rings (the in-plane arrangement being achieved through cyclometalation) increases the reactivity, although the strong σ-donor carbon weakens the π-acceptor effect dramatically since the electron donating properties of the σ-donor counteract the electron withdrawing effect of the π-acceptors. Taking the nucleophilic discrimination factor as an indicator for the electrophilicity of the metal center, it can be seen that the decrease in the π-acceptor effect is smaller for cis than for trans carbon donors, indicating that, in the case of a Pt−C bond trans to the leaving group, the additional benefit from π-acceptor pyridyl/phenyl rings is small but still significant. The reactivity of the **NCN** complex is therefore the highest observed among comparable complexes of the type *trans*-[Pt(C)(L_1)(L_2)Cl] due to the highly destabilized ground state (labilization of the Pt−Cl bond by the trans influence of phenyl) and the additional small π-acceptor contributions.

In the case of the **NNC** complex, the nucleophilic discrimination is lower than for **NNN**, which results in slower substitution reactions with all investigated nucleophiles except for methanol. The intrinsic reactivity of **NNC** is not affected by the introduction of the cis σ-donor phenyl and remains equal to that of **NNN**. On the basis of the present work and earlier investigations,[1,17,18,59] the cis effect in Pt(II) substitution chemistry can be summarized in the following way. The direction (acceleration or deceleration) and

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magnitude of the cis effect (as compared to the trans effect of the same ligand) depends on three factors, viz. the σ-donor strength, π-acceptor ability, and steric property of the cis ligand. (i) With increasing σ-donor strength, the reactivity decreases because nucleophilic discrimination is reduced. Whether this deceleration is larger or smaller than the accelerating trans effect of the same σ-donor depends on the nucleophilicity of the investigated nucleophile. (ii) With increasing π-acceptor ability of the cis ligand, the reactivity is increased by an enhanced nucleophilic discrimination of the complex. This π-cis-effect is larger than the corresponding π-trans-effect.[17,18] (iii) With increasing steric bulk of the cis ligand, the reaction is slowed due to an increase in steric hindrance in the five-coordinate transition state. This steric cis effect reduces the reactivity more than the corresponding steric trans effect.[1,59]

The results of this and earlier studies[3−21,58,63−67,71] clearly demonstrate the ability to systematically tune the reactivity of Pt(II) complexes via σ-donor and π-acceptor effects, to the point where a fine-tuning as a result of a combination of these effects is indeed possible. This may be of significance in the systematic tuning of the reactivity of Pt(II) complexes in applications such as antitumor drug design, C−H activation, and homogeneous catalysis.

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Supporting Information Available: Summary of the selected wavelengths used in the kinetic measurements, all measured rate constants, two representative plots to illustrate the pressure dependence of the observed rate constants, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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