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Structural Features and Dynamical Behavior of Heteroleptic *trans-C,C*-Bisaryl-Platinum(II) and -Palladium(II) Complexes

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Several heteroleptic *trans*-bisaryl-Pt^{II} complexes, *trans-C,C*-[Pt(NCN)R] (**6**−**9**), have been prepared starting from the readily available precursor [PtCl(NCN)] (**1**, NCN = [$C_6H_3(CH_2NMe_2)_2$-2,6]$^-$) and *ortho*-substituted phenyl- or naphthyllithium reagents, respectively. Variable-temperature ^{1}H NMR spectroscopy shows that in solution the NCN ligand is η^3-coordinated and that rotation of the *trans*-aryl ligand about the Pt−C$_{ipso}$ bond is slow or even nonexistent on the NMR time scale. Moreover, in the temperature range −80 to +90 °C no dissociation of the Pt−N (NCN) coordination occurs. In contrast, the analogous Pd^{II} complex **13** shows fluxional behavior of the nitrogen-to-metal coordination (above 0 °C). The dynamic properties of this type of complexes can thus be tuned by the choice of metal. The crystal structure determinations of two *trans-C,C*-[M(NCN)($C_{10}H_6(CH_2NMe_2)$-2)] complexes (**8** (M = Pt), **13** (M = Pd)) are reported. The most significant feature in these structures is that the η^3-*N,C,N*-coordinating NCN ligand present in **1** has been retained in **8** and **13**; that is, the *ortho*-(dimethylamino)methyl group of the naphthyl ligand remains noncoordinating and cannot compete with the *ortho*-(dimethylamino)methyl groups of the NCN ligand.

Introduction

Due to the increasing interest in the use of monoanionic, potentially terdentate coordinating bischelating pincer ligands, a number of interesting applications simultaneously emerged for the corresponding (transition) metal pincer complexes as homogeneous catalysts[1] and as materials with interesting physical properties.[1c−e,2]

At present, a large diversity within this class of terdentate monoanionic ligands is known and includes *N,C,N*-[1a,b,e] *P,C,P*-,[1a−c] and *S,C,S*-chelating[1a,b] systems, as well as hetero-mixed combinations.[3] In square-planar Pt^{II} or Pd^{II} complexes the residual ligand, usually a halide, is positioned *trans* to the aryl C$_{ipso}$ due to the meridional *E,C,E*-terdentate coordination mode of the pincer ligand. Anion exchange is possible via halide abstraction procedures using silver salts. With noncoordinating anions, cationic metal centers can be formed in which the square-planar coordination sphere is completed by a neutral monodentate donor molecule, e.g., a pyridine ligand.[2,4] For example, recently reported cationic *trans*-[Pt^{II}(η^3-N,C,N)]$^+$ (N = NCy$_2$) reacts with terpyridine (tpy), to form *trans*-[Pt^{II}(η^1-N,C,N)(η^3-tpy)]$^+$ having instead of an η^3-*N,C,N*- an η^1-*C*-coordinated pincer ligand.[2] Treatment of [MX(NCN)] complexes (M = Pd, Pt; X = Cl, Br) with lithium (LiR)[5−7] or SnMe$_3$ (SnMe$_3$R, R = aryl)[6] reagents provided access to neutral heteroleptic [M(NCN)R] species. These complexes were the subject of a number of investigations that involved both homoleptic[8] and heteroleptic[7] bisaryl species. A method for introduction of a *trans* ligand is via transcyclometalation of [PtCl(NCN)] with a PC(H)P ligand (PCP = [$C_6H_3(CH_2PPh_2)_2$-2,6]$^-$), resulting in the formation of *trans*-[Pt(η^1-*C*-NCN)(η^3-*P,C,P*-PCP)]Cl.[9]

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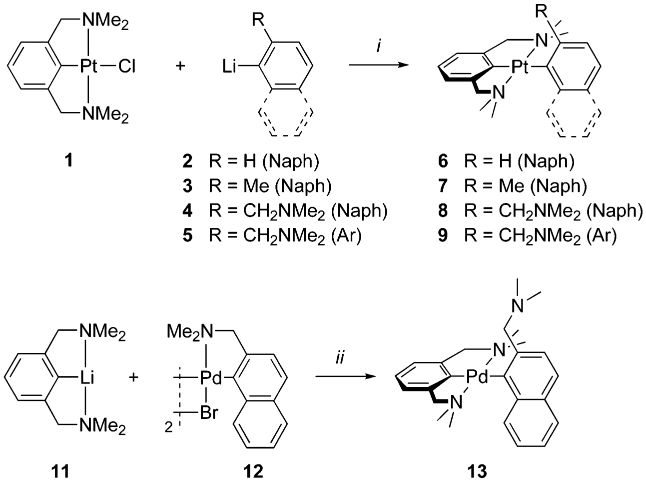
Scheme 1. Synthesis of Complexes 6−9 and 13[a]



[a] *i.* Et_2O, -78 °C → RT. *ii.* THF, -78 °C → RT.

In this paper, the syntheses of some heteroleptic bisaryl-Pt^{II} and -Pd^{II} complexes containing both a terdentate coordinating NCN ligand and a monodentate coordinating phenyl or naphthyl ligand are described. The structural and dynamical properties of these complexes with either no *ortho*-substituent (η^1-*C*-naphthyl) or one *ortho*-substituent (η^1-*C*-naphthyl, phenyl) were investigated. With CH_2NMe_2 as *ortho*-substituent, the potentially bidentate coordinating ligand may force a change in η^3-*N,C,N*-coordination of the NCN ligand. This could lead to an exchange between [Pt(η^3-*N,C,N*-NCN)(η^1-*C*-CN)] and [Pt(η^2-*C,N*-NCN)(η^2-*C,N*-CN)] (CN = $[C_6H_4(CH_2NMe_2)\text{-}2]^-$) complexes. Moreover, protonation of the free *ortho*-CH_2NMe_2 substituent in [Pt(η^3-*N,C,N*-NCN)(η^1-*C*-CN)], which may lead to a compound with a stable intramolecular $Pt^{II}\cdots H{-}N$ bond, was investigated.[10]

Results and Discussion

Synthesis of Heteroleptic Bisaryl-Platinum and -Palladium Complexes 6−9 and 13. A number of asymmetric platinum complexes containing both η^3-*N,C,N*-terdentate and η^1-*C*-monodentate coordinating aryl ligands have been prepared in a two-step synthetic route. The first step is the introduction of the NCN ligand onto a Pt^{II} metal center, a process already reported for [PtCl(NCN)] (**1**).[11] In the second step, **1** was treated with a selection of phenyl- and naphthyllithium reagents (**2**−**5**) to afford the Pt^{II} complexes **6**−**9** [Pt(NCN)(R)], respectively (R = $[C_{10}H_7]^-$ (**6**), $[C_{10}H_6Me\text{-}2]^-$ (**7**), $[C_{10}H_6(CH_2NMe_2)\text{-}2]^-$ (**8**),[12] and $[C_6H_4(CH_2NMe_2)\text{-}2]^-$ (**9**) (Scheme 1)).

Synthesis of the palladium analogue of **8** was not successful by this methodology. Upon treatment of [PdCl(NCN)][13] (**10**) with $[Li(C_{10}H_6\{CH_2NMe_2\}\text{-}2)]$ (**4**), only a mere 5% of **13** was obtained, a result that could not be improved by using either higher or lower reaction temperatures. Although the conversion could be (slightly) improved, the low thermal stability of the lithium reagent in ethereal solvents excluded the use of prolonged reaction times, and thus a high yield of **13** was thwarted.[14] However, the inverse route turned out to be more successful, i.e., first attachment of the 1-naphthyl group to the palladium metal center,[12] followed by the introduction of the NCN ligand. Following this sequence, $[Pd(NCN)(C_{10}H_6(CH_2NMe_2)\text{-}2)]$ (**13**) was prepared in 55% yield (Scheme 1).

Solid-State Structures of 8 and 13. Unambiguous confirmation of the connectivity pattern of the NCN and CN ligands in complexes **8** and **13** was accomplished by a single-crystal X-ray structure analysis. Suitable crystals were grown by slow diffusion of pentane into saturated solutions of **8** and **13**, respectively, in benzene at room temperature. Figure 1 presents displacement ellipsoid plots of both **8**·C_6H_6 and **13**·C_6H_6. Pertinent bond lengths, bond angles, and torsion angles are listed in Table 1.

Both molecular structures reveal a metal center that is ligated by a terdentate η^3-*N,C,N*-bound NCN ligand and a monodentate, η^1-*C*-bound 2-({dimethylamino}-methyl)naphthalene ligand. Both complexes have a relative perpendicular positioning of the two aryl rings around the metal center as exemplified by the torsion angle N2−M−C13−C18 (−82.9(4)° and −90.2(4)° for **8** and **13**, respectively). The puckered five-membered chelate ring conformations, bond lengths, and bond angles of the [M(η^3-*N,C,N*-NCN)] moieties fall in the range normally observed for square-planar platinum(II) and palladium(II) complexes containing this type of ligand.[8,11,13] An interesting feature of the structures is the positioning of the benzylic protons H(23B) (**8**) and H(23A) (**13**) near the virtual *z*-axis of the metal center (M···H 2.8872 and 2.793(5) Å for **8** and **13**, respectively). These distances are significantly shorter than the sum of the van der Waals radii of both nuclei (3.50 Å), indicating an additional interaction with the filled d_{z^2} orbital of the metal centers, providing extra stability to these structures. This phenomenon has also been observed for related NCN-pincer platinum(II) complexes [Pt(η^3-*N,C,N*-NCN)(η^1-*C*-NCN)][8] and [Pt(η^3-*N,C,N*-NCN)(η^1-*N*-$C_5H_3N\{CH_2OMe\}_2$-2,6)].[15] As a consequence of the different denticities of the ligands, the M−C bonds of the monodentate bonded naphthalene ligands are considerably longer (2.131(4) and 2.139(5) Å for **8** and **13**, respectively) as compared to those that involve the NCN ligand (1.959(4) and 1.952(5) Å for **8** and **13**, respectively). Moreover, the aromatic rings of the naphthalene ligand systems are severely distorted. The internal angles at C_{ipso} are approximately 115° for the η^1-*C*-naphthalene ligands, whereas the same angles of the

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[14] To determine whether the lithium species was still present, the Et_2O layer was reacted with S_2Me_2, stirred for 2 h, and washed with brine. The product (analyzed by ^1H NMR and GC/MS spectroscopy) was 2-({dimethylamino}methyl)naphthalene, indicating that the lithium compound had decomposed.

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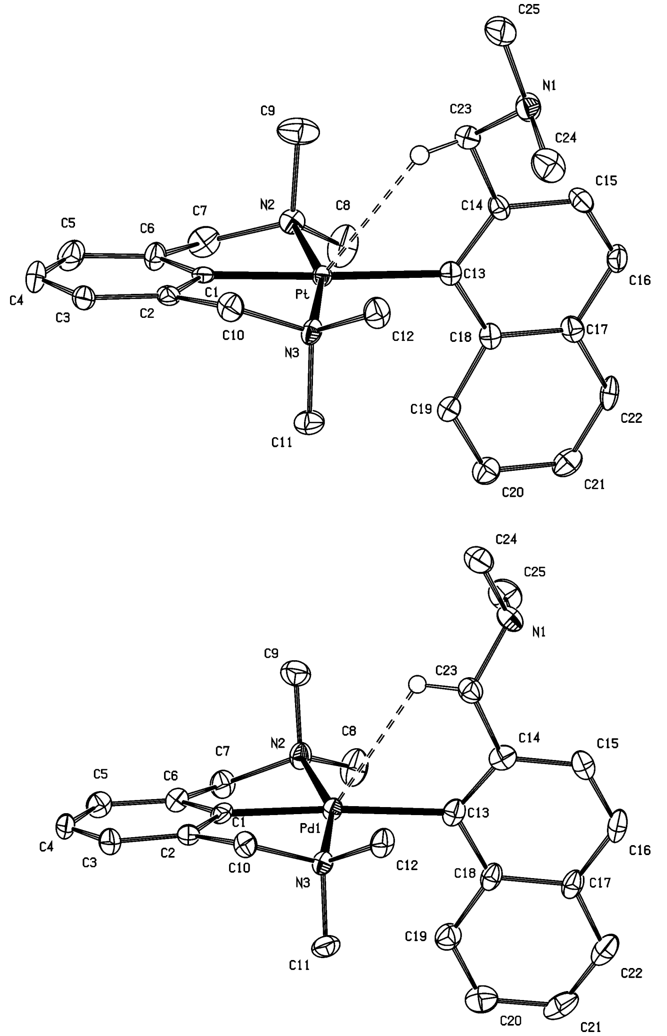

Figure 1. Displacement ellipsoid plots (ORTEP, 50% probability level) of the molecular structures of complexes **8** (top) and **13** (bottom) together with the adopted numbering schemes. Benzene solvent molecules and hydrogen atoms (except for H(23B) (**8**) and H(23A) (**13**)) have been omitted for clarity.

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Torsion Angles (deg) for 8·C_6H_6 and 13·C_6H_6

	8·C_6H_6 (M = Pt)	**13**·C_6H_6 (M = Pd)
	Bond Lengths	
M−C(1)	1.959(4)	1.952(5)
M−C(13)	2.131(4)	2.139(5)
M−N(2)	2.083(3)	2.123(4)
M−N(3)	2.086(3)	2.116(4)
M···H(23)	2.8872 (H23B)	2.793(5) (H23A)
	Bond Angles and Torsion Angles	
N(2)−M−N(3)	161.60(14)	160.04(13)
N(2)−M−C(1)	81.03(16)	80.03(17)
N(2)−M−C(13)	95.71(15)	101.79(16)
N(3)−M−C(1)	80.58(16)	80.02(17)
N(3)−M−C(13)	102.68(15)	98.16(16)
C(1)−M−C(13)	176.72(18)	176.34(19)
C(2)−C(1)−C(6)	120.6(4)	120.6(4)
C(14)−C(13)−C(18)	115.3(4)	115.1(4)
N(2)−M−C(13)−C(18)	−82.9(4)	−90.2(4)
N(2)−M−C(13)−C(14)	87.3(4)	95.9(4)
N(3)−M−C(13)−C(18)	96.5(4)	89.1(4)
N(3)−M−C(13)−C(14)	−93.4(4)	−84.7(4)

η^3-*N,C,N*-bonded ligands are equal to 120.6(4)°. The difference is presumably a consequence of the steric crowding around the metal center.

Structural Aspects of the Complexes in Solution. At room temperature the ^1H NMR spectra (C_6D_6 solution) of the platinum(II) complexes **6**−**9** showed two distinct signals for the magnetically inequivalent NMe_2 groups of the NCN ligand, whereas the corresponding NMe_2 methyl groups of the palladium derivative **13** appeared as one singlet (see Table 2). For the platinum complexes distinct coupling patterns ($^3J_{H,Pt}$ = 41−44 Hz) were observed that are diagnostic for nitrogen-to-metal coordination.[7] The NMe_2 group of the η^1-*C* bound ligands in **8**, **9**, and **13** appeared as one singlet resonance, which is in line with their noncoordinating behavior as observed in the solid-state structure of both **8** and **13**.[8] Interestingly the methyl resonances of the noncoordinating NMe_2 groupings are shifted downfield in comparison to the free ligands ($\Delta\delta$(H) ≈ 0.40 ppm for **8**, **9**, and **13**).[8] The low-field shift of the CH_2N protons in this noncoordinating CH_2NMe_2 substituent ($\Delta\delta$(H) ≈ 0.90 ppm for **8**, **9**, and **13**) is remarkable and points to deshielding of these nuclei, which may originate from weak intramolecular interactions (e.g., hydrogen bonding) with the nucleophilic platinum(II) center.[8,15] The naphthalene methyl group in **7** appeared as a single line at δ = 3.23 ppm.

In the spectra of **6**, **8**, and **9**, clear AB patterns were observed for the benzylic protons of the NCN ligand, with distinct Pt satellites ($^3J_{H,Pt}$ = 45 Hz). For palladium complex **13** an AA′ pattern was observed. Remarkably, for complex **7** a singlet signal with Pt satellites ($^3J_{H,Pt}$ = 44 Hz) was observed for the benzylic protons of the NCN ligand, whereas an AB pattern was expected, vide infra. For the naphthalene-substituted complexes the doublet signals of the H-8 protons were shifted downfield as compared to the free ligands ($\Delta\delta$(H) ≈ 2.4 ppm), and in the case of **6**−**8**, no platinum couplings were observed. The doublet signal of the H-6 proton of the η^1-*C* aryl unit of **9** showed Pt satellites ($^3J_{H,Pt}$ = 33 Hz). This signal was also shifted downfield ($\Delta\delta$(H) ≈ 0.7 ppm) compared to the free ligand.

Further structural confirmation was derived from $^{13}C\{^1H\}$ NMR spectroscopy. The ArC_{ipso} of the η^3-*N,C,N* and η^1-*C* aryl ligands were found between 172.6−174.2 and 181.5−187.5 ppm, respectively (Table 2), in line with the previously reported values for complexes of general formula [Pt(NCN)R].[7,8]

Variable-temperature ^1H NMR experiments were carried out to study the dynamic aspects of the complexes. The AB patterns (**6**, **8**, **9**) and AA′ patterns (**7**, **13**) for the benzylic protons did not change in the temperature range 25−90 °C. The signals for the NMe_2 groups of the NCN units of platinum complexes **6**−**9** did not show coalescence or line broadening at temperatures up to 90 °C. Low-temperature ^1H NMR spectra were recorded (CD_2Cl_2), and for all complexes line broadening was observed for the benzylic and NMe_2 protons upon lowering the temperatures. Below −50 °C, the AB patterns were not resolved. Below approximately −80 °C, the Pt satellites on the CH_2N and NMe_2 groups were not discernible due to severe line broadening. The signals for H-8 (and H-6 in the case of **9**) remained sharp. Lowering the temperature for the palladium complex **13** resulted in broadening of the singlet signal corresponding to the NMe_2 methyl groups of the NCN

Table 2. Selected ^1H and $^{13}C\{^1H\}$ NMR Data for Complexes 6−9 and 13[a]

	NMe$_2$ ($^3J_{H,Pt}$)		CH$_2$N ($^3J_{H,Pt}$)		ArMe	ArH-8 (d)	C$_{ipso}$ ($^1J_{C,Pt}$)	
complex	η^3-NCN	η^1-C	η^3-NCN	η^1-C	η^1-C	η^1-C	η^3-NCN	η^1-C
6	2.37/2.42 (44)		3.50/3.55 (45)[b]			9.53	172.6[c]	187.5[c]
7	2.37/2.40 (43)		3.53[e] (44)		3.23 (8)	9.73	172.7 (598)	181.5 (826)
8	2.36/2.49 (41)	2.47	3.47/3.51 (45)[b]	4.50 (39)		9.89	172.8[c]	183.6[c]
9	2.49/2.54 (44)	2.43	3.43/3.61 (45)[b]	4.25 (126)		8.07[d]	173.0 (591)	183.8 (790)
13	2.47	2.43	3.50/3.51[e]	4.46		9.65	174.2	183.4

[a] In C_6D_6 solutions; chemical shifts in ppm, coupling in hertz; singlet resonances unless stated otherwise, doublet (d). [b] AB pattern $^2J_{H,H}$ = 14 Hz. [c] $^1J_{C,Pt}$ unresolved. [d] ArH-6. [e] AA′ pattern.

ligand, which decoalesced into two broad singlets ($\Delta G^{\ddagger}$ = 56 kJ·mol^{-1}) at 0 °C.[16]

The spectral features are interpreted as follows: the structures of the platinum and palladium naphthalene complexes in solution have a perpendicular positioning of the two aryl rings around the metal center in the ground state. This is apparent from the similar downfield shift of the H-8 proton, which is situated above the metal coordination plane near the metal center, as being displayed in the X-ray crystal structures of **8** and **13** (M(1)···H(19) = 2.8338 Å (Pt, **8**) and 2.794(6) Å (Pd, **13**)). The resonances at 9.53−9.89 ppm for the H-8 protons are higher than those for similar Pt^{II} and Pd^{II} complexes (δ(H) = 8.39−8.91 ppm),[17] but are comparable to those found for 1,8-diplatinum-anthracene complexes (9.33−9.54 ppm).[18] The absence of platinum couplings on H-8 excludes an agostic type of interaction.[19] The presence of both AB patterns for **6**, **8**, **9**, an AA′ pattern for **13**, and two singlets for the NMe$_2$ groups of the NCN ligand for **6**−**9** indicates that under these conditions there is no molecular symmetry plane containing the benzylic carbon and nitrogen centers of the NCN ligand.[20] This can only be explained by assuming that an asymmetric environment is created by the manifold NCN−arene and naphthalene−arene planes. This asymmetry causes the NMe$_2$ methyl groups and the benzylic protons of the NCN ligand to be diastereotopic and as such result in the observation of two distinct singlets and an AB pattern, respectively. It must be noted that a process involving rapid rotation on the NMR time scale of the η^1-*C*-coordinated naphthalene ligand about its Pt−C$_{ipso}$ axis would create an apparent molecular symmetry plane resulting in coalescence of the two NMe$_2$ singlets to one singlet as well as coalescence of the AB pattern (CH$_2$N) to one singlet. Consequently it can be concluded that for complexes **6**, **8**, **9**, and **13** rotation about the Pt−C$_{ipso}$ axis is either slow or completely arrested on the NMR time scale. The methyl-substituted complex **7** does not show an AB pattern for the benzylic protons of the NCN ligand in the temperature range −80 to 90 °C,[21] but two singlets for the NMe$_2$ methyl groups were observed. In principle, the asymmetric environment created by the naphthalene ligand causes benzylic protons to be diastereotopic, and therefore, an AB pattern is expected. For **7** an AA′ system with a small relative chemical shift $\Delta\nu$ is observed; that is, the center lines lie so close to one another that the spectral resolution is not sufficient to separate them and the intensity of the outer lines is too small to detect, resulting in a "deceptively simple" spectrum.[22] To confirm that aryl rotation about the Pt−η^1-*C* axis does not take place, calculations on the rotation barrier were performed (354 kJ/mol), suggesting that rotation was not feasible.[23]

In the case of the platinum complexes, the diastereotopicity of the NMe methyl groups indicates that the nitrogen-to-metal coordination is rigid and stable five-membered chelate rings exist on the NMR time scale up to 90 °C (Figure 1). As anticipated, the palladium analogue **13** shows a fast exchange between the coordinated and uncoordinated amino functionalities on the NMR time scale at room temperature. It is at 0 °C that Me$_2$N−Pd coordination becomes rigid on the NMR time scale.[24] Since coalescence of the singlet absorptions of the NMe$_2$ groups in the NCN ligand (up to 90 °C) was not observed for the platinum complexes **6**−**9**, it can be concluded that the strength of the platinum−nitrogen bond in these complexes is higher than those of the palladium−nitrogen bond in **13**.

In principle, a dynamic exchange process between the chelating and free CH$_2$NMe$_2$ groups of the η^3- and η^1-coordinated ligands could occur in both **8** and **9**. However, neither ^1H NMR spectra in toluene-d_8 solution at 90 °C nor spectra measured at low temperatures to −80 °C in CD_2Cl_2 solution revealed any evidence for such a dynamic behavior of **8** and **9** on the NMR time scale. This dynamic process was also not observed for a related complex, [Pt(η^3-*N,C,N*-NCN)(η^1-*C*-NCN)].[8]

Reactivity toward HCl and I$_2$. Wehman-Ooyevaar et al. reported platinum complexes of the general formula [PtCl(η^2-*C,N*-CN)(η^2-*C,H*-CN{H})]. These com-

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(20) If the NMe$_2$ groups of the C,N ligand would be coordinated to the platinum center, the molecular symmetry plane could contain the N atom, resulting in a singlet signal resonance. The absence of Pt satellites, however, indicates that the C,N ligand is η^1-*C* bound.

(21) Also the ^1H NMR spectrum measured on a 500 MHz spectrometer did not show an AB pattern.

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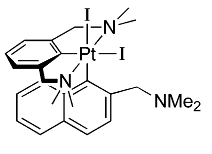
(23) Calculations on the rotation about the Pt−C bond were carried out using the coordinate drive routine, on a molecular mechanics level using the SPARTAN 5.1.1 (UNIX) package (*SPARTAN SGI version 5.5.1*; Wavefunction Inc.: 18401 Von Karman Ave., Ste. 370, CA 92612), with a MMFF94 force field. The energy profile of a rotation around 720° was determined, and for the barrier of the rotation, the difference between minimum (−88.50 kJ/mol) and maximum energy (266.04 kJ/mol) was 354 kJ/mol.

(24) Above 0 °C, a fast exchange between coordinated and noncoordinated dimethylamino groups of the NCN ligand in the palladium complex **13** takes place and the two methyl groups of the NMe$_2$ moiety appear as a single (averaged) peak. At these relatively higher temperatures both pyramidal inversion and rotation about the benzylic carbon−nitrogen axis can take place, which are processes with very small activation barriers.

plexes contain a zwitterionic $Pt(II)^{-}\cdots H-N^{+}$ moiety as result of the reaction of $[Pt(CN)_2]$ with dry HCl.[10] In view of the similarity in structural features between these complexes on one hand and **6**−**9** on the other hand, we tested the reactivity of **8** and **9** toward gaseous HCl as well as HCl formed in situ by reaction of $[SnClMe_3]$ with MeOH.[25] Rather than quaternerization of the free NMe groups, cleavage of the Pt−C bond of the η^1-coordinated ligand occurred, resulting in formation of the starting Pt^{II} compound **1** and the protonated, monodentate ligand. Under the applied conditions no disruption of either the Pt−N or the Pt−C bond of the η^3-*N,C,N*-coordinated NCN ligand was noted. The general higher stability of the $[Pt^{II}(NCN)]$ unit is thus an intrinsic feature of these type of complexes, as was previously described by Albrecht et al.[8]

For complex **8**, the reactivity toward I_2 was also tested. Van Beek et al. have reported the stereoselective oxidative−addition reaction of I_2 and Br_2 to organoplatinum(II) complexes $[Pt(C,N)_2]$.[26] It was found that reactions with *cis*-$[Pt(C,N)_2]$ afforded selectively *trans,cis*-$[Pt^{IV}X_2(C,N)_2]$ (X = Br, I) products, whereas with *trans*-$[Pt(C,N)_2]$ both *trans,cis*- and *cis,cis*-$[Pt^{IV}X_2(C,N)_2]$ products were obtained. The crowded environment around the metal center in **8** and the presence of a noncoordinating aminomethyl group prompted us to investigate if formation of a five-coordinate cationic complex with I^- as counteranion was possible. Preliminary results showed the formation of a platinum(IV) species. Upon addition of I_2 to a colorless solution of **8** in CD_2Cl_2, a bright red colored solution was obtained, in which a dramatic upfield shift of the H-8 proton to $\delta(H) = 6.66$ ppm ($\Delta\delta(H) = 2.96$ ppm) was observed. The red color is diagnostic for a Pt^{IV} species.[26,27] The upfield shift of the H-8 proton indicates that the naphthalene ligand is not in the same *trans*-position anymore. Such an upfield shift has also been observed for the *ortho*-proton of the *cis*-positioned aryl groups in the related complex *cis,cis*-$[PtI_2(\eta^3\text{-}N,C,N\text{-NCN})(\eta^1\text{-}C\text{-}p\text{-tolyl})]$.[28] It is likely that the naphthyl ligand is shifted to a *cis*-position, in which the H-8 proton is positioned under the aromatic ring of the NCN ligand. This proton feels a strong influence from the ring current, which results in the large upfield shift in the NMR spectrum.[22] Therefore, the formed product has the following structure, *cis,cis*-$[PtI_2(\eta^3\text{-}N,C,N\text{-NCN})(\eta^1\text{-}C\text{-}C_{10}H_6\{CH_2NMe_2\}\text{-}2)]$ (**14**). Such a change of position of the *trans*-bonded ligand was also observed by Loeb and co-workers, who have performed an oxidative addition of I_2 on a cationic crown thioether η^4-*S,C,S,S*-platinum(II) complex, $[Pt^{II}(TT[11]MC)](BF_4)$ (TT[11]MC = 2,6,10-trithia[11]-*m*-cyclophane).[29] Formation of an octahedral platinum(IV) complex, *cis*-$[Pt^{IV}I_2(TT[11]MC)](BF_4)$ (**15**), was observed in which the I atoms were mutually *cis* and TT[11]CC was folded such that the *trans*-oriented S atom was coordinated perpendicular to the $PtIS_2C$ plane.



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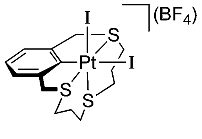

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Conclusions

A series of new heteroleptic bisaryl Pd^{II} and Pt^{II} complexes comprising both a potentially terdentate NCN and a monodentate aryl or naphthyl ligand were isolated and fully characterized. Variable-temperature ^1H NMR experiments pointed out that for the Pt^{II} complexes no significant dynamic behavior could be observed over a large temperature range, apparently due to rigid nitrogen-to-platinum coordination. For Pd^{II} complex **13**, however, the nitrogen-to-palladium coordination above 0 °C becomes less rigid and fluxional behavior of the NCN ligand was clearly noted. Reaction of HCl with complexes **8** and **9** resulted in breaking the M−C(naph) bond, whereas addition of I_2 to **8** resulted in the formation of a *cis,cis*-platinum(IV) complex (**14**). Currently, we are investigating this latter process more thoroughly.

Experimental Section

General Comments. The complexes [PtCl(NCN)] (**1**),[11] $[Li\{C_{10}H_7\}]$ (**2**),[12] $[Li\{C_{10}H_6(Me)\text{-}2\}]$ (**3**),[12] $[Li\{C_{10}H_6(CH_2NMe_2)\text{-}2\}]$ (**4**),[12] $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]$ (**5**),[30] [PdCl(NCN)] (**10**),[13] [Li(NCN)] (**11**),[11,31] and $[PdBr\{C_{10}H_6(CH_2NMe_2)\text{-}2\}]_2$ (**12**)[12] were prepared according to (modified) literature procedures. Reactions involving organolithium derivatives were carried out under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Et_2O and THF were distilled from Na/benzophenone prior to use. All other solvents and other reagents were obtained from commercial sources and were used without further purification unless stated otherwise. Melting points were measured on an Electrothermal 8100 apparatus. All NMR spectra were recorded on a Varian Inova 300 MHz spectrometer at room temperature using benzene-d_6 as solvent and TMS as an external standard. Chemical shifts are reported in ppm. Elemental analyses were obtained from Kolbe, Mikroanalytisches Laboratorium (Mülheim a.d. Ruhr, Germany).

Crystal Structure Determination of 8 and 13. X-ray data were collected on an Enraf-Nonius TurboCAD$_4$ on a rotating anode using graphite-monochromated Mo Kα radiation at 150 K. Both structures were solved by automated Patterson methods (DIRDIF)[32] and refined on F^2 with SHELXL-97,[33] and an empirical correction for absorption was done for **13** using PLATON/DELABS. Geometrical calculations, the ORTEP illustrations, and structure validation were done with PLATON.[34]

Crystal data for 8: $C_{25}H_{33}N_3Pt\cdot 0.5(C_6H_6)$, monoclinic, spacegroup $P2_1/c$ (#14), $a = 8.3484(6)$ Å, $b = 19.6218(10)$ Å, $c = 15.6521(10)$ Å, $\beta = 108.384(5)°$, $V = 2433.1(3)$ Å^3, $Z = 4$, d_x

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[25] $[SnClMe_3] + MeOH \rightarrow HCl + [SnMe_3OMe]$.

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$= 1.664$ g/cm^3, μ(Mo Kα) $= 5.787$ mm^{-1}, crystal size $0.10 \times 0.15 \times 0.45$ mm, colorless; 11 874 reflections measured ($\theta_{max} = 27.5°$), 5565 unique reflections, $R_{int} = 0.044$, 4326 reflections with $I > 2\sigma(I)$. $R = 0.0303$, $wR_2 = 0.0591$, $S = 0.99$, $-0.85 < \Delta\rho < 1.05$ e/Å^3.

Crystal data for 13: $C_{25}H_{33}N_3Pd{\cdot}0.5(C_6H_6)$, triclinic, spacegroup $P\bar{1}$(#2), $a = 9.199(2)$ Å, $b = 11.3015(10)$ Å, $c = 12.6747(10)$ Å, $\alpha = 101.723(7)°$, $\beta = 99.966(12)°$, $\gamma = 101.409(13)°$, $V = 1233.1(3)$ Å^3, $Z = 2$, $d_x = 1.403$ g/cm^3, μ(Mo Kα) $= 0.773$ mm^{-1}, crystal size $0.05 \times 0.10 \times 0.62$ mm, yellowish; 7096 reflections measured, 5620 unique, $R_{int} = 0.06.4331$ reflections with $I > 2\sigma(I)$. $R = 0.0532$, $wR_2 = 0.1227$, $S = 1.05$, $-0.89 < \Delta\rho < 1.19$ e/Å^3.

General Procedure for the Synthesis of NCN-Pt-aryl Complexes 6–9. A solution of the aryl/naphthyllithium compound (1.5 mmol) in Et_2O (30 mL) was added dropwise to a white suspension of [PtCl(NCN)] **1** (1.2 mmol, 0.8 equiv) in Et_2O (20 mL) at −78 °C over a period of 30 min. The resulting suspension was allowed to warm to room temperature, whereupon the color changed to pale yellow. The reaction mixture was stirred for 4 h, and then all volatiles were removed in vacuo. The solid residue was dissolved in CH_2Cl_2 (50 mL) and filtered through a short path of Celite. The solvent was removed under reduced pressure and the product thoroughly washed with acetone (15 mL) and pentane (15 mL) to yield an (off-)white powder.

[Pt(NCN)($C_{10}H_7$)] (6). Yield: 0.52 g (1.01 mmol, 91%). Mp: 213 °C (dec). ^1H NMR (300 MHz): δ 2.37 (s, $^3J_{H,Pt} = 44$ Hz, 6H, NMe_2), 2.42 (s, $^3J_{H,Pt} = 44$ Hz, 6H, NMe_2), 3.50/3.55 (AB, $^2J_{H,H} = 14$ Hz, $^3J_{H,Pt} = 45$ Hz, 4H, CH_2N), 6.91 (d, $^3J_{H,H} = 7$ Hz, 2H, ArH-3,5 (η^3-NCN)), 7.19 (t, $^3J_{H,H} = 8$ Hz, 1H, ArH-4 (η^3-NCN)), 7.49 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.67 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.71 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.80 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.03 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.17 (d, $^3J_{H,H} = 8$ Hz, $^4J_{H,Pt}$ unresolved, 1H, ArH (η^1-C)), 9.53 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH-8 (η^1-C)). $^{13}C\{^1H\}$ NMR (75.5 MHz): δ 54.4 (NMe_2), 55.2 (NMe_2), 81.0 ($ArCH_2$), 118.8 (ArC-3,5 (η^3-NCN)), 121.8, 122.7, 123.0, 124.2, 126.5, 129.1, 135.0, 135.7, 136.0, 145.2, 145.6, 172.6 (ArC_{ipso} (η^3-NCN)), 187.5 (ArC_{ipso} (η^1-C)). Anal. Calcd for $C_{22}H_{26}N_2Pt$: C, 51.45; H, 5.10; N, 5.45. Found: C, 51.34; H, 5.08; N, 5.38.

[Pt(NCN)($C_{10}H_5$(Me)-2)] (7). Yield: 0.45 g (0.85 mmol, 71%). Mp: 189 °C (dec). ^1H NMR (300 MHz): δ 2.37 (s, $^3J_{H,Pt} = 43$ Hz, 6H, NMe_2), 2.40 (s, $^3J_{H,Pt} = 43$ Hz, 6H, NMe_2), 3.23 (s, $^3J_{H,Pt} = 8$ Hz, 3H, ArMe), 3.53 (AA′, $^3J_{H,Pt} = 44$ Hz, 4H, CH_2N), 6.91 (d, $^3J_{H,H} = 7$ Hz, 2H, ArH-3,5 (η^3-NCN)), 7.19 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH-4 (η^3-NCN)), 7.44 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH-6,7 (η^1-C)), 7.61 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 7.66 (t, $^3J_{H,H} = 8$ Hz, 1H, ArH-6,7 (η^1-C)), 7.80 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.00 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 9.73 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH-8 (η^1-C)). $^{13}C\{^1H\}$ NMR (75.5 MHz): δ 25.8 ($^3J_{C,Pt} = 32$ Hz, ArMe), 54.7 (NMe_2), 55.1 (NMe_2), 81.0 ($^3J_{C,Pt} = 28$ Hz, CH_2N), 118.7, 122.5, 122.6, 123.3, 128.9, 129.1, 133.9, 134.3, 140.9, 145.2 ($^2J_{C,Pt} = 43$ Hz), 172.7 ($^1J_{C,Pt} = 598$ Hz, C_{ipso} (η^3-NCN)), 181.5 ($^1J_{C,Pt} = 826$ Hz, C_{ipso} (η^1-C)). Anal. Calcd for $C_{23}H_{28}N_2Pt$: C, 52.36; H, 5.35; N, 5.31. Found: C, 52.43; H, 5.41; N, 5.03.

[Pt(NCN)($C_{10}H_6$(CH_2NMe_2)-2)] (8). Yield: 0.40 g (0.70 mmol, 65%). Crystallization by slow diffusion of pentane into a benzene solution of **8** afforded needle-shaped crystals suitable for single-crystal X-ray structure determination. Mp: 160 °C (dec). ^1H NMR (300 MHz): δ 2.36 (s, $^3J_{H,Pt} = 41$ Hz, 6H, NMe_2 (η^3-NCN)), 2.47 (s, 6H, NMe_2 (η^1-C)), 2,49 (s, $^3J_{H,Pt} = 41$ Hz, 6H, NMe_2 (η^3-NCN)), 3.47/3.51 (AB, $^2J_{H,H} = 14$ Hz, $^3J_{H,Pt} = 45$ Hz, 4H, CH_2N (η^3-NCN)), 4.50 (s, 2H, $^3J_{H,Pt} = 39$ Hz, CH_2N (η^1-C)), 6.92 (d, $^3J_{H,H} = 7$ Hz, 2H, ArH-3,5 (η^3-NCN)), 7.19 (t, $^3J_{H,H} = 8$ Hz, 1H, ArH-4 (η^3-NCN)), 7.46 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.65 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.86 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.00 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.15 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 9.89 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH-8 (η^1-C)). $^{13}C\{^1H\}$ NMR (75.5 MHz): δ 46.3 (NMe_2 (η^1-C)), 55.1 (NMe_2 (η^3-NCN)), 55.5 (NMe_2 (η^3-NCN)), 68.6 (CH_2N (η^1-C)), 81.3 (CH_2N (η^3-NCN)), 119.4 (ArC-3,5 (η^3-NCN)) 122.7, 122.9, 123.3, 124.1, 129.3, 134.7, 135.4, 143.9, 145.6, 146.1, 172.8 (ArC_{ipso} (η^3-NCN)), 183.6 (ArC_{ipso} (η^1-C)). Anal. Calcd for $C_{25}H_{33}N_3Pt$: C, 52.62; H, 5.83; N, 7.36. Found: C, 52.47; H, 5.72; N, 7.31.

[Pt(NCN)(C_6H_4(CH_2NMe_2)-2)] (9). Yield: 0.53 g (1.01 mmol, 85%). Mp: 209 °C (dec). ^1H NMR (300 MHz): δ 2.43 (s, 6H, NMe_2 (η^1-C)), 2.49 (s, $^3J_{H,Pt} = 44$ Hz, 6H, NMe_2 (η^3-NCN)), 2.54 (s, $^3J_{H,Pt} = 44$ Hz, 6H, NMe_2 (η^3-NCN)), 3.43/3.61 (AB, $^2J_{H,H} = 14$ Hz, $^3J_{H,Pt} = 45$ Hz, 4H, CH_2N (η^3-NCN)), 4.25 (s, 2H, $^3J_{H,Pt} = 126$ Hz, CH_2N (η^1-C)), 6.91 (d, $^3J_{H,H} = 7$ Hz, 2H, ArH-3,5 (η^3-NCN)), 7.17 (t, $^3J_{H,H} = 8$ Hz, 1H, ArH-4 (η^3-NCN)), 7.34 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH (η^1-C)), 7.48 (t, $^3J_{H,H} = 6$ Hz, 1H, ArH (η^1-C)), 7.85 (d, $^3J_{H,H} = 7$ Hz, 1H, ArH-3 (η^1-C)), 8.07 (d, $^3J_{H,H} = 6$ Hz, $^3J_{H,Pt} = 33$ Hz, 1H, ArH-6 (η^1-C)). $^{13}C\{^1H\}$ NMR (75.5 MHz): $\delta = 46.0$ (NMe_2 (η^1-C)), 54.5 (NMe_2 (η^3-NCN)), 54.7 (NMe_2 (η^3-NCN)), 69.1 ($^2J_{C,Pt} = 34$ Hz, CH_2N (η^1-C)), 81.0 ($^3J_{C,Pt} = 34$ Hz, CH_2N (η^3-NCN)), 118.8 (ArC-3,5 (η^3-NCN)), 122.2, 122.8, 125.8 ($^2J_{C,Pt} = 34$ Hz), 139.5, 145.5 ($^2J_{C,Pt} = 50$ Hz), 147.1, 173.0 ($^1J_{C,Pt} = 591$ Hz, ArC_{ipso} (η^3-NCN)), 183.8 ($^1J_{C,Pt} = 790$ Hz, ArC_{ipso} (η^1-C)). Anal. Calcd for $C_{21}H_{31}N_3Pt$: C, 48.45; H, 6.00; N, 8.07. Found: C, 48.36; H, 5.94; N, 7.96.

[Pd(NCN)($C_{10}H_6$(CH_2NMe_2)-2)] (13). To a suspension of $[PdBr\{C_{10}H_6(CH_2NMe_2)\text{-}2\}]_2$ (**12**) (0.57 g, 1.54 mmol) in THF (30 mL) was added dropwise a solution of $[Li(NCN)]_2$ (**11**) (0.41 g, 2.07 mmol, 1.3 equiv) in THF (20 mL) at −78 °C. The yellow solution was allowed to warm to room temperature and stirred for 1 h, after which time all volatiles were evaporated in vacuo. The solid residue was dissolved in toluene (30 mL) and filtered through a path of Celite. After removal of the solvent in vacuo and subsequent washing with Et_2O (5×10 mL), **13** was isolated as an off-white powder (0.41 g, 0.84 mmol, 55%). Needle-shaped crystals suitable for an X-ray crystal structure determination were obtained by slow diffusion of pentane into a benzene solution of **13**. Mp: 149 °C (dec). ^1H NMR (300 MHz): δ 2.30 (s, 6H, NMe_2 (η^1-C)), 2.47 (s, 12H, NMe_2 (η^3-NCN)), 3.50/3.51 (AA′, $^2J_{H,H} = 15$ Hz, 4H, CH_2N (η^3-NCN)), 4.46 (s, 2H, CH_2N (η^1-C)), 6.80 (d, $^3J_{H,H} = 8$ Hz, 2H, ArH-3,5 (η^3-NCN)), 7.09 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH-4 (η^3-NCN)), 7.47 (dt, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 1$ Hz, 1H, ArH (η^1-C)), 7.64 (dt, $^3J_{H,H} = 7$ Hz, $^4J_{H,H} = 1$ Hz, 1H, ArH (η^1-C)), 7.81 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 7.96 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 8.06 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH (η^1-C)), 9.65 (dd, $^3J_{H,H} = 8$ Hz, $^4J_{H,H} = 1$ Hz, 1H, ArH-8 (η^1-C)). $^{13}C\{^1H\}$ NMR (75.5 MHz): δ 46.4 (NMe_2 (η^1-C)), 53.9 (NMe_2 (η^3-NCN)), 69.8 (CH_2N (η^1-C)), 78.4 (CH_2N (η^3-NCN)), 119.6 (ArC-3,5 (η^3-NCN)) 123.3, 123.5, 124.0, 124.4, 127.1, 129.4, 134.6, 135.2, 143.8, 144.9, 146.2, 174.2 (ArC_{ipso} (η^3-NCN)), 183.4 (ArC_{ipso} (η^1-C)). Anal. Calcd for $C_{25}H_{33}N_3Pd$: C, 62.30; H, 6.90; N, 8.72. Found: C, 62.18; H, 6.86; N, 8.64.

Reaction of 8 and 9 with HCl. Method A. Through a solution of **8** (0.07 g, 0.12 mmol) or **9** (0.07 g, 0.13 mmol) in CH_2Cl_2 (10 mL) was bubbled dry gaseous HCl for 5 min. The solutions were evaporated in vacuo, after which pentane (5 mL) was added. Removal of the solvent yielded white powders. ^1H NMR analysis in C_6D_6 showed for both complexes only the presence of **1**. **Method B.** To a solution of **8** (23 mg, 0.04 mmol) or **9** (21 mg, 0.04 mmol) in CH_2Cl_2/MeOH (5 and 0.5 mL, respectively) was added a solution of $[SnMeCl_3]$ (9 mg, 0.4 mmol) in CH_2Cl_2 (2 mL). After being stirred for 1.5 h, the solutions were concentrated in vacuo. ^1H NMR analysis in $CDCl_3$ showed the presence of **1** and $[C_{10}H_7(CH_2NMe_2)\text{-}2]$ or $[C_6H_5(CH_2NMe_2)]$ for **8** or **9**, respectively.

Reaction of 8 with I_2. To a solution of **8** (9 mg, 16 μmol) in CD_2Cl_2 (0.5 mL) was added a solution of I_2 in CD_2Cl_2 (0.1 mL, 0.16 M, 1 equiv). Immediately, a bright red colored solution was obtained. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 1.53 (s, 6H, NMe_2 (η^1-C)), 2.37 (s, $^3J_{Pt,H} = 47$ Hz, 12H, NMe_2 (η^3-NCN)), 4.05/4.58 (AB, $^2J_{H,H} = 14$ Hz, $^3J_{Pt,H} = 57$ Hz, 4H, CH_2N (η^3-NCN)), 4.79 (s, 2H, CH_2N (η^1-C)), 6.66 (d, $^3J_{H,H} = 9$ Hz, 1H, ArH-8 (η^1-C)), 7.07 (t, $^3J_{H,H} = 7$ Hz, 1H, ArH), 7.25 (d, $^3J_{H,H} =$ 8 Hz, 2H, ArH), 7.33 (d, $^3J_{H,H} = 8$ Hz, 1H, ArH), 7.83 (m, 3H, ArH).

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