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PAPER

Unexpectedly efficient activation of push–pull nitriles by a Pt^{II} center toward dipolar cycloaddition of *Z*-nitrones†

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Pt^{II}-coordinated $NCNR'_2$ species are so highly activated towards 1,3-dipolar cycloaddition (DCA) that they react smoothly with the acyclic nitrones $ArCH{=}N^+(O^-)R''$ (Ar/R″ = C_6H_4Me-*p*/Me; C_6H_4OMe-*p*/CH_2Ph) in the *Z*-form. Competitive reactivity study of DCA between *trans*-$[PtCl_2(NCR)_2]$ (R = Ph and NR'_2) species and the acyclic nitrone 4-$MeC_6H_4CH{=}N^+(O^-)Me$ demonstrates comparable reactivity of the coordinated NCPh and $NCNR'_2$, while alkylnitrile ligands do not react with the dipole. The reaction between *trans*-$[PtCl_2(NCNR'_2)_2]$ (R'_2 = Me_2, Et_2, C_5H_{10}) and the nitrones proceed as consecutive two-step intermolecular cycloaddition to give *mono*-(**1a–d**) and *bis*-2,3-dihydro-1,2,4-oxadiazole (**2a–d**) complexes (Ar/R″ = *p*-tol/Me: R'_2 = Me_2 **a**, R'_2 = Et_2 **b**, R'_2 = C_5H_{10} **c**; Ar/R″ = *p*-$MeOC_6H_4$/CH_2Ph: R'_2 = Me_2 **d**). All complexes were characterized by elemental analyses (C, H, N), high resolution ESI-MS, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The structures of *trans*-**1b**, *trans*-**2a**, *trans*-**2c**, and *trans*-**2d** were determined by single-crystal X-ray diffraction. Metal-free 5-NR'_2-2,3-dihydro-1,2,4-oxadiazoles **3a–3d** were liberated from the corresponding (dihydrooxadiazole)$_2Pt^{II}$ complexes by treatment with excess NaCN and the heterocycles were characterized by high resolution ESI^+-MS, ^1H and $^{13}C\{^1H\}$ spectroscopy.

Introduction

Nitriles can be strongly activated upon their ligation to a metal center, which often results in promotion of nucleophilic[1–3] and electrophilic addition,[2] or 1,3-dipolar cycloaddition (DCA);[1,4–6] many of these processes are not feasible for the corresponding metal-free RCN species. In particular, reactions of metal-activated RCN ligands with 1,3-dipoles leads to nitrogen heterocycles, which are stabilized by metal centers and some of them do not even exist after liberation and they split to the starting reactants.[7]

Although a rather wide variety of allyl- [acyclic nitrones (A, Fig. 1),[8–13] cyclic nitrones such as pyrroline-*N*-oxide (B),[14–16] imidazoline-*N*-oxides (C),[7] oxazoline-*N*-oxides (D),[17] and nitronates (E)[18]] and propargyl/allenyl- [azides (F)[6,19–22] and nitrile oxides (G)[23,24]] anion type dipoles have been applied for metal-mediated DCA to nitriles, the range of employed RCN substrates is usually restricted to the conventional species such as alkyl- and arylnitriles. Application of DCA in another important category of nitrile substrates, the so-called *push–pull nitriles* (a push–pull system is highly polarized and it is characterized by an electron-withdrawing substituent or electronegative atom on one side of the multiple bond and an electron-donating substituent on the other side),[25–27] *e.g.* dialkylcyanamides $NCNR'_2$, so far have attracted only little attention despite the fact that data gradually accumulated in the literature indicates intriguing reactivity differences between the *conventional* and the *push–pull* RCN species.[27–31]

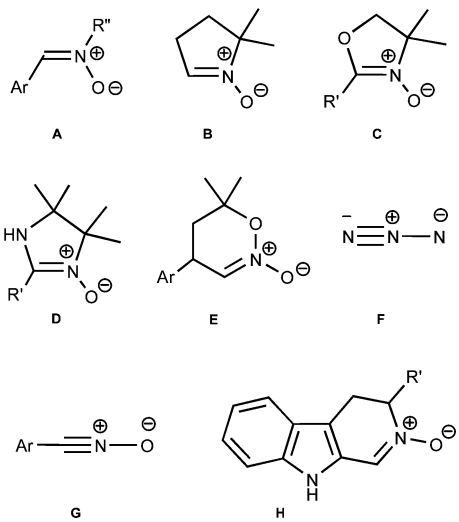

Fig. 1 1,3-Dipoles applied for DCA to nitriles.

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† Electronic supplementary information (ESI) available: crystal cif file; view of **2a** and **2d** with the atomic numbering scheme. CCDC reference numbers 803620–803623. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01689f

Indeed, to the best of our knowledge only one report[32] is devoted to metal-free DCA of the highly reactive cyclic *E*-configurated indole-based nitrone (H, Fig. 1) to $NCNMe_2$ performed in toluene under rather harsh conditions (80 °C, 3.5 h). In addition, few examples of DCA to push–pull nitrile ligand, *i.e.* Pd^{II}- and Pt^{IV}-mediated DCA of nitrile oxides to $NCNR'_2$[23,24] and also reactions of *E*-configurated imidazoline-*N*-oxides (D)[7] or oxazoline-*N*-oxides (C)[17] with the dialkylcyanamide ligands at Pt^{II} centers, were previously reported by our group.

As can be inferred from the inspection of all these works,[7,17,32] highly reactive dipoles in the *E*-form[33] have so far been applied for DCA, while reactivity of much less reactive[33,34] acyclic nitrones in the *Z*-configuration was not studied. It is worthwhile mentioning that Hermkens *et al.*[32] pointed out that the acyclic nitrone *Z*-PhCH=$N^+(O^-)$Me reacts only with RCN substrates bearing electron withdrawing substituents (R = CCl_3, Ph) and no examples of DCA with nitriles having donor groups (R = Me, NMe_2) were observed.

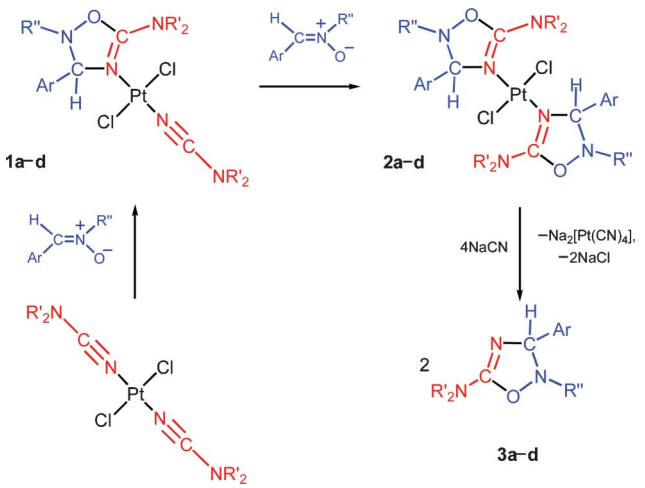
As an amplification of our previous studies on metal-mediated DCA,[7,13,17,18,23] and in view of our general interest in reactivity of nitriles (for reviews see[1,2,4,5,35,36] and for recent works see[7,17,18,27,30,31,37,38]) and isonitriles (for recent works see ref. 39,40), we studied DCA of the acyclic nitrones ArCH=$N^+(O^-)$R″ (Ar/R″ = C_6H_4Me-*p*/Me; C_6H_4OMe-*p*/CH_2Ph)[41,42] in the *Z*-configuration to the push–pull nitriles in the complexes $[PtCl_2(NCNR'_2)_2]$ (R'_2 = Me_2, Et_2, C_5H_{10}). The scenario of this work was the following: (i) to discover the reactivity of $NCNR'_2$ ligands toward DCA of the acyclic nitrones *Z*-ArCH=$N^+(O^-)$R″ and to characterize the DCA products; (ii) to decoordinate the 5-NR'_2-2,3-dihydro-1,2,4-oxadiazoles and to characterize these metal-free heterocycles; (iii) to perform a comparative kinetic study on the reactivity of dialkylcyanamide ligands and the conventional coordinated RCN species (*i.e.*, PhCN and EtCN).

Results and discussion

DCA of the acyclic nitrones to dialkylcyanamide ligands

The reaction between *Z*-ArCH=$N^+(O^-)$R″ (Ar/R″ = C_6H_4Me-*p*/Me; C_6H_4OMe-*p*/CH_2Ph) and *trans*-$[PtCl_2(RCN)_2]$ (R = NMe_2, NEt_2, NC_5H_{10}) in a molar ratio 1 : 1.5 in chloroform at 20–25 °C was monitored by both TLC and ^{1}H NMR. It leads to **1a–d** (Scheme 1) for 30 h. These species are formed in almost quantitative NMR spectroscopy yields and 70–75% isolated yields after column chromatography; both yields are based on the nitrone.

When DCA was performed at a 2 : 1 molar ratio at room temperature, we observed generation of **1a–d** followed by their transformation to **2a–d** (Scheme 1). However, under these conditions the conversion is slow and DCA is accompanied with a gradual degradation of the nitrone. Furthermore, upon heating at 50 °C, the reaction loses its selectivity providing a broad spectrum of products originated from degradations of both nitrones and DCA products. The performance of DCA in a molar ratio 15 : 1 proceeds much faster, more selective, and with the complete conversion of *trans*-$[PtCl_2(RCN)_2]$ to *bis*-CA species **2a–d** (after 24 h NMR yields *ca.* 100% based on the starting complexes; isolated yields 70–86%) *via* intermediate formation of **1a–d** (NMR yields *ca.* 95–97% after 2 h).



Scheme 1 Two-step Pt^{II}-mediated DCA and liberation of the oxadiazoles (Ar/R″ = *p*-tol/Me: R'_2 = Me_2 **a**, R'_2 = Et_2 **b**, R'_2 = C_5H_{10} **c**; Ar/R″ = *p*-$MeOC_6H_4$/CH_2Ph: R'_2 = Me_2 **d**).

Thus, the reaction of *Z*-ArCH=$N^+(O^-)$R″ and *trans*-$[PtCl_2(NCNR_2)_2]$ proceeds as a consecutive two-step DCA; the first step occurs faster than the second one. These observations are coherent with the previous report[12] indicating that DCA of the acyclic nitrone *Z*-PhCH=$N^+(O^-)$Ph to the nitrile ligands in *trans*-$[PtCl_2(PhCN)_2]$ also occurs *via* two consecutive steps. The significant difference in the reaction rates between the two steps of the DCA could be accounted for by a higher electron donor ability of the newly formed heterocycle, compared to the corresponding push–pull nitrile ligand that leads to an increase in the LUMO of the remaining *trans*-located $NCNR'_2$ ligand and deactivate the dipolarophile towards DCA.

Complexes **1a–d** and **2a–d** were obtained as yellow solids and characterized by elemental analyses (C, H, N), high resolution ESI^+-MS, IR, and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopies, and also by X-ray diffraction (for **1b**, **2a**, **2c**, and **2d**). All complexes gave satisfactory microanalyses. In the ESI^+-MS, the typical ions that were detected are $[M]^+$ and $[M + Na]^+$. A comparison of the IR spectra of the products with those of the starting *trans*-$[PtCl_2(RCN)_2]$ indicated the absence of ν(C≡N) stretching vibrations at *ca.* 2300 cm^{-1} for **2a–d**, while for **1a–d** these stretches emerge in the region from 2289 to 2299 cm^{-1}. The presence of intensive ν(C=N) vibrations in the range 1640–1670 cm^{-1} was detected in the IR spectra of all complexes.

For **1a–d** and **2a–d**, signal integration in the ^{1}H NMR spectra gives evidence that the reaction between each of the coordinated nitriles and the nitrone proceeds in a 1 : 1 ratio. The ^{1}H NMR spectra of **1a–d** and **2a–d** display the broad (owing to the quadrupole effect of two ^{14}N) singlets of the C^3H protons in the range 5.33–5.85 ppm. The signals from the C^3H protons for **2a–d** are low-field shifted from those for the corresponding **1a–d**. In the $^{13}C\{^1H\}$ NMR spectra, the peaks due to C^5=N (157.4–160.4 ppm) and C^3 (89.8–93.4 ppm) were recognized. Both ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **1a–d** exhibit the signals from the oxadiazole and the nitrile ligands.

Complexes **1b** (Fig. 2), **2a** (Fig. S1, supplementary†), **2c** (Fig. 3), and **2d** (Fig. S2, supplementary†) were characterized by single-crystal X-ray diffraction. In **1b**, the coordination polyhedron of the Pt atom is a slightly distorted square plane with the hetetocyclic

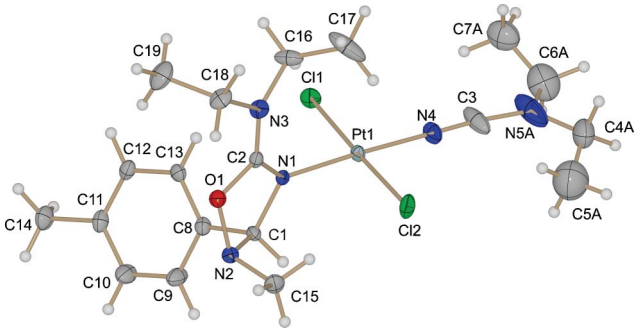


Fig. 2 View of **1b** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(4) 1.960(3), Pt(1)–N(1) 2.003(3), Pt(1)–Cl(1) 2.2983(9), Pt(1)–Cl(2) 2.3002(10), N(1)–C(2) 1.299(4), N(1)–C(1) 1.480(4), O(1)–N(2) 1.474(4), O(1)–C(2) 1.364(4), N(3)–C(2) 1.328(5), N(4)–C(3) 1.141(5), N(4)–Pt(1)–N(1) 177.65(13), Cl(1)–Pt(1)–Cl(2) 178.13(3).

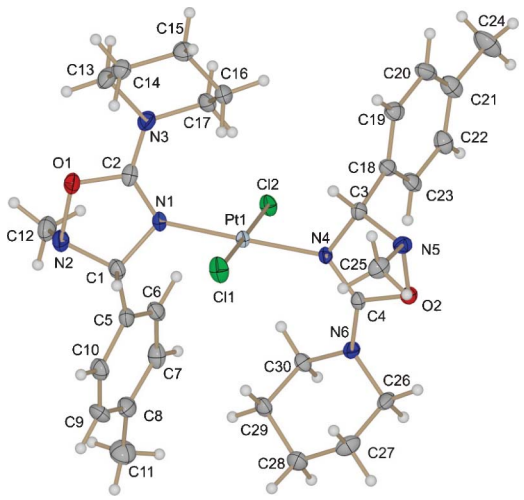


Fig. 3 View of **2c** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(4) 2.006(2), Pt(1)–N(1) 2.016(2), Pt(1)–Cl(1) 2.3087(8), Pt(1)–Cl(2) 2.3108(7), N(1)–C(2) 1.316(4), N(1)–C(1) 1.485(4), N(2)–C(1) 1.482(4), N(4)–C(4) 1.302(4), N(4)–C(3) 1.482(4), N(5)–C(3) 1.486(4), N(4)–Pt(1)–N(1) 177.74(9), Cl(1)–Pt(1)–Cl(2) 177.81(3).

and nitrile ligands in the *trans*-position (Fig. 3). The N(4)C(3) bond (1.141(5) Å) is the typical C≡N triple bond in the coordinated dialkylcyanamide and nitrile ligands.[43] The distance N(1)–C(2) (1.299(4) Å) is typical for the N=C double bond,[44] the N(1)–C(1), and N(2)–C(1), are characteristic for the N–C (1.480(4) and 1.478(5) Å) single bonds. The NEt_2 fragment of the nitrile ligand is strongly disordered and this prevents the comparison of the geometrical parameters. To the best of our knowledge, the mixed (nitrile)(2,3-dihydro-1,2,4-oxadiazole)Pt^{II} complex **1b** represents the first example of a structurally characterized platinum(II) species of this type.

The structure of **2d** is strongly disordered, however the X-ray data confirm its formulation. In **2a** (Fig. S1, supplementary†), **2c** (Fig. 3), and **2d** (Fig. S2, supplementary†), the oxadiazole ligands are located in the *trans* position. The Pt(1)–N(1) and Pt(1)–N(4) bond lengths in each complex are typical for (imine)Pt^{II} species.[44] N(1)–C(2) and N(4)–C(4) (1.305(5) Å, 1.303(5) Å in **2a** and 1.316(4) Å, 1.302(4) Å in **2c**) are characteristic for the N=C double bond,[44] while the N(1)–C(1), N(2)–C(1), N(4)–C(3), and N(5)–C(3) bond lengths in **2a** (1.475(4), 1.480(5), 1.469(4) and 1.480(4) Å), and in **2c** (1.485(4), 1.482(4), 1.482(4), and 1.486(4) Å) are specific for the N–C single bonds. In **2a** and **2c**, both asymmetric atoms C^3 in the heterocyclic ligands exhibit the same configuration (*RR*/*SS*), while in **2d** the configuration of the C^3 atoms in two heterocyclic ligands is different (*RS*). It is worthwhile mentioning that in **2a**, **2d**, and **1b**, the alkyl (Me for **2a** and **1b**; CH_2Ph for **2d**) and aryl (*p*-tol for **2a** and **1b**; *p*-$MeOC_6H_4$ for **2d**) groups of the heterocyclic ligands adopt the *trans*-orientation, while in **2c** one of the heterocyclic ligands has the *trans*-orientation of Me and *p*-tol and another one has Me and *p*-tol from the nitrone situated in the *cis*-position.

The previous studies[9] demonstrated that Pt^{IV} centers activate nitrile substrates towards DCA of acyclic nitrones in a significantly more efficient way than Pt^{II} centers. Having an aim to enhance the cycloaddition and to achieve higher yields of (2,3-dihydro-1,2,4-oxadiazole)Pt species, we attempted DCA of the nitrones to the dialkylcyanamides at a Pt^{IV} center. The reaction between the nitrone *Z*-$MeC_6H_4CH{=}N^+(O^-)Me$ and *trans*-$[PtCl_4(NCNMe_2)_2]$[29]—performed under the same conditions as for Pt^{II}-mediated DCA—does not accomplish the corresponding oxadiazole complexes. Instead, a wide range of products (up to seven spots on the TLC; additionally a signal corresponding to the $(oxadiazole)_2Pt^{IV}$ complex was detected in ESI^+-MS: found 798.4552, calcd. $[PtCl_4(2,3\text{-dihydro-}1,2,4\text{-oxadiazole})_2]$ 798.4445) was formed after a few minutes. After two weeks at 20–25 °C we were able to identify in the solution several additional species, *i.e.* the platinum(II) complex **2a** and the aldehyde MeC_6H_4CHO. The formation of **2a** can be accounted for by the reduction of the Pt^{IV} complex with the nitrone and/or products of its degradation (*i.e.* hydroxylamine and the aldehyde formed upon hydrolysis) and/or DCA to the Pt^{II} nitrile complex also generated *in situ* upon reduction. The orange precipitate released from the reaction mixture, based on IR spectroscopy, ESI mass-spectrometry and ^{13}C CP-MAS NMRdata, was formulated as $[NH_2Me_2]_2[PtCl_6]$. This complex was previously observed in another Pt^{IV}-mediated reaction of dialkylcyanamide, *i.e.* when $[PtCl_4(MeCN)_2]$ was kept in the neat undried $NCNMe_2$ and this process afforded the metal-mediated C–N bond cleavage of $NCNMe_2$ to furnish $[NH_2Me_2]_2[PtCl_6]$.[29] Thus, the Pt^{IV} center activates $NCNR_2$ ligands so greatly, that DCA loses its selectivity and generates a broad mixture of products.

Liberation of 2,3-dihydro-1,2,4-oxadiazoles from 2a–d

In the past few years, several methods for liberation of the strongly bound imines and nitrogen heterocycles from their Pt^{II} complexes have been developed and they are based on displacement with an excess of a diphosphine,[37,45–48] or monodentate and bidentate amines bearing two sp^3-*N*-donor centres.[11,17,49] We observed that in **2a–d** the newly formed heterocyclic ligands are so strongly bound to the platinum(II) center that the decoordination cannot be achieved even with 1,2-bis-(diphenylphosphino)ethane (6-fold excess, 35–40 °C, 2 d) and ethane-1,2-diamine (10-fold excess, 35–40 °C, 1 d). However, it was previously reported that the alkali metal cyanides could be applied for the decoordination of some chelated phosphine ligands, and this observation indicates that the cyanide species are highly potent reactants for the displacement

of strongly bound ligands at Pt^{II} centers.[50] In accord with this assumption, we observed that treatment of **2a–d** with NaCN (6 equivs., 35–40 °C, 1 d) leads to almost quantitative formation of the metal-free oxadiazoles (Scheme 1). These species were characterized by high resolution ESI^+ mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. In the ESI^+-MS, the observed peaks were attributed to the quasi-ions $[M + H]^+$ and $[M + Na]^+$. The ^1H and $^{13}C\{^1H\}$ NMR spectra of the uncomplexed oxadiazoles demonstrate all signals specific for these ring systems. Thus, the heterocycles exhibit signals from the C^{3a} (88.9–92.3 ppm) and the C=N (159.4–161.2 ppm) carbons in the $^{13}C\{^1H\}$ spectra, the former signal is high field shifted (*ca.* 1.0–1.5 ppm) and the latter is low field shifted (1–3 ppm) relative to the corresponding signals in the $(oxadiazole)_2Pt^{II}$ species, although chemical shifts are not directly comparable because the spectra of the complexed and metal-free oxadiazoles were measured in different solvents.

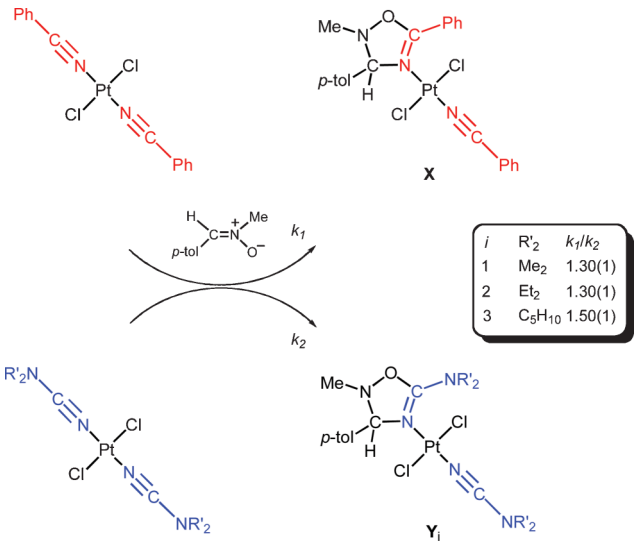
Competitive reactivity study

The synthetic data of the current work and those previously obtained for DCA of nitrones to platinum complexes bearing the conventional nitrile ligands (for discussion see ref. 4,9) explicitly indicate that the alteration of the substituent of R of RCN in $(nitrile)_2Pt^{II}$ complexes plays a dramatic role on the reactivity. In general, the reactivity toward DCA of nitrones increases with the increase of electron-deficiency of RCN species. The most intriguing issue of the current work is the observation of unexpectedly high reactivity of the push–pull dialkylcyanamide ligands $NCNR'_2$ bearing the strong donor substituents $NAlk_2$ (as confirmed by considering their Pickett P_L and Lever E_L parameters[51,52]) toward DCA. As it was revealed in the preparative experiments, the reactivity of the nitriles with $NAlk_2$ is comparable with that of a moderate acceptor group Ph. To get a quantitative estimate of the reactivity dependence on the nature of the R group, we conducted a competitive reactivity study of DCA to $NCNR'_2$ (R'_2 = Me_2, Et_2, NC_5H_{10}) and PhCN coordinated species. The method employed includes DCA between the equimolar mixture of two complexes and one dipole, *i.e.* $4\text{-}MeC_6H_4CH{=}N^+(O^-)Me$, with a 2 : 1 overall molar ratio between the metal-containing species and the dipole (see Experimental); under these conditions the first step of DCA was monitored (Scheme 2).

In the context of the similar reactivity of $NCNR'_2$ and NCPh ligands, attention should be drawn to the work by Hermkens *et al.*[32] who found (based purely on synthetic experiments) that the uncomplexed nitriles RCN react with the highly reactive indole-derived cyclic nitrone in the *E*-form (H, Fig. 1) and the reactivity in DCA generally increases with an increase in the electron-withdrawing ability of the substituents R in the following order $Me \ll Ph < NMe_2 < CO_2Et < CCl_3$. Position of the strong electron-donating group NMe_2 between the moderate (Ph) and strong (CO_2Et) accepting groups in the metal-free experiment[32] and the similar reactivity of the dialkylcyanamides and PhCN, verified in our kinetic study, apparently could be explained by the crossover in FMO control of DCA, specific for dialkylcyanamides.

Final remarks

Despite the wealth of chemistry associated with reactions of metal-bound *conventional* nitriles RCN (R = alkyl, aryl), the coordination chemistry of the *push–pull* nitriles such as, *e.g.* dialkylcyanamides R'_2NCN, has so far been little explored, although data gradually accumulated in the literature indicates that the R'_2NCN ligands might exhibit some exciting reactivity modes unknown for alkyl- or arylnitrile ligands.[27,29,30,53–55]



Scheme 2 Competitive reactivity study of DCA to PhCN and $NCNR'_2$ ligands.

DCA of the rather unreactive acyclic *Z*-nitrones to dialkylcyanamide ligands, conducted under mild conditions and described above, represents a novel example of reactivity for metal-activated push–pull nitriles. These reactions constitute a facile route to the coordinated and metal-free (after the liberation) 5-NR'_2-2,3-dihydro-1,2,4-oxadiazoles. In this context, it is worth mentioning that platinum(II) 5-Ph-2,3-dihydro-1,2,4-oxadiazole complexes exhibit significant antitumor activity[56,57] and we believe that the antitumor activity study of more water soluble $(5\text{-}NR'_2\text{-}2,3\text{-dihydro-}1,2,4\text{-oxadiazoles})_2Pt^{II}$ complexes could be an interesting further task.

The competitive reactivity study of DCA between $[PtCl_2(RCN)_2]$ (R = Ph, NMe_2, NEt_2, NC_5H_{10}) and the acyclic nitrone demonstrates comparable reactivity of coordinated NCPh and $NCNR'_2$. Unexpectedly high activation of the $NCNR'_2$ species due to the coordination in contrast to alkylnitrile ligands (see results and discussion) requires additional investigation. Further works on the reactivity differences between the push–pull and the conventional nitrile species ligated to various metal centers are under way in our group.

Experimental

Materials and instrumentation

Solvents were obtained from commercial sources and used as received. Complexes $[PtCl_2(RCN)_2]$ ($R = NEt_2$, NMe_2, NC_5H_{10}) were synthesized in accordance with the published procedures.[29] The nitrones $ArCH{=}N^+(O^-)R''$ ($Ar/R'' = C_6H_4Me\text{-}p/Me$; $C_6H_4OMe\text{-}p/CH_2Ph$) were obtained by the known protocol based on condensation of the aldehydes $p\text{-}MeC_6H_4CHO$ and $p\text{-}MeOC_6H_4CHO$ with $R''NHOH{\cdot}HCl$ ($R'' = Me$, CH_2Ph).[41,42] C, H, and N elemental analyses were carried out by the Department of Organic Chemistry

Table 1 Crystal data

	1b	**2a**	**2c**	**2d**
Empirical formula	$C_{19}H_{31}Cl_2N_5OPt$	$C_{24}H_{34}Cl_2N_6O_2Pt$	$C_{30}H_{42}Cl_2N_6O_2Pt$	$C_{36}H_{42}Cl_2N_6O_4Pt$
Fw	611.48	704.56	784.69	888.75
Temp (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Cryst syst	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	8.2227(2)	16.0916(4)	9.6768(2)	8.4287(7)
b (Å)	11.0745(3)	9.3706(2)	12.1702(2)	11.1631(8)
c (Å)	13.7740(4)	18.3895(3)	26.9509(3)	19.8266(14)
α (deg)	102.4393(13)	90	90	90
β (deg)	99.8321(14)	91.5729(13)	96.1540(11)	97.669(4)
γ (deg)	102.6972(13)	90	90	90
V (Å^3)	1163.15(5)	2771.87(10)	3155.68(9)	1848.8(2)
Z	2	4	4	2
ρ_{calc} (Mg m^{-3})	1.746	1.688	1.652	1.596
μ (Mo Kα) (mm^{-1})	6.280	5.287	4.653	3.986
No. reflns.	16522	45783	44178	11105
Unique reflns.	5325	6354	9211	3320
GOOF (F^2)	1.080	1.069	1.037	1.105
R_{int}	0.0274	0.0533	0.0556	0.0465
$R1^a$ ($I \geq 2\sigma$)	0.0250	0.0283	0.0313	0.0515
$wR2^b$ ($I \geq 2\sigma$)	0.0558	0.0534	0.0558	0.1025

^{a} $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. ^{b} $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]]^{1/2}$.

of St. Petersburg State University on a 185B Carbon Hydrogen Nitrogen Analyzer Hewlett Packard. Electrospray ionization mass spectra were obtained on a Bruker micrOTOF spectrometer equipped with an electrospray ionization (ESI) source. The instrument was operated both in positive and negative ion mode using a m/z range of 50–3000. The capillary voltage of the ion source was set at –4500 V (ESI$^+$-MS) and the capillary exit at ± (70–150) V. The nebulizer gas flow was 0.4 bar and the drying gas flow 4.0 L min^{-1}. For ESI, species were dissolved in MeOH or MeCN, $NaBF_4$ was used as an addition ionization agent. In the isotopic pattern, the most intensive peak is reported for both the complexes and the free heterocycles. TLC was performed on Merck 60 F_{254} SiO_2 plates. Infrared spectra (4000–400 cm^{-1}) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. ^{1}H and ^{13}C{^{1}H} NMR spectra were measured in $CDCl_3$ on Bruker DPX-300 and AMX-400 spectrometers at ambient temperature.

X-ray crystal structure determination

The crystals of **2a**, **2c**, **2d**, and **1b** and were immersed in cryo-oil, mounted in a nylon loop, and measured at a temperature of 100 K. The X-ray diffraction data were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The Denzo-Scalepack[58,59] program package was used for cell refinements and data reductions. The structures were solved by direct methods using SIR2004[59] or SHELXS-97[60] programs with a WinGX[61] graphical user interface. A semi-empirical (SADABS) method[62] was applied to all of the data. Structural refinements were carried out using SHELXL-97.[60] In **1b**, the *N,N*-diethylcyanamide ligand was heavily disordered. The N(5), C(6), and C(7) atoms were disordered over two sites with occupancies 0.9 and 0.1. The C(4) and C(5) carbon atoms were disordered over three sites with occupancies 0.7, 0.2, and 0.1. The anisotropic displacement parameters of the disordered atoms were constrained to be similar. Also, the C–C and N–C distances in the *N,N*-diethylcyanamide ligand were restrained to be similar. The hydrogen atoms were positioned geometrically and constrained to ride on their parent carbon atoms, with C–H = 0.95–1.00 Å, U_{iso} = 1.2–1.5 U_{eq} (parent atom). The crystallographic details are summarized in Table 1.

Competitive reactivity study

The reactions were performed in a $CDCl_3$ solution (0.5 mL $CDCl_3$, 0.5 mmol of each of two studied complexes, 0.5 mmol of the nitrone) at 25 °C and the reactions were monitored by ^{1}H NMR spectroscopy. Hexamethyldisiloxane was used as an internal standard. The spectra were registered immediately after the addition of the dipole to the reaction mixture and then after 0.25, 0.75, 2, 4, 9, and 20 h; after 36 h the nitrone was not detected in the ^{1}H NMR spectra.

The ratio $\frac{k_1}{k_2}$ was obtained in accord with the formula

$$\frac{k_1}{k_2} = \frac{S(X)_t}{S(Y_i)_t},$$

where $S(X)_t$ and $S(Y_i)_t$ are integral intensities of signals of the C^{3}H proton of the oxadiazole ring from X and Y_i (Scheme 2). The mean value was calculated based on the timepoints for 0.25, 0.75, 2 and 4 h since the constant ratio $\frac{k_1}{k_2}$ is stable within the specified time period.

Synthetic work

Synthesis of the (2,3-dihydro-1,2,3-oxadiazole)(nitrile)Pt^{II} complexes (a general procedure). The solutions of each of the nitrones (0.1 mmol) in $CHCl_3$ (1 mL) were added to a solution of the corresponding *trans*-[$PtCl_2(NCR)_2$] (0.15 mmol; R = NMe_2, NC_5H_{10}, NEt_2) in $CHCl_3$ (1 mL). The mixture was stirred at

room temperature for 30 h and the progress of the reaction was monitored by TLC. The separation of **1a–d** was achieved by column chromatography on SiO_2 (the first fraction; eluent $CHCl_3/Me_2CO$, 10/1, v/v). The solvent was evaporated *in vacuo* at 20–25 °C to give yellow oily residues. The residues were crystallized under *n*-hexane to form the yellow powders of **1a–d**. The complexes were dried in air at 20–25 °C. Yields 70–75%.

1a (42 mg, 75%); Found: C, 32.84; H, 4.36; N, 12.29 (Calc. for $C_{15}H_{23}N_5Cl_2OPt$: C, 32.48; H, 4.18; N, 12.63); *m/z* (high resolution ESI$^+$) 556.0876 ([M + H]$^+$, requires 556.1029); 578.0700 ([M + Na]$^+$, requires 578.0849); 594.0432 ([M + K]$^+$, requires 594.0588); R_f = 0.35 (eluent $CHCl_3/Me_2CO$, 50/1, v/v); ν_{max}(KBr)/cm^{-1}: 2927 m (C–H), 2289 m (C≡N), 1666 s (C=N); δ_H (300 MHz, $CDCl_3$): 2.32 (3H, s, CH_3 from *p*-tol), 2.89 (9H, br s, N(O)Me, NMe_2 of the nitrile ligand), 3.61 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 5.56 (1H, s, CH), 7.16 (2H, d, *m*-H from *p*-tol), 7.45 (2H, d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$): 21.8 (CH_3 from *p*-tol), 40.3 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 40.4 (NMe_2 of the nitrile ligand), 46.3 (N(O)Me), 93.2 (N–CH–N), 128.6, 129.4, 135.09, and 139.1 ($C_{aromatic}$), 158.5 (C(O)=N); the C≡N carbon was not detected.

1b (43 mg, 70%); Found: C, 37.21; H, 5.10; N, 11.53 (Calc. for $C_{19}H_{31}N_5Cl_2OPt$: C, 37.36; H, 5.12; N, 11.47); *m/z* (high resolution ESI$^+$) 612.1488 ([M + H]$^+$, requires 612.1658); 634.1311 ([M + Na]$^+$, requires 634.1475); R_f = 0.46 (eluent $CHCl_3/Me_2CO$, 60/1, v/v); ν_{max}(KBr)/cm^{-1}: 2976, 2933 m (C–H), 2291 m (C≡N), 1653 s (C=N); δ_H (300 MHz, $CDCl_3$): 1.25 (6H, t, *J* = 7 Hz, CH_3 from NEt_2 of the nitrile ligand), 1.39 (6H, t, *J* = 7 Hz, CH_3 from $CNEt_2$ of the 2,3-dihydro-1,2,4-oxadiazole ligand), 2.31 (3H, s, CH_3 from *p*-tol), 2.94 (3H, br s, N(O)Me), 3.10 (4H, q, *J* = 7 Hz, CH_2 from NEt_2 of the nitrile ligand, 4.10 (4H, br s, CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 5.63 (1H, s, CH), 7.17 (2H, d, *m*-H from *p*-tol), 7.37 (2H, d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$): 13.3 (CH_3 from NEt_2 of the nitrile ligand), 14.2 (CH_3 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 21.7 (CH_3 from *p*-tol), 44.6 (CH_2 from NEt_2 of the nitrile ligand), 46.2 (CH_2 from NEt_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 46.7 (N(O)Me), 93.2 (N–CH–N), 128.1, 129.3, 138.5, and 138.9 ($C_{aromatic}$), 158.5 (C(O)=N); the C≡N carbon was not detected. The crystals suitable for X-ray study were obtained by a slow evaporation of the solvent (heptane/acetone = 1/1, v/v) at room temperature.

1c (45 mg, 71%); Found: C, 39.52; H, 4.91; N, 11.02 (Calc. for $C_{21}H_{31}N_5Cl_2OPt$: C, 39.73; H, 4.92; N, 11.04); *m/z* (high resolution ESI$^+$) 636.1471 ([M + H]$^+$, requires 636.1655); 658.1290 ([M + Na]$^+$, requires 658.1475); 674.1013 ([M + K]$^+$, requires 674.1214); R_f = 0.47 (eluent $CHCl_3/n\text{-}C_6H_{14}/Me_2CO$, 4/5/1, v/v/v); ν_{max}(KBr)/cm^{-1}: 2927 m (C–H), 2289 m (C≡N), 1666 s (C=N); δ_H (300 MHz, $CDCl_3$): 1.60 (12H, br m; β- and γ-CH_2 from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole and nitrile ligands), 2.33 (3H, s, CH_3 from *p*-tol), 2.90 (3H, br s, N(O)Me), 3.23 (4H, 7, *J* = 5 Hz, α-CH_2 from NC_5H_{10} of the nitrile ligand), 4.27 (4H, br s, α-CH_2 from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 5.57 (1H, s, CH), 7.43 (2H, d, *m*-H from *p*-tol), 7.19 (2H, d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$): 21.8 (CH_3 from *p*-tol), 22.9 (γ-CH_2 from NC_5H_{10} of the nitrile ligand), 24.3 (γ-CH_2 from NC_5H_{10} of the nitrile ligand), 24.9 (β-CH_2 from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 25.9 (β-CH_2 from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 46.2 (N(O)Me and α-CH_2 from NC_5H_{10} of the 2,3-dihydro-1,2,4-oxadiazole ligand), 50.0 (α-CH_2 from NC_5H_{10} of the nitrile ligand), 93 (N–CH–N), 128.6, 129.4, 135.2, and 139 ($C_{aromatic}$), 157.7 (C(O)=N); the C≡N carbon was not detected.

1d (47 mg, 73%); Found: C, 39.04; H, 4.21; N, 10.82; (Calc. for $C_{21}H_{27}N_5Cl_2O_2Pt$: C, 39.00; H, 4.21; N, 10.84); *m/z* (high resolution ESI$^+$): 647.1254 ([M + H]$^+$, requires 647.1267); R_f = 0.49 (eluent $CHCl_3/Me_2CO$, 15/1, v/v); ν_{max}(KBr)/cm^{-1}: 3475 m (C–H), 2299 m (C≡N), 1670 s (C=N); δ_H (300 MHz, $CDCl_3$): 2.96 (6H, s, NMe_2 of the nitrile ligand), 3.63 (6H, br s, NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 3.78 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 4.29 (2H, br s, N(O)CH_2Ph), 5.85 (1H, br s, CH), 6.87 (2H, br d, $H_{aromatic}$), 7.34, 7.46 (7H, m and s, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$): 40.4 (NMe_2 of the 2,3-dihydro-1,2,4-oxadiazole ligand), 40.5 (NMe_2 of the nitrile ligand), 55.6 (N(O)CH_2Ph), 62.1 (CH_3 from *p*-$MeOC_6H_4$), 89.8 (N–CH–N), 113.9, 128.4, 129.0, 129.6, 130.3, and 135.0 ($C_{aromatic}$), 160.2 (C(O)=N); the C≡N carbon was not detected.

Synthesis of the (2,3-dihydro-1,2,3-oxadiazole)$_2$Pt^{II} complexes (a general procedure). The solutions of each of the nitrones (1.5 mmol) in $CHCl_3$ (1 mL) were added to a solution of the corresponding *trans*-[$PtCl_2(NCR)_2$] (0.1 mmol; R = NMe_2, $N(C_5H_{10})$, NEt_2) in $CHCl_3$ (1 mL). The mixture was stirred at room temperature for 24 h and the progress of the reaction was monitored by TLC. The separation of **2a–d** was achieved by column chromatography on SiO_2 (the first fraction; eluent $CHCl_3/Me_2CO$, 15/1, v/v). The solvent was evaporated *in vacuo* at 20–25 °C to give yellow oily residues. The residues were crystallized under *n*-hexane to form the yellow powders of **2a–d**. The complexes were dried in air at 20–25 °C. Yields 70–86%.

2a (58 mg, 82%); Found: C, 41.42; H, 4.82; N, 11.80 (Calc. for $C_{24}H_{34}N_6Cl_2O_2Pt$: C, 40.95; H, 4.87; N, 11.94); *m/z* (high resolution ESI$^+$) 743.1330 ([M + K]$^+$, requires 743.1429); R_f = 0.44 (eluent $CHCl_3/Me_2CO$, 40/1, v/v); ν_{max}(KBr)/cm^{-1}: 2933 m (C–H), 1665 s (C=N); δ_H (300 MHz, $CDCl_3$): 2.34 (3H, s, CH_3 from *p*-tol), 2.73 (3H, s, N(O)Me), 3.13 (6H, br s, NMe_2), 5.33 (1H, br s, CH), 7.17 (2H, two d, *m*-H from *p*-tol), 7.44 (2H, br d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$): 21.7 (CH_3 from *p*-tol), 39.6 (NMe_2), 44.5 (N(O)Me), 93.4 (N–CH–N), 129.1, 130.2, 135.08, and 139.3 ($C_{aromatic}$), 157.4 (C(O)=N). The crystals suitable for X-ray study were obtained by a slow evaporation of the solvent (heptane/acetone = 1/1, v/v) at room temperature.

2b (65 mg, 80%); Found: C, 44.37; H, 5.59; N, 11.02 (Calc. for $C_{28}H_{42}N_6Cl_2O_2Pt$: C, 44.25; H, 5.57; N, 11.06); *m/z* (high resolution ESI$^+$) 761.2265 ([M + H]$^+$, requires 761.2418); 783.2131 ([M + Na]$^+$, requires 783.2316); 799.1843 ([M + K]$^+$, requires 799.2055); R_f = 0.56 (eluent $CHCl_3/Me_2CO$, 60/1, v/v); ν_{max}(KBr)/cm^{-1}: 2967, 2929 m (C–H), 1645 s (C=N); δ_H (300 MHz, $CDCl_3$): 1.19 (6H, br s, CH_3 from NEt_2), 2.33 (3H, s, CH_3 from *p*-tol), 2.83 (3H, s, N(O)Me), 3.9 (4H, br s, CH_2 from NEt_2), 5.49 (1H, br s, CH), 7.15 (2H, two d, *m*-H from *p*-tol), 7.35 (2H, br d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$) 14.1 (CH_3 from NEt_2), 21.7 (CH_3 from *p*-tol), 44.1 (CH_2 from NEt_2), 46 (N(O)Me), 93.4 (N–CH–N), 129.2, 128.57, 135.5, and 138.8 ($C_{aromatic}$), 158 (C(O)=N).

2c (55 mg, 70%); Found: C, 45.72; H, 5.43; N, 10.63 (Calc. for $C_{30}H_{42}N_6Cl_2O_2Pt$: C, 45.96; H, 5.40; N, 10.72); *m/z* (high resolution ESI$^+$) 783.2146 ([M – H]$^+$, requires 783.2339); 807.2114

([M + Na]$^+$, requires 807.2315); 823.1834 ([M + K]$^+$, requires 823.2055); R_f = 0.60 (eluent $CHCl_3$/*n*-C_6H_{14}/Me_2CO, 4/5/1, v/v/v); ν_{max}(KBr)/cm^{-1}: 2924 and 2856 m (C–H), 1647 s (C═N); δ_H (300 MHz, $CDCl_3$): 1.53 (6H, br s, β- and γ-CH_2 from NC_5H_{10}), 2.32 (3H, s, CH_3 from *p*-tol), 2.76 (s, 3H, N(O)Me) 3.88 and 4.00 (4H, br d, α-CH_2 from NC_5H_{10}), 5.39 (1H, br s, CH), 7.15 (2H, two d, *m*-H from *p*-tol), 7.38 (2H, two s, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$): 21.7 (CH_3 from *p*-tol), 24.3 (γ-CH_2 from NC_5H_{10}), 25.9 (β-CH_2 c from NC_5H_{10}), 48.6 (α-CH_2 from NC_5H_{10}), 45.3 (N(O)Me), 93.3 (N–CH–N), 129.2, 135.5, 138.8, and 138 ($C_{aromatic}$), 157 (C(O)═N). The crystals suitable for X-ray diffraction study were obtained by a slow evaporation of the solvent (heptane/acetone = 1/1, v/v) at room temperature.

2d (73 mg, 82%); Found: C, 48.62; H, 4.75; N, 9.45; (Calc. for $C_{36}H_{42}N_6Cl_2O_4Pt$: C, 48.65; H, 4,76; N, 9.45); *m*/*z* (high resolution ESI$^+$) 911.2139 ([M + Na]$^+$, requires 911.2214); R_f = 0.36 (eluent $CHCl_3$: Me_2CO, 40 : 1, v/v); ν_{max}(KBr)/cm^{-1}: 2929 m (C–H), 1662 s (C═N); δ_H (300 MHz, $CDCl_3$): 3.19, 3.29 (6H, two s, NMe_2), 3.82 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 4.10 (2H, br s, N(O)CH_2Ph), 5.69 (1H, br s, CH), 6.89 (2H, br d, $H_{aromatic}$), 7.43 (7H, m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$): 39.8 (NMe_2), 55.7 (CH_3 from *p*-$MeOC_6H_4$), 61.4 (N(O)*C*H_2Ph), 90.4 (N–CH–N), 113.8, 128.2, 129.7, 130.5, 130.8, 131.2, 135.5 ($C_{aromatic}$), 160.4 (C(O)═N). The crystals suitable for X-ray study were obtained by a slow evaporation of the solvent (heptane/acetone = 1/1, v/v) at room temperature.

Liberation of the oxadiazoles from 2a–d. An excess of NaCN (8.2 mg, 0.168 mmol) in methanol-d_4 (0.5 mL) was added to a suspension of each of **2a–d** (0.028 mmol) in $CDCl_3$ (0.1 mL) and the reaction mixture was left to stand for 1 d at 35–40 °C. During this time, the initially pale yellow suspension turned to a colorless solution. Completeness of the reaction was monitored by ^{1}H NMR and high resolution ESI-MS indicating that the conversion was completed after 1d. The metal-free heterocycles were separated from excess NaCN, and also from NaCl and $Na_2[Pt(CN)_4]$, formed in the reaction, by evaporation of the solvent at room temperature and treating of the colorless oily residue with $CHCl_3$. The liquid phase was separated by filtration, whereupon evaporation of the solvent afforded in almost quantitative yields **2a–d** as colorless oily residues.

3a; *m*/*z* (high resolution ESI$^+$) 242.1262 ([M + Na]$^+$, requires 242.1269); δ_H (300 MHz, $CDCl_3$/CD_3OD) 2.33 (3H, s, CH_3 from *p*-tol), 2.89 (3H, s, N(O)Me), 2.98 (6H, br s, NMe_2), 5.39 (1H, br s, CH), 7.18 (2H, br d, *m*-H from *p*-tol), 7.24 (2H, br d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$/CD_3OD): 20.5 (CH_3 from *p*-tol), 37.4, (NMe_2), 45.9 (N(O)Me), 92.3 (N–CH–N), 124.2, 126.7, 129.1, and 138.3 ($C_{aromatic}$), 160.8 (C(O)═N).

3b; *m*/*z* (high resolution ESI$^+$) 248.1750 ([M + H]$^+$, requires 248.1762); δ_H (300 MHz, $CDCl_3$/CD_3OD): 1.20 (6H, t, *J* = 7 Hz, CH_3 from NEt_2), 2.33 (3H, s, CH_3 from *p*-tol), 2.90 (3H, s, N(O)Me), 3.32 (4H, m, CH_2 from NEt_2), 5.37 (1H, br s, CH), 7.17 (2H, d, *m*-H from *p*-tol), 7.21 (2H, d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$/CD_3OD) 13.3 (CH_3 in NEt_2), 20.7 (CH_3 in *p*-tol), 43.5, (CH_2 in NEt_2), 45.9 (N(O)Me), 92.1 (N–CH–N), 126.6, 128.9, and 138.3 ($C_{aromatic}$), 159.7 (C(O)═N).

3c; *m*/*z* (high resolution ESI$^+$) 260.1746 ([M + H]$^+$, requires 260.1762); δ_H (300 MHz, $CDCl_3$/CD_3OD): 1.65 (6H, br s, β- and γ-CH_2 from NC_5H_{10}), 2.34 (3H, s, CH_3 from *p*-tol), 2.89 (s, 3H, N(O)Me), 3.33 (4H, br d, α-CH_2 from NC_5H_{10}), 5.39 (1H, br s, CH), 7.18 (2H, d, *m*-H from *p*-tol), 7.23 (2H, d, *o*-H from *p*-tol); δ_C (75.5 MHz, $CDCl_3$/CD_3OD): 20.4 (CH_3 from *p*-tol), 24.0 (γ-CH_2 from NC_5H_{10}), 25.5 (β-CH_2 from NC_5H_{10}), 45.8 (N(O)Me), 91.9 (N–CH–N), 124.1, 126.7, 130.9, and 138.3 ($C_{aromatic}$), 160.0 (C(O)═N).

3d; *m*/*z* (high resolution ESI$^+$) 312.1685 ([M + H]$^+$, requires 312.1711); δ_H (300 MHz, $CDCl_3$/CD_3OD): 3.32 (6H, br s, NMe_2), 3.77 (3H, s, CH_3 from *p*-$MeOC_6H_4$), 4.12, 4.27 (2H, two br d, N(O)CH_2Ph), 5.60 (1H, br s, CH), 6.86, (2H, br d, $H_{aromatic}$), 7.14 (2H, br d, $H_{aromatic}$), 7.36 (5H, br m, $H_{aromatic}$); δ_C (75.5 MHz, $CDCl_3$/CD_3OD): 37.4 (NMe_2), 54.9 (CH_3 from *p*-$MeOC_6H_4$), 62.8 (N(O)*C*H_2Ph), 88.9 (N–CH–N), 113.7, 124.2, 127.9, 128.0, 128.5, 131.2, and 160.1 ($C_{aromatic}$), 161.2 (C(O)═N).

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