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Dialkylcyanamides are more reactive substrates toward metal-mediated nucleophilic addition than alkylcyanides†

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The dialkylcyanamide complexes Q[$PtCl_3(NCNR_2)$] (Q = Ph_3PCH_2Ph, R_2 = Me_2 **1**, Et_2 **2**, C_5H_{10} **3**, C_4H_8O **4**; Q = NMe_4, R_2 = Me_2 **5**; Q = NEt_4, R_2 = Me_2 **6**) were synthesized either by dissolving $Q_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$ in neat $NCNR_2$ (**1–4**) or by substitution of a $NCNR_2$ ligand with Cl^- in [$PtCl_2(NCNR_2)_2$] by its treatment with QCl (**5**, **6**). Nucleophilic addition of dibenzylhydroxylamine, $HON(CH_2Ph)_2$, to **1–6** results in the formation of the complexes Q[$PtCl_3${*N*HC(NR_2)ON($CH_2Ph)_2$}] (Q = Ph_3PCH_2Ph, R_2 = Me_2, **7**; Et_2, **8**; C_5H_{10}, **9**; C_4H_8O, **10**; Q = Me_4N, R_2 = Me_2 **11**; Q = Et_4N, R_2 = Me_2, **12**) that further convert at room temperature in the solid state (1–24 h) or in a solution (0.5–2 h) to the imine complexes Q[$PtCl_3${*N*(CH_2Ph)=C(H)Ph}] (Q = Ph_3PCH_2Ph, **13**; Me_4N, **14**; Et_4N, **15**) and the corresponding dialkylureas $H_2NC(=O)NR_2$. The competitive reactivity study of the nucleophilic addition of $HON(CH_2Ph)_2$ to (Ph_3PCH_2Ph)[$PtCl_3$(NCR′)] (R′ = Ph, NR_2, CH_2Ph) indicated that the reactivity of the coordinated $NCNR_2$ is comparable to NCPh, while $NCCH_2Ph$ appeared to be much less reactive than the former two ligands. Compounds **1–6** and **13** were fully characterized by elemental analyses (C, H, N), high resolution ESI-MS, IR, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The structure of **1** was additionally verified by a single-crystal X-ray diffraction.

Introduction

In contrast to the wealth of chemistry associated with conventional NCR′ (R′ = Alk, Ar) nitriles,[1–17] the coordination chemistry of dialkylcyanamides, $NCNR_2$—ligands that fall into the category of the so-called push–pull nitriles—is still a very little explored field. The data, gradually accumulated in the literature (for reviews see ref. 1–3, 5 and 6; for recent works see ref. 18–27), demonstrated that reactivity modes of $NCNR_2$ ligands can substantially vary from those of the conventional nitriles.[18–20,28] These distinctions were recognized at qualitative level when the same metal-mediated reactions of NCR′ and $NCNR_2$ ligands furnish different products,[18–20,29] or at quantitative level when kinetic experiments showed that $NCNR_2$ species exhibit an unexpectedly high activation toward metal-mediated 1,3-dipolar cycloaddition of nitrones as compared to NCAlk.[30,31] In addition, synthetic experiments indicate that dialkylcyanamide ligands, despite a strong donor character of the NR_2 group (that becomes evident upon inspection of the Pickett and Lever parameters for $NCNR_2$ [32]), exhibit high reactivity toward nucleophilic addition.[33] However, all these differences were observed exclusively at a qualitative level and no convincing quantitative or semi-quantitative data were reported.

In the framework of our ongoing project on the reactivity of metal-activated substrates with the C≡N bond,[1–6] we focused our attention on kinetic studies[34,35] of platinum-mediated nucleophilic addition to nitrile species and verified the effects of the oxidation state and the nature of a HON-nucleophile on reaction rates. In this work, we attempted to compare the nitrile ligands and to establish a relative degree of activation for platinum(II)-bound $NCNR_2$ and NCR′ (R′ = Alk, Ph) ligands.

The scenario of this work was the following: we intended, first, to synthesize the previously unknown platinum(II) anionic complexes [$PtCl_3(NCNR_2)$]$^-$ featuring only one dialkylcyanamide ligand; second, to study the nucleophilic addition of $HON(CH_2Ph)_2$ to a platinum(II)-activated $NCNR_2$; third, to

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conduct a comparative kinetic study for $[PtCl_3(NCR')]^-$ (R′ = NR_2, CH_2Ph, Ph) complexes with an aim to verify the reactivity differences between the dialkylcyanamide and the conventional nitrile ligands.

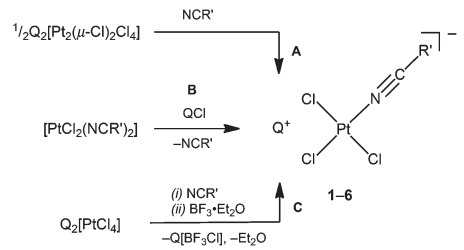
Results and discussion

Synthesis and characterization of $Q[PtCl_3(NCNR_2)]$

For this study, we addressed the platinum(II) compounds $Q[PtCl_3(NCNR_2)]$ (Q = Ph_3PCH_2Ph, Me_4N, Et_4N). These complexes have only one ligand that can be involved in the nucleophilic addition and this reaction can be easily monitored by ^1H NMR spectroscopy. In addition, the kinetic inertness of platinum(II) complexes minimizes the possibility of ligand exchange. Moreover, the anionic mono-nitrile complexes $Q[PtCl_3(NCNR_2)]$ do not have geometric isomers and do not contain other organic ligands that could complicate the reactions with the nitrile functionality. The idea behind the synthesis of different anionic complexes was to obtain platinum species suitable for kinetic studies that could be easily monitored by a NMR method. For this purpose, complexes bearing different cations, having different solubilities in the commonly used deuterated solvents, were synthesized.

Anionic complexes of the type $[PtCl_3(L)]^-$, analogous to the Cossá salt $K[PtCl_3(NH_3)]$,[36–38] are important species in the coordination chemistry of platinum(II). Complexes of this type are known for the conventional nitriles (L = NCAlk, NCAr) and were unknown until now for dialkylcyanamides (L = $NCNR_2$). The reported complexes bearing the conventional nitriles, *viz.* $Q[PtX_3(NCR')]$, were generated *via* (i) splitting the $Q_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$ species by their dissolution in NCR′ (Scheme 1, **A**; Q = Et_4N, R′ = Me, X = Br),[39] (ii) substitution of a NCR′ ligand with X^- in $[PtX_2(NCR')_2]$ by treatment with Q[X] (Scheme 1, **B**; Q = Et_4N, R′ = Me, CH_2Ph, Ph, CH_2CO_2Et, X = Cl; Q = Ph_3PCH_2Ph, R′ = Me, X = Cl; Q = Et_4N, R′ = Me, X = Br),[40] or (iii) substitution of the X^- ligand with NCMe in $Q_2[PtX_4]$ in acetonitrile in the presence of $BF_3{\cdot}Et_2O$ as the halide-abstracting reagent (Scheme 1, **C**; Q = Ph_3PCH_2Ph, R′ = Me, X = Cl).[41]

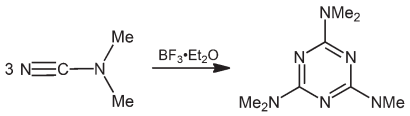
All these methods were examined in the syntheses of the target $Q[PtCl_3(NCNR_2)]$ species (Scheme 1, Table 1). In the case of Q = Ph_3PCH_2Ph, the best yields were achieved by using method **A** (reflux in $NCNR_2$ for 3–5 min) and **B** (reflux in $EtNO_2$ for 5–7 min).



Scheme 1 Routes to $Q[PtX_3(NCR')]$ complexes.

Table 1 Numbering of **1–6**

i	R′	Q
1	NMe_2	Ph_3PCH_2Ph
2	NEt_2	Ph_3PCH_2Ph
3	NC_5H_{10}	Ph_3PCH_2Ph
4	NC_4H_8O	Ph_3PCH_2Ph
5	NMe_2	NMe_4
6	NMe_2	NEt_4



Scheme 2 Trimerization of dimethylcyanamide.

Method **C** led to the trimerization of the dimethylcyanamide (Scheme 2) along with the generation of $(Ph_3PCH_2Ph)[PtCl_3(NCNR_2)]$. The major product of the reaction is hexamethylmelamine (HRESI$^+$-MS, *m*/*z*: 509.3335 $[2M + H_2BF_3]^+$ [509.3407 calcd]; ^1H NMR in $CDCl_3$, δ: 3.23 (s, 9*H*, Me). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 30.1; *lit*. ESI$^+$-MS, *m*/*z*: 210 $[M]^+$; ^1H NMR in $CDCl_3$, δ: 3.25 (s, 9*H*, Me)[42]), which is known for its antitumor properties.[43] This trimerization was previously studied by Dornan *et al.* using aluminum amide as a Lewis acid catalyst.[42]

The complexes $(Ph_3PCH_2Ph)[PtCl_3(NCNR_2)]$ (R_2 = Me_2, **1**; R_2 = Et_2, **2**; R_2 = C_5H_{10}, **3**; R_2 = C_4H_8O, **4**) were prepared from $(Ph_3PCH_2Ph)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$[41] by suspending the bridged complex in neat $NCNR_2$ and further heating to 110–125 °C until homogenization of the reaction mixture (3–5 min) by the literature method reported for the generation of similar platinum(II) NCR′ species (Scheme 1, **A**).[39] Compounds **1–4** were isolated in good (*ca*. 90%) yields as pale orange solids.

In the synthesis of $Q[PtCl_3(NCNR_2)]$ (Q = Et_4N, Me_4N), the best yields were achieved using method **B** (see ESI†). The complexes $Q[PtCl_3(NCNMe_2)]$ (Q = Me_4N, **5**; Q = Et_4N, **6**) were prepared from the corresponding *cis*-$[PtCl_2(NCNMe_2)_2]$ *via* substitution of one coordinated $NCNMe_2$ by treatment with [Q]Cl (Q = Me_4N, Et_4N) in refluxing $MeNO_2$ (Scheme 1, **B**).[40] Compounds **5** and **6** were isolated in good (*ca*. 80%) yields as bright orange solids.

Compounds **1–6** were characterized by C, H, and N elemental analyses, high resolution ESI$^{+/-}$-MS, IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopic techniques, and single-crystal X-ray diffraction (for **1**). The HRESI$^-$ mass spectra of **1–6** display the peaks from $[M - Q]^-$ with the characteristic isotopic distribution. The IR spectra of **1–6** exhibit one strong band in the range 2270–2297 cm^{-1} attributed to the C≡N stretching vibrations. These values agree well with those observed for *cis*/*trans*-$[PtCl_2(NCNR_2)_2]$ (ν(C≡N) 2284–2294 cm^{-1})[18,44] and are higher than those for the corresponding uncomplexed $NCNR_2$ species (ν(C≡N) *ca.* 2215 cm^{-1}) indicating the electrophilic activation of the nitrile upon its coordination.[13] In the ^1H NMR spectra of **1–6**, the protons of the NR_2 groups were detected in the

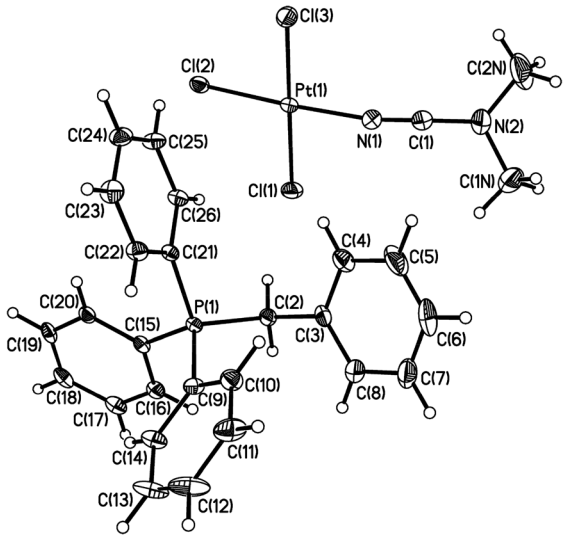


Fig. 1 View of **1** with the atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–Cl(1) 2.303(1), Pt(1)–Cl(2) 2.281(1), Pt(1)–Cl(3) 2.295(1), Pt(1)–N(1) 1.971(4), N(1)–C(1) 1.132(6), C(1)–N(2) 1.301(7), N(1)–Pt(1)–Cl(2) 176.29(14), N(1)–Pt(1)–Cl(3) 88.7(1), Cl(1)–Pt(1)–N(1) 89.7(1), Cl(2)–Pt(1)–Cl(3) 90.59(4), Cl(2)–Pt(1)–Cl(1) 91.20(4), Cl(3)–Pt(1)–Cl(1) 176.46(6), Pt(1)–N(1)–C(1) 169.7(5), N(1)–C(1)–N(2) 179.5(6).

ranges 1.23–1.76 and 2.78–3.77 ppm. The PCH_2 moiety appeared as a doublet in the interval between 5.11 and 5.24 (for **1–4**), and the NR_4 cation emerges as a singlet at 3.48 ppm (R = Me) (for **5**) or as triplet and quartet at 1.43 and 3.51 ppm, correspondingly (R = Et) (for **6**). In the $^{13}C\{^1H\}$ NMR spectra of **1–4**, the carbons of the NR_2 cation were observed in the aliphatic region, while the PCH_2 carbon was detected as a doublet at 118.0 ppm (for **1–4**).

Molecular structure of **1** (Fig. 1) is built up by the cation $[Ph_3PCH_2Ph]^+$ and the anionic complex $[PtCl_3(NCNMe_2)]^-$. The coordination polyhedron has one dialkylcyanamide and three Cl^- ligands resulting in a typical square-planar geometry. All bond angles around the platinum(II) center are close to 90° varying from 88.68(13) to 91.20(4)°. The Pt–Cl distances (2.2808(11)–2.3026(12) Å) are typical for the single Pt–Cl bonds.[18,29,44–46] The Pt–N(1)–C(1)–N(2) fragment is not linear (Pt–N(1)–C(1) 169.7(5)° and N(1)–C(1)–N(2) 179.5(6)°) similarly to the bent $NCNMe_2$ in *trans*-$[PtCl_2(NCNMe_2)\{S(O)Me_2\}]$.[46] The Pt–N(1) distance (1.971(4) Å) agrees well with the corresponding values observed in *trans*-$[PtCl_2(NCNMe_2)_2]$[18] and *cis*-$[PtCl_2(NCNMe_2)\{S(O)Me_2\}]$[29] (1.973(8) and 1.970(6) Å, respectively). The C(1)–N(1) distance (1.132(6) Å) is the normal C≡N bond[47] and it is comparable to the values observed for the similar platinum(II) complexes *trans*-$[PtCl_2(NCNMe_2)_2]$[18] and *cis*-$[PtCl_2(NCNMe_2)\{S(O)Me_2\}]$[29] (1.129(14) and 1.137(9) Å, correspondingly). The NMe_2 group is disordered over two positions with equal occupancies.

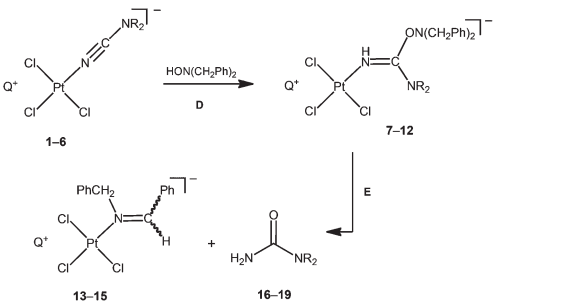
Dialkylcyanamide–hydroxylamine coupling

The nucleophilic addition of *N*,*N*-substituted hydroxylamines to coordinated nitriles was previously studied by our group for high oxidation state metal centers, *viz.* Pt^{IV} [48] and Re^{IV}.[49] In addition, this coupling was used for the synthesis of metal-containing or metal-free phthalocyanines.[50] In this work, we addressed, on the one hand, new platinum(II) compounds $Q[PtCl_3(NCNR_2)]$ and, on the other hand, dibenzylhydroxylamine as a nucleophile referring to the system we studied in our previous works.[34,35] This hydroxylamine has two equivalent methylene groups that resonate at *ca.* 4 ppm (^1H NMR), *viz.* in the area that is free from other signals, and therefore the application of $HON(CH_2Ph)_2$ facilitates the kinetic studies (see later). In addition, this compound is stable, solid and can easily be weighted.

We observed that addition of excess $HON(CH_2Ph)_2$ to any one of **1–6** in $CHCl_3$ at RT resulted in the generation of the new imino species $Q[PtCl_3\{NHC(NR_2)ON(CH_2Ph)_2\}]$ (Q = Ph_3PCH_2Ph, R_2 = Me_2, **7**; Et_2, **8**; C_5H_{10}, **9**; C_4H_8O, **10**; Q = Me_4N, R_2 = Me_2 **11**; Q = Et_4N, R_2 = Me_2, **12**) (Scheme 3, **D**; Table 2).

In the ^1H NMR spectra of **9–12**, the NCH protons of the NR_2 group were detected in the range of 3.27–3.60 ppm that is deshielded than those of starting complexes **1–4** (2.78–3.33 ppm). The proton of the newly formed NH group was detected in the range of 5.86–6.14 ppm as a broad singlet. Compounds **9–12** gave satisfactory C, H, and N elemental analyses, which are consistent with their formulae. Although these compounds are rather reactive and undergo further conversion, the elemental analyses agree well with the composition of the nucleophilic addition product rather than with the substitution product.

A benzyl group in the hydroxylamine can be easily deprotonated. We attempted the application of the other hydroxylamine, *viz.* $HONEt_2$, as a nucleophile in our reactions, and found that its reaction with $Q[PtCl_3(NCNR_2)]$ (NR_2 = Me_2, Et_2, C_5H_{10}, C_4H_8O) does not proceed selectively. Based on ESI-MS^- and NMR data both nucleophilic addition and coordination of



Scheme 3 Studied reactions.

Table 2 Numbering of the compounds

i	R	Q	*i*	Q	*i*	R
7	NMe_2	Ph_3PCH_2Ph	**13**	Ph_3PCH_2Ph	**16**	NMe_2
8	NEt_2	Ph_3PCH_2Ph	**14**	NMe_4	**17**	NEt_2
9	NC_5H_{10}	Ph_3PCH_2Ph	**15**	NEt_4	**18**	NC_5H_{10}
10	NC_4H_8O	Ph_3PCH_2Ph			**19**	NC_4H_8O
11	NMe_2	NMe_4				
12	NMe_2	NEt_4				

$HONEt_2$ was detected. Importantly, reaction **E** (Scheme 3) specific for dibenzylhydroxylamine was not observed.

Dehydration of iminoacylated dibenzylhydroxylamine

In the current work, complexes with iminoacylated dibenzylhydroxylamine **7–9** appeared to convert in the solid state at RT for 4–24 h (R_2 = Me_2, 6 h; R_2 = Et_2, 4; R_2 = C_5H_{10}, C_4H_8O, 24 h) to the imino complexes Q[$PtCl_3${*E*/*Z*-*N*(CH_2Ph)=C(H)Ph}] (*ca.* 1 : 1 *E*/*Z* mixture; Q = Ph_3PCH_2Ph, **13**; Q = Me_4N, **14**, Q = Et_4N, **15**) and the corresponding dialkylureas $H_2NC(=O)NR_2$ (R_2 = Me_2, **16**; R_2 = Et_2, **17**; R_2 = C_5H_{10}, **18**; R_2 = C_4H_8O, **19**) (Scheme 3, **E**) that were detected in the ^{1}H NMR (signals of the NCH protons of the NR_2 group in the range of 3.19–3.95 ppm) and HRESI$^+$ mass spectra ($[M + H]^+$ or $[M + Na]^+$). Compound **13** was purified by column chromatography on silica gel and characterized by C, H, and N elemental analyses, HRESI$^{+/-}$-MS, IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic techniques, while **14** and **15** were identified by HRESI$^{+/-}$-MS and ^{1}H NMR methods.

In the ^{1}H NMR spectrum of **13**, the characteristic signals at 9.30 and 9.33 ppm are from the protons of the N=CH group in the *Z* and *E* forms. Protons of the NCH_2 group were detected at 5.38 and 5.39 ppm as two singlets corresponding to the *Z* and *E* forms. In the $^{13}C\{^1H\}$ NMR spectrum, the resonance of the N=CH carbon was found at 168.0 ppm, while the carbon of the NCH_2 group emerged at 66.0 ppm.

Herein we observed the first example of the formation of an imine complex *via* elimination of substituted ureas from iminoacylated hydroxylamine ligand at the platinum(II) center. Complexes bearing imines of this type, *e.g. cis*/*trans*-[$PtCl_2$-{$N(CH_2C_6H_4Cl\text{-}4')$=CH(4-$ClC_6H_4$)}{$S(O)Me_2$}], were previously obtained by the substitution of a Me_2SO ligand in *cis*-[$PtCl_2$-{$S(O)Me_2$}$_2$] with the imine (4-ClC_6H_4)CH=NCH_2(4′-ClC_6H_4).[51–53] A similar imine complex, *viz.* [Pt(pip_2NCN){N(Me)=CMe_2}]-[CF_3SO_3] (pip_2NCN = the pincer 1,3-($MeNC_6H_9$)$_2C_6H_3$ ligand), was produced upon the addition of $MeNH_2$ to the [Pt-(pip_2NCN)(acetone)]$^{2+}$ in an acetone solution.[54] The complex with the same imine, *trans*-[$Pt(MeNH_2)_2(MeN{=}CMe_2)_2]I_2$, was synthesized by the reaction of acetone with the amine in $[Pt(MeNH_2)_4]I_2$.[55] A similar imine complex, *viz.* [PtCl-($NH_2CH_2CH_2N$=CMe_2)(PBu^n_3)]$^+$, was generated in the reaction between $[Pt_2(\mu\text{-}Cl)_2Cl_2(PBu^n_3)_2]$ and ethanediamine in acetone.[56]

It is also worthwhile noting that only two examples of metal-mediated dehydration of substituted hydroxylamines were previously reported and they include the Ti^{III}-mediated dehydration of *N*,*N*-disubstituted hydroxylamines giving imines[57] and stepwise conversion of *N*-arylhydroxylamines to 1,4-naphthoquinone imines after the oxidation of the former with Ag_2O or air giving 1-naphthyl phenyl nitroxides, which then convert to the corresponding imines.[58]

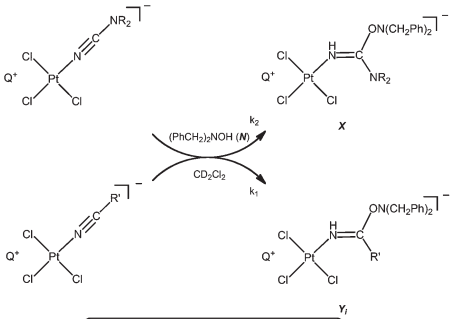
Competitive reactivity study

The synthetic data of the current work and those previously obtained for the nucleophilic addition to platinum complexes with the conventional nitrile and dialkylcyanamide ligands[59–62] indicate unexpectedly high reactivity of $NCNR_2$ bearing the strong donor substituents N*Al*k_2 as compared to conventional nitriles NCR′ with donor groups R′ (as confirmed by considering their Pickett P_L and Lever E_L parameters[32,63,64]) toward the nucleophilic addition. As was revealed from the preparative experiments, the reactivity of the $NCNR_2$ ligands is even comparable to that of benzonitrile bearing the moderate acceptor group Ph.

In the previous work, we studied the kinetics of the nucleophilic addition of dibenzylhydroxylamine to coordinated conventional nitriles at Pt^{IV} and Pt^{II} centers.[35] In the current work, the conventional kinetic study of the nucleophilic addition of dibenzylhydroxylamine to the coordinated push–pull nitriles is not straightforward because of the observed dehydration (see above). Therefore, to get a quantitative estimate of the dependence for the reactivity on the nature of the R group and in order to compare the differences between the reactivity of coordinated and uncomplexed NCR′ species, we conducted a competitive reactivity study of the nucleophilic addition to NCR′ (R′ = NMe_2, NEt_2, NC_5H_{10}, NC_4H_8O) and NCR′ (R′ = Ph, CH_2Ph) ligands. The method employed includes the reaction between the equimolar mixture of two complexes and the nucleophile, *viz.* $HON(CH_2Ph)_2$, in a 2 : 1 molar ratio (see the Experimental section) (Scheme 4).

The competitive reactivity study demonstrates that the reactivity of the NCR′ species decreases in the following order: NR_2 ≈ Ph > CH_2Ph, which points out the unexpectedly high reactivity of the dialkylcyanamide ligand bearing the strong donor NR_2 substituent toward the nucleophilic addition. A similar result was obtained earlier in our group for 1,3-dipolar cycloaddition of nitrones to coordinated dialkylcyanamides and conventional nitriles.[30]

We also observed the coupling between the uncomplexed conventional NCR′ (R′ = Ph, CH_2Ph) and the push–pull nitrile $NCNR_2$ and $HON(CH_2Ph)_2$ followed by the dehydration of the resulting HN=C(R)O$N(CH_2Ph)_2$ (**20–22**). Although the addition of the hydroxylamine to coordinated and uncomplexed nitrile species proceeds under different conditions (which preclude a quantitative comparison of the reaction rates), we made a qualitative estimate of the accelerating effect of the coordination. Thus, the nucleophilic addition of



i	R′	NMe_2	NEt_2	NC_5H_{10}	NC_4H_8O
		k_1/k_2			
1	Ph	1.4(3)	1.4(2)	1.5(1)	1.6(2)
2	CH_2Ph	0.018(6)	0.03(1)	0.016(4)	0.015(8)

Scheme 4 Competitive reactivity study.

$HON(CH_2Ph)_2$ proceeds more slowly in the case of uncomplexed NCR′ (in C_6D_6 at 65 °C the full conversion was reached after 2 d for R′ = NR_2, or 7 d for R′ = Ph; 5 mmol of NCR′, 5 mmol of $HON(CH_2Ph)_2$ in 0.5 mL of C_6D_6) rather than in the case of the coordinated NCR′ (20 °C, the full conversion was reached after 40 min for R′ = NMe_2, or 30 min for R′ = Ph; 0.5 mmol of $(Ph_3PCH_2Ph)[PtCl_3(NCR')]$, 0.5 mmol of dibenzylhydroxylamine in 0.5 mL of CD_2Cl_2). Therefore, these synthetic data indicate that coordination to the metal dramatically affects the reactivity of the nitrile species.

Final remarks

The result of this work can be considered from a few perspectives. First, we succeeded in synthesis of the Cossá-type complexes $[PtCl_3(NCNR_2)]^-$ featuring the dialkylcyanamide ligands. In the platinum chemistry, complexes $[PtCl_3(L)]^-$ play an important role in synthesis of the compounds having two different neutral ligands, *viz.* $[PtCl_2(L)(L')]$, that otherwise are difficult-to-obtain. We believe that an easy access to $[PtCl_3(NCNR_2)]^-$ should stimulate progress in the synthetic chemistry of dialkylcyanamides and open up a route to various yet unknown $[PtCl_2(L)(NCNR_2)]$ species.

Second, although the nucleophilic addition of dibenzylhydroxylamine to platinum(II)-activated conventional nitriles was thoroughly studied,[35] this reaction with metal-bound dialkylcyanamides has a specific feature consisting in further transformation of the iminoacylated hydroxylamine producing ligated imine and uncomplexed urea (Scheme 3). It is anticipated that the generation of the latter drives the reaction and the observed transformation represents yet another example of different reactivity modes between dialkylcyanamides and conventional nitriles.

Third, the competitive reactivity study of the nucleophilic addition of $HON(CH_2Ph)_2$ to NCR′ (R′ = Ph, NR_2, CH_2Ph) ligands demonstrates that the reactivity changes in the following order: $NR_2 \approx Ph > CH_2Ph$. Dimethylcyanamide appears to be highly activated by the platinum(II) center and its reactivity toward $HON(CH_2Ph)_2$ is comparable to benzonitrile ligand bearing the moderate electron acceptor group. In addition, $NCNR_2$ ligands behave like stronger σ-donors[32] and, consequently, they are better ligands than conventional nitriles. These complementary properties of dialkylcyanamides, *i.e.* better donor properties of the nitrile N atom and high electrophilic activation of the nitrile C atom, make them perfect candidates for the nucleophilic addition studies and open up new horizons for further work in the area of metal-activated nitriles.[1,2]

Experimental section

Materials and instrumentation

The dialkylcyanamides $NCNR_2$ (R_2 = Me_2, Et_2, Acros; R_2 = C_4H_8O, C_5H_{10}, Aldrich) and solvents were obtained from commercial sources and used as received. The complexes $(Ph_3PCH_2Ph)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$[41] and *cis*/*trans*-$[PtCl_2(NCR')_2]$[18] were prepared by the reported procedures. The compounds $(Ph_3PCH_2Ph)[PtCl_3(NCR')]$ (R′ = Ph, CH_2Ph) were synthesized from the corresponding *cis*-$[PtCl_2(NCR')_2]$ according to the method described earlier.[40] For column chromatography silica gel 60 F_{254}, 0.063–0.200 mm (Merck) was used.

Elemental analyses were performed using EuroVector 3000 and 185B Carbon Hydrogen Nitrogen Analyzer Hewlett-Packard instruments. Electrospray ionization mass spectra were obtained using a Bruker micrOTOF spectrometer equipped with an electrospray ionization source and MeCN or MeOH was used as the solvent. The instrument was operated both in positive and negative ion modes using an *m*/*z* range of 50–3000. The capillary voltage of the ion source was set at −4500 V (ESI^+-MS) or 3500 V (ESI^--MS) and the capillary exit ±(70–150) V. In the isotopic pattern, the most intensive peak is reported. Infrared spectra were recorded using a Shimadzu FTIR 8400S instrument in KBr pellets. ^1H and $^{13}C\{^1H\}$ NMR spectra were measured using Bruker-DPX 300 and Bruker Avance II + 400 MHz (UltraShield^{tm} Magnet) spectrometers at ambient temperature.

X-ray determination

A single-crystal X-ray diffraction experiment was carried out with a Bruker SMART APEX II diffractometer[65] (graphite monochromated Mo-Kα radiation, l = 0.71073 Å, ω-scan technique, T = 100(2) K). A multi-scan absorption correction based on equivalent reflections (*SADABS*[66]) was applied to the data. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic thermal parameters for all non-hydrogen atoms using the *SHELXTL* program package.[67] Hydrogen atoms were positioned geometrically and included in the structure factor calculations in the riding motion approximation. The crystallographic details are summarized in Table S1 (ESI†).

Synthetic work

Preparation of $(Ph_3PCH_2Ph)[PtCl_3(NCNR_2)]$. Suspension of $(Ph_3PCH_2Ph)_2[Pt_2(\mu\text{-}Cl)_2Cl_4]$ (80 mg, 0.061 mmol) in $NCNR_2$ (0.244 mmol) was refluxed until the starting complex was dissolved (*ca.* 5 min). The reaction mixture was then cooled to RT and the product was precipitated by addition of benzene (1 mL), washed with Et_2O (three 1 mL portions) and dried in air at RT. Yields: 84 mg, 95% (R_2 = Me_2, **1**), 78 mg, 86% (R_2 = Et_2, **2**), 87 mg, 93% (R_2 = C_5H_{10}, **3**), 89 mg, 93% (R_2 = C_4H_8O, **4**).

*$(Ph_3PCH_2Ph)[PtCl_3(NCNMe_2)]$ (**1**).* Anal. Calcd for $C_{28}H_{28}N_2Cl_3PPt$: C, 46.39; H, 3.89; N, 3.86%. Found: C, 46.06; H, 3.84; N, 3.58%. HRESI$^+$-MS, *m*/*z*: 353.1514 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 370.9254 $[PtCl_3(NCNMe_2)]^-$ [370.9196 calcd]. IR spectrum in KBr, selected bands, cm^{-1}: 2289 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 2.78 (s, 5*H*, NCH_3), 5.11 (d, $^2J_{PH}$ 14.0 Hz, 2*H*, PCH_2), 7.03–7.13 and 7.67–7.77 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 40.1 (NCH_3), 117.9 (d, $^1J_{PC}$ 335 Hz, PCH_2), 127.4–132.0 (Ph); the NCN carbon was not detected.

*$(Ph_3PCH_2Ph)[PtCl_3(NCNEt_2)]$ (**2**).* Anal. Calcd for $C_{30}H_{32}N_2Cl_3PPt$: C, 47.85; H, 4.28; N, 3.72%. Found: C, 47.83; H, 4,05; N, 3.74%. HRESI$^+$-MS, *m*/*z*: 353.1635 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 398.9464 $[PtCl_3(NCNEt_2)]^-$ [398.9509 calcd]. IR spectrum in KBr, selected bands, cm^{-1}: 2280 s ν(C≡N). ^1H NMR in CD_2Cl_2, δ: 1.23 (t, $^3J_{HH}$ 7.2 Hz, 6*H*, CH_3), 3.08 (q, $^3J_{HH}$ 7.2 Hz, 4*H*, NCH_2), 5.02 (d, $^2J_{PH}$ 13.7 Hz, 2*H*, PCH_2), 7.05–7.35 (m, 5*H*, Ph from CH_2Ph), 7.67–7.88 (m, 15*H*, PPh_3). $^{13}C\{^1H\}$ NMR in CD_2Cl_2, δ: 13.1 (CH_3), 46.1 (NCH_2), 117.7 (d, $^1J_{PC}$ 330 Hz, PCH_2), 127.3–135.6 (Ph); the NCN carbon was not detected.

*$(Ph_3PCH_2Ph)[PtCl_3(NCNC_5H_{10})]$ (**3**).* Anal. Calcd for $C_{31}H_{32}N_2Cl_3PPt$: C, 48.67; H, 4.22; N, 3.66%. Found: C, 48.63; H, 4.26; N, 3.66%. HRESI$^+$-MS, *m*/*z*: 353.1427 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 410.9458 $[PtCl_3(NCNC_5H_{10})]^-$ [410.9509 calcd]. IR spectrum in KBr, selected bands, cm^{-1}: 2274 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 1.52–1.76 (m, br, 6*H*, β-CH_2 and γ-CH_2), 3.12–3.33 (m, br, 4*H*, α-CH_2), 5.12 (d, $^2J_{PH}$ 14.0 Hz, 2*H*, PCH_2), 7.03–7.28 and 7.68–7.80 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 23.0 (γ-CH_2), 25.0 (β-CH_2), 49.8 (α-CH_2), 118.0 (d, $^1J_{PC}$ 347 Hz, PCH_2), 127.5–135.4 (Ph); the NCN carbon was not detected.

*$(Ph_3PCH_2Ph)[PtCl_3(NCNC_4H_8O)]$ (**4**).* Anal. Calcd for $C_{30}H_{30}N_2Cl_3OPPt$: C, 46.97; H, 3.94; N, 3.65%. Found: C, 47.02; H, 4.10; N, 3.78%. HRESI$^+$-MS, *m*/*z*: 353.1589 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 412.9309 $[PtCl_3(NCNC_4H_8O)]^-$ [412.9301 calcd]. IR spectrum in KBr, selected bands, cm^{-1}: 2285 s ν(C≡N). ^1H NMR in $CDCl_3$, δ: 3.19–3.28 (m, br, 4*H*, NCH_2), 3.63–3.77 (m, br, 4*H*, OCH_2), 5.12 (d, $^2J_{PH}$ 14.1 Hz, 2*H*, PCH_2), 7.04–7.23 and 7.67–7.80 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 48.2 (NCH_2), 66.0 (OCH_2), 117.9 (d, $^1J_{PC}$ 338 Hz, PCH_2), 127.6–135.4 (Ph); the NCN carbon was not detected.

Reaction of $Q[PtCl_3(NCNR_2)]$ with $HON(CH_2Ph)_2$. $(PhCH_2)_2NOH$ (53 mg, 0.25 mmol) was added to a solution of any one of **1–4** (0.05 mmol) in $CHCl_3$ (0.5 mL) at RT. After 5 min the reaction mixture was evaporated under a stream of air and an oily residue was formed. The product was crystallized under Et_2O (1 mL) and washed with Et_2O (two 1 mL portions). Yields: 43 mg, 92% (R_2 = Me_2, **7**), 46 mg, 95% (R_2 = Et_2, **8**), 43 mg, 89% (R_2 = C_5H_{10}, **9**), 46 mg, 94% (R_2 = C_4H_8O, **10**).

*$(Ph_3PCH_2Ph)[PtCl_3\{NHC(NMe_2)ON(CH_2Ph)_2\}]$ (**7**).* HRESI$^+$-MS, *m*/*z*: 353.1424 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 584.0314 $[PtCl_3(NCNMe_2)]^-$ [584.0349 calcd]. ^1H NMR in $CDCl_3$, δ: 3.41 (s, 6*H*, NMe), 4.03 and 4.05 (s + s, br, 4*H*, NCH_2), 5.29 (d, $^2J_{PH}$ 13.9 Hz, 2*H*, PCH_2), 5.87 (s, br, 1*H*, NH), 7.50–7.80 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR was not recorded because of the fast conversion of **7** in solution.

*$(Ph_3PCH_2Ph)[PtCl_3\{NHC(NEt_2)ON(CH_2Ph)_2\}]$ (**8**).* HRESI$^+$-MS, *m*/*z*: 353.1425 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 612.0766 $[PtCl_3(NCNEt_2)]^-$ [612.0662 calcd]. ^1H NMR in $CDCl_3$, δ: 1.28 (t, $^3J_{HH}$ 6.3 Hz, 6*H*, Me), 3.27 (q, $^3J_{HH}$ 6.4 Hz, 4*H*, CH_2 from Et), 3.95 and 4.02 (s + s, br, 4*H*, NCH_2), 5.24 (d, $^2J_{PH}$ 14.0 Hz, 2*H*, PCH_2), 5.86 (s, br, 1*H*, NH), 7.04–7.75 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR was not recorded because of the fast conversion of **8** in solution.

*$(Ph_3PCH_2Ph)[PtCl_3\{NHC(NC_5H_{10})ON(CH_2Ph)_2\}]$ (**9**).* HRESI$^+$-MS, *m*/*z*: 353.1425 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 624.0894 $[PtCl_3(NCNC_5H_{10})]^-$ [624.0662 calcd]. ^1H NMR in $CDCl_3$, δ: 1.49–1.66 (m, 6*H*, β-CH_2 and γ-CH_2), 3.33–3.38 (m, 4*H*, α-CH_2), 4.01 (s, 4*H*, NCH_2), 5.35 (d, $^2J_{PH}$ 14.0 Hz, 2*H*, PCH_2), 5.92 (s, br, 1*H*, NH), 7.09–7.76 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR was not recorded because of the fast conversion of **9** in solution.

*$(Ph_3PCH_2Ph)[PtCl_3\{NHC(NC_4H_8O)ON(CH_2Ph)_2\}]$ (**10**).* HRESI$^+$-MS, *m*/*z*: 353.1413 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 626.0740 $[PtCl_3(NCNC_4H_8O)]^-$ [626.0455 calcd]. ^1H NMR in $CDCl_3$, δ: 3.57–3.60 (m, 4*H*, NCH_2 from NC_4H_8O), 4.15–4.18 (m, 4*H*, OCH_2), 4.03 (s, 4*H*, NCH_2), 5.25 (d, $^2J_{PH}$ 13.7 Hz, 2*H*, PCH_2), 6.14 (s, br, 1*H*, NH), 7.06–7.77 (m, 20*H*, Ph). $^{13}C\{^1H\}$ NMR was not recorded because of the fast conversion of **10** in solution.

Products **7–10** are unstable and they convert at RT after 1–24 h (in solid state) or 0.5–2 h (in a solution) to the imine complex $(Ph_3PCH_2Ph)[PtCl_3\{(PhCH_2)N{=}CHPh\}]$ (**13**) and the *N*,*N*-dialkyl urea $H_2NCO(NR_2)$ (R_2 = Me_2, **16**, R_2 = Et_2, **17**, R_2 = C_5H_{10}, **18**, R_2 = C_4H_8O, **19**). Complex **13** was separated by column chromatography on SiO_2.

*$(Ph_3PCH_2Ph)[PtCl_3\{N(CH_2Ph){=}CH)Ph\}]$ (**13**).* Anal. Calcd for $C_{39}H_{35}NCl_3PPt{\cdot}1/5[PtCl_2\{N(CH_2Ph){=}C(H)Ph\}_2]$: C, 52.10; H, 3.97; N, 2.12%. Found: C, 51.95; H, 3.96; N, 2.45%. $[PtCl_2\{N(CH_2Ph){=}CHPh\}_2]$ additive was detected by ^1H NMR and ESI$^-$-MS spectroscopic techniques, and the ratio **13** : $[PtCl_2\{N(CH_2Ph){=}CHPh\}_2]$ = 5 : 1 was determined by using ^1H NMR (the ratio does not change in repeated syntheses). It could not be separated from **13** by column chromatography (due to close retention indexes) or by recrystallization from $CHCl_3$–Et_2O or $MeNO_2$–Et_2O mixtures in various ratios of their components. HRESI$^+$-MS, *m*/*z*: 353.1427 $[Ph_3PCH_2Ph]^+$ [353.1459 calcd]. HRESI$^-$-MS, *m*/*z*: 495.9759 $[PtCl_3\{N(CH_2Ph){=}CHPh\}]^-$ [495.9713 calcd]. IR spectrum in KBr, selected bands, cm^{-1}: 3057–2893 s ν(C–H), 1586 m ν(C=N). ^1H NMR in $CDCl_3$, δ: 5.11 (d, $^2J_{PH}$ 13.8 Hz, 2*H*, PCH_2), 5.38 and 5.39 (*E*/*Z* ratio is 1 : 1, s + s, br, 2*H*, NCH_2), 7.02–7.84 (m, 20*H*, Ph), 9.30 and 9.33 (s + s, 1*H*, N=CH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 66.0 (NCH_2), 117.7 (d, $^1J_{PC}$ 335 Hz, PCH_2), 128.5–135.6 (Ph), 168.0 (N=CH).

Identification of the ureas formed upon dehydration. **$NH_2C(=O)NMe_2$** (**16**). HRESI$^+$-MS, *m*/*z*: 111.0491 $[M + Na]^+$ [111.0534 calcd], 129.0570 $[M + H_2O + Na]^+$ [129.0640 calcd]. **$NH_2C(=O)NEt_2$** (**17**). HRESI$^+$-MS, *m*/*z*: 117.1074 $[M + H]^+$ [117.1028 calcd. **$NH_2C(=O)NC_5H_{10}$** (**18**). HRESI$^+$-MS, *m*/*z*: 129.1130 $[M + H]^+$ [129.1028 calcd]. **$NH_2C(=O)NC_4H_8O$** (**19**). HRESI$^+$-MS, *m*/*z*: 131.0892 $[M + H]^+$ [131.0821 calcd].

Competitive reactivity studies. The reaction of (Ph_3PCH_2Ph)-$[PtCl_3(NCNR_2)]$ (0.5 mmol) and $(Ph_3PCH_2Ph)[PtCl_3(NCR')]$ (0.5 mmol, R′ = Ph, CH_2Ph) with $HON(CH_2Ph)_2$ (0.5 mmol) was performed in a CD_2Cl_2 solution (0.5 mL) at 20 °C and was monitored by ^1H NMR spectroscopy. The spectra were registered immediately after the addition of $HON(CH_2Ph)_2$ to the reaction mixture and then after 5, 10, 15, 20, and 30 min; after 80 min $HON(CH_2Ph)_2$ was not detected in the ^1H NMR spectra. The signals of the imine complex $(Ph_3PCH_2Ph)PtCl_3$-$\{N(CH_2Ph){=}CHPh\}$ were found in the spectrum recorded 20 min after the addition of $HON(CH_2Ph)_2$. The mean value k_1/k_2 was calculated

based on the time points for 5, 10, and 15 min; the k_1/k_2 ratio was stable within the specified time period.

The ratio k_1/k_2 (R = CH_2Ph) was calculated according to the formula

$$\frac{k_1}{k_2} = \frac{(S(N)^0 - S(N)_t)}{(S(X)^0 - S(X)_t)},$$

where $S(X)_t$ and $S(N)_t$ are integral intensities of signals of the protons of the NMe_2 or NCH_2 group of $NCNR_2$ and the CCH_2 group of $NCCH_2Ph$, respectively, and $S(X)^0$ and $S(N)^0$ are the starting integral intensities of these signals in the spectrum recorded immediately after the addition of $HON(CH_2Ph)_2$. All the intensities were reduced to the number of protons in the group (reduced to 6 for NMe_2, 4 for $N(CH_2–)_2$ and 2 for CCH_2).

Because of signal overlap of the aromatic protons of the NCPh ligand (7.01–7.22 ppm) and the resulting imine ligand $NHC(Ph)ON(CH_2Ph)_2$ (7.01–7.50 ppm), NMR integrations in the calculations of the k_1/k_2 (R = Ph) ratio were not possible. Also, taking into account that the imino complexes generated during the reaction were unstable, it was necessary to use the formula that allows the calculation of the conversion of NCPh knowing the difference in conversions of $HON(CH_2Ph)_2$ and $NCNMe_2$ (formula (a)) or $NCNR_2$ (R = NEt_2, NC_5H_{10}, NC_4H_8O; formula (b)):

$$\frac{k_1}{k_2} = \frac{\frac{1}{2}(S(N)^0 - S(N)_t) - \frac{1}{3}(S(X)^0 - S(X)_t)}{\frac{1}{3}(S(X)^0 - S(X)_t)} \quad \text{(a)}$$

$$\frac{k_1}{k_2} = \frac{(S(N)^0 - S(N)_t) - (S(X)^0 - S(X)_t)}{(S(X)^0 - S(X)_t)} \quad \text{(b)}$$

where $S(X)_t$ and $S(N)_t$ are integral intensities of signals of the protons of the NMe_2 or NCH_2 group of the $NCNR_2$ and the NCH_2 group of $HON(CH_2Ph)_2$, respectively, and $S(X)^0$ and $S(N)^0$ are starting integral intensities of these signals in the spectrum recorded immediately after the addition of $HON(CH_2Ph)_2$ (Scheme 4).

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