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Regioselective HON-addition of bifunctional hydrazone oximes to Pt(IV)-bound nitriles †

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Received 11th February 2004, Accepted 20th February 2004
First published as an Advance Article on the web 5th March 2004

Treatment of *trans*-[$PtCl_4(RCN)_2$] (R = Me, Et) with the hydrazone oximes MeC(=NOH)C(R′)=NNH_2 (R′ = Me, Ph) at 45 °C in CH_2Cl_2 led to the formation of *trans*-[$PtCl_4${NH=C(R)ON=C(Me)C(R′)=NNH_2}$_2$] (R/R′ = Me/Ph **1**, Et/Me **2**, Et/Ph **3**) due to the regioselective OH-addition of the bifunctional MeC(=NOH)C(R′)=NNH_2 to the nitrile group. The reaction of **3** and Ph_3P=$CHCO_2Me$ allows the formation of the Pt(II) complex *trans*-[$PtCl_2${NH=C(Et)ON=C(Me)C(Ph)=NNH_2}$_2$] (**4**). In **4**, the imine ligand was liberated by substitution with 2 equivalents of bis(1,2-diphenylphosphino)ethane (dppe) in $CDCl_3$ to give, along with the free ligand, the solid [$Pt(dppe)_2$]Cl_2. The free iminoacyl hydrazone, having a restricted life-time, decomposes at 20–25 °C in about 20 h to the parent organonitrile and the hydrazone oxime. The Schiff condensation of the free NH_2 groups of **4** with aromatic aldehydes, *i.e.* 2-OH-5-NO_2-benzaldehyde and 4-NO_2-benzaldehyde, brings about the formation of the platinum(II) complexes *trans*-[$PtCl_2${NH=C(Et)ON=C(Me)C(Ph)=NN=CH(C_6H_3-2-OH-5-NO_2}$_2$] (**5**) and *trans*-[$PtCl_2${NH=C(Et)ON=C(Me)C(Ph)=NN=CH(C_6H_4-4-NO_2}$_2$] (**6**), respectively, containing functionalized remote peripherical groups. Metallization of **5**, which can be considered as a novel type of metallaligand, was achieved by its reaction with $M(OAc)_2 \cdot nH_2O$ (M = Cu, n = 2; M = Co, n = 4) in a 1 : 1 molar ratio furnishing solid heteronuclear compounds with composition [Pt] : [M] = 1 : 1. The complexes were characterized by C, H, N elemental analyses, FAB^+ mass-spectrometry, IR, ^1H, $^{13}C\{^1H\}$ and ^{195}Pt NMR spectroscopies; X-ray structures were determined for **3**, **4** and **5**.

Introduction

In general, organonitriles are among the most common precursors in chemistry due to both their synthetic versatility and a great potential for syntheses of compounds with intrinsic industrial (*e.g.* acrylamide) or pharmacological interest (*e.g.* nicotineamide or *S*-(+)-ibuprofen).[1–5] In particular, the control of the reactivity of nitriles by coordination to a metal allows reactions to be carried out, which are not possible with free nitriles. Many of these reactions have been reviewed by two of us.[1,2] Despite the vast current interest in metal-mediated and metal-catalyzed nucleophilic additions to nitriles relatively few investigations have been carried out with the addition of potentially *bifunctional nucleophiles* to the nitrile C atom. Among the latter, attention should be drawn to the coupling between metal-complexed nitriles and symmetric (*e.g.* diphosphines,[6] dioximes[7,8] and diamines[9,10]) and unsymmetrical (aminoalcohols,[11] salicylaldoximes,[12] mixed sulfimide/sulfides[13] and hydroxy/phosphines[14]) bifunctional nucleophiles.

Following our ongoing project on ligand reactivity[15] and, especially, on metal-mediated coupling reactions between organonitriles and various nucleophiles giving novel type products and/or having certain applications in organic synthesis involving metal complexes,[16–19] we extended our previous studies[7–9,11–13] on the additions of bifunctional nucleophiles to ligated nitriles to other unsymmetrical nucleophiles, *i.e.* hydrazone oximes (Scheme 1). The essential interests to this project are at least three-fold: (i) to study regioselectivity of the addition and to verify preferences in either C–O or C–N bond making; (ii) to liberate a ligand, formed in the course of metal-mediated reaction, thus contributing to the development of methods for metal-mediated organic synthesis; (iii) in the case of one-end addition of the hydrazone oximes to coordinated nitriles, to study the possibility of reactions of a free uncoordinated group for further assembly by building-block methodology. A scenario of our work, described in this article, follows these lines.

† Dedicated to Professor Ilya I. Moiseev on the occasion of his 75th birthday.

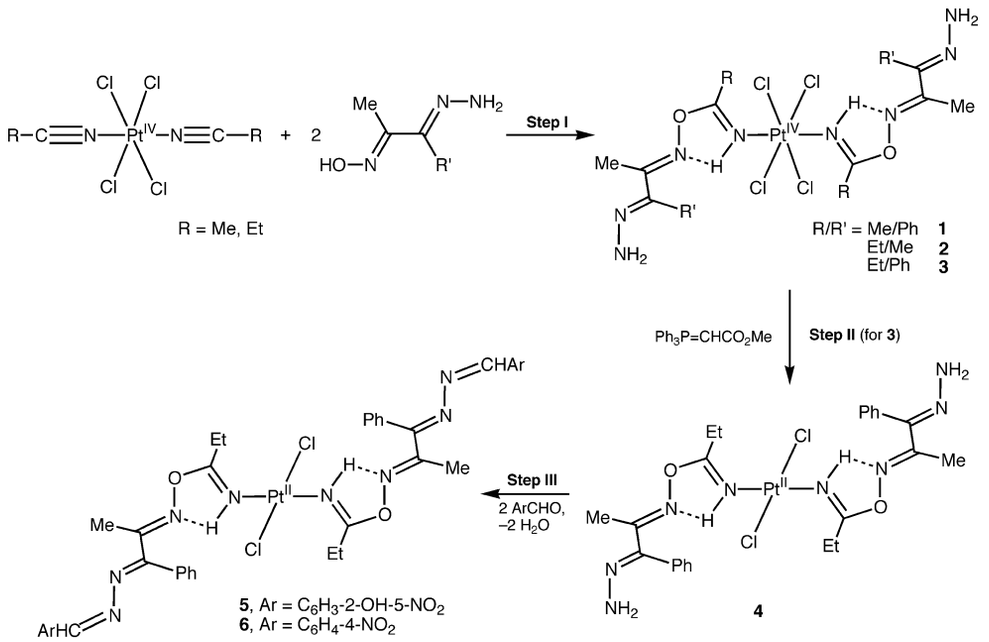
Results and discussion

Hydrazone oxime–nitrile coupling

For this study we addressed the platinum(IV) nitrile complexes *trans*-[$PtCl_4(RCN)_2$] (R = Me, Et) because it was proved that the Pt(IV) center provides a substantial electrophilic activation of nitriles toward even very weak nucleophiles.[1] The treatment of these complexes with the hydrazone oximes MeC(=NOH)-C(R′)=NNH_2 (R′ = Me, Ph) at 45 °C in CH_2Cl_2 led to the formation of the *trans*-[$PtCl_4${NH=C(R)ON=C(Me)C(R′)=NNH_2}$_2$] (**1**–**3**) (Scheme 1, step I) species.

All isolated compounds (**1**–**3**) gave satisfactory C, H and N elemental analyses and the expected molecular ion and fragmentation patterns in FAB^+ mass spectra. Complexes were characterized by IR spectroscopy [the absence of C≡N stretching vibrations, the presence of ν(N–H) bands due to the imino and NH_2 groups and characteristic vibrations from ν(C=N) and ν(C–O) were recognized]. NMR data confirmed the regio-

DOI: 10.1039/b402105c



Scheme 1

selective formation of the addition products formed *via* HON rather than H_2NN addition of the bifunctional reagent to the nitrile N≡C group. Thus, ^{1}H NMR spectra of **1**–**3** show the presence of a broad signal due to the imino NH proton involved in H-bonding displayed in the usual[7,12] range from 8.2 to 8.8 ppm, and the singlet at 6.0–6.2 ppm of the protons from the NH_2 group of the hydrazone fragment; the latter are slightly low-field shifted relatively to $\delta(NH_2)$ of the free reagent (5.60 ppm). In the $^{13}C\{^1H\}$ NMR spectra of **3**, the signals of three different imino (*C*=N) carbons [142.0 (C=NNH_2), 165.5 (C=NO) and 176.8 (C=NH)] were observed, while **1** and **2** are not soluble enough to measure their $^{13}C\{^1H\}$ NMR spectra even with long acquisition times. ^{195}Pt NMR chemical shifts for **2** (−141 ppm) and **3** (−129 ppm) are in the expected range for *trans*-[$PtCl_4$(imino)$_2$] complexes,[7,11–13] whereas the low solubility of **1** precluded the measurement.

The structure of **3** was determined by single-crystal X-ray diffraction (Fig. 1) The coordination geometry of this complex is a slightly distorted octahedron. The values of the Pt–Cl bond distances [2.3246(5) Å] agree well with previously characterized platinum(IV) chloride compounds.[7,11–13] The two newly formed ligands N(H)=C(Et)ON=C(Me)C(Ph)=NNH_2 are mutually

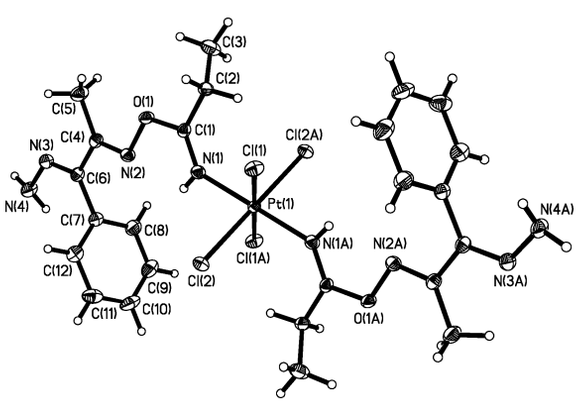


Fig. 1 Molecular structure of **3**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1): 2.024(2), N(1)–C(1): 1.271(3), C(1)–O(1): 1.350(3), N(2)–C(4): 1.283(3), C(4)–C(6): 1.471(3), C(6)–N(3): 1.295(3), N(3)–N(4): 1.360(3); Cl(2)–Pt(1)–Cl(1): 89.85(2); N(1)–Pt(1)–Cl(1): 95.33(6), N(1)–Pt(1)–Cl(2): 86.54(6), N(1)–C(1)–O(1): 121.3(2), C(1)–O(1)–N(2): 112.4(2), C(4)–N(2)–O(1): 109.9(2), N(2)–C(4)–C(6): 113.9(2), C(6)–N(3)–N(4): 118.5(2).

trans, which is thermodynamically stable form for complexes having metal centers in a high oxidation state.[20] Values of the three C=N bonds are almost identical within 3σ (1.273(3), 1.283(3) and 1.295(3) Å for C(1)–N(1), C(2)–N(2), and C(6)–N(3), respectively) and correspond to the mean value of C=N double bonds.[21] The ligands are in *E*-configuration as a result of a rather *weak* hydrogen bond between the N(1)–H hydrogen and the oxime nitrogen [the distances N(1) ··· N(2), N(1)–H(1) and N(1)–H ··· N(2) are 2.573(3), 0.79(3) and 2.15(3) Å; the angle N(1)–H(1) ··· N(2) is 113(2)°]. The *E*-configuration and hydrogen bonding was observed in all structurally characterized complexes with [Pt(IV)]–N(H)=C(R)ON=CR′R″ moieties.[7,11–13] The NH_2 group has an amine character [N(3)–N(4)–H(41): 115(2)°, N(3)–N(4)–N(42): 110(2)°, H(41)–N(4)–H(42): 116(3)°, H(41)–N(4)–H(42)–N(3): −134(3)°].

Reduction of 3 and liberation of the imine ligand

Previously our group[1] and Michelin *et al.*[22] found that the liberation of ligated imines is efficient when (imine)Pt(II) complexes are treated with bidentate diphosphines, *e.g.* 1,2-bis(diphenylphosphino)ethane (dppe), in CH_2Cl_2 to give quantitative yield of the imine in solution and the solid [Pt(diphosphine)$_2$]Cl_2. In addition, the phosphorus ylide Ph_3P=$CHCO_2Me$ has previously proved to be a mild and selective reducing agent for the conversion of Pt(IV) complexes to the appropriate Pt(II) compounds in *non-aqueous* solvents.[23] The liberation of the ligated imines from this study was performed by combination of these two methods for the relatively well soluble, in CH_2Cl_2, complex **3**.

The reaction of **3** and a 1.5-fold excess of Ph_3P=$CHCO_2Me$ proceeds at room temperature in CH_2Cl_2 and allows the formation of the Pt(II) complex **4** (Scheme 1, step II), which was purified by column chromatography. The general features of the IR, ^{1}H and $^{13}C\{^1H\}$ NMR spectra of **4** are similar to those observed for **3** (see Experimental section). The most remarkable spectroscopic difference between the two complexes is their ^{195}Pt NMR spectra, displaying an almost 2000 ppm shift on going from Pt(IV) [−129 ppm] to Pt(II) [−2023 ppm].

The X-ray structure of **4** (Fig. 2) revealed a square planar environment around the metal center and *trans* geometry, with iminoacyl hydrazone ligands in the *E*-configuration stabilized by the same type of weak hydrogen bonding (the distances N(1) ··· N(2), N(1)–H(1) and N(1)–H ··· N(2) were 2.618(4), 0.90(4) and 2.14(4) Å; the angle N(1)–H(1) ··· N(2) is 112(3)°) as in the case of **3**. The inspection of the bond lengths and

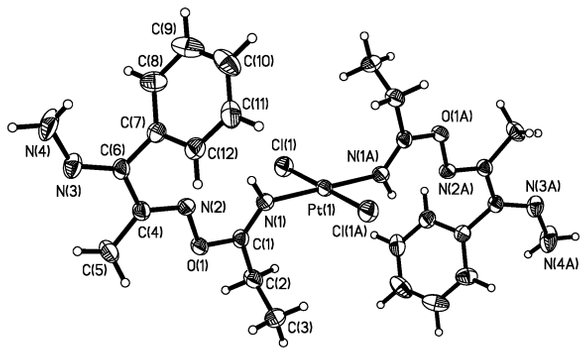
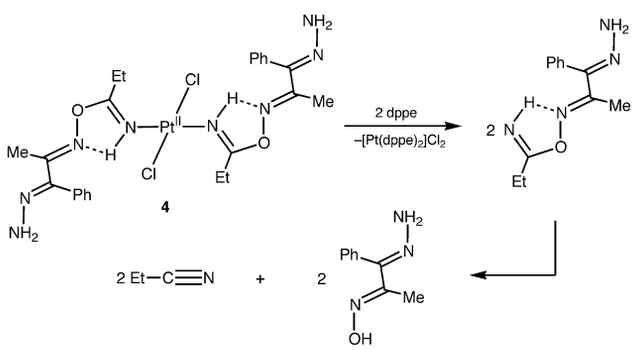


Fig. 2 Molecular structure of **4**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1): 2.018(3), Pt(1)–Cl(1): 2.3098(9), N(1)–C(1): 1.271(4), O(1)–C(1): 1.348(4), N(2)–O(1): 1.442(3), N(2)–C(4): 1.278(4), N(3)–C(6): 1.293(4), N(3)–N(4): 1.355(4); N(1)–Pt(1)–Cl(1): 90.30(9), N(1)–C(1)–O(1): 124.1(3), C(1)–O(1)–N(2): 112.1(2), C(4)–N(2)–O(1): 109.2(2), C(6)–N(3)–N(4): 119.6(3).

angles indicates good agreement with those of the corresponding platinum(IV) complex **3**. The NH_2 group has an amine character [N(3)–N(4)–N(4A): 117(3)°, N(3)–N(4)–H(4B): 115(3)°, H(4A)–N(4)–H(4B): 120(4)°, H(4A)–N(4)–H(4B)–N(3): −149(5)°].

In **4**, the imine ligand was liberated by substitution with 2 equivalents of dppe, as previously[1] described. The reaction proceeds in $CDCl_3$ and the solid $[Pt(dppe)_2]Cl_2$ precipitates and it is removed by filtration. The NMR monitoring of the filtrate allows the identification of the free iminoacyl hydrazone ligand (see Experimental section) (Scheme 2).



Scheme 2

The liberated imine, having a restricted life-time, decomposes in an NMR tube at 20–25 °C after about 20 h to the parent organonitrile and the hydrazone oxime. Additional ^{1}H NMR experiments show that neither MeCN nor EtCN react with the hydrazone oximes under the reaction or even more drastic (45 °C, 3 d) conditions and all these observations together support the idea of the metal-mediated reaction. The complexes are conceivably formed by nucleophilic attack of the oxime oxygen on the highly electrophilically activated carbon atom of the organonitrile. Most likely, the formation of highly stable Pt(IV)-bound imine additionally drives the reaction.

Schiff condensation of complex 4 with aromatic aldehydes giving a novel type of metallaligands

Complex **4** bears two hydrazone groups which are not involved in coordination and we anticipated that certain reactions centered at these functionalities might lead to systems available for further assembly by complexation. This methodology is illustrated below by application of well-known Schiff condensation often explored in the chemistry of hydrazones.[24,25]

Thus, the Schiff condensation of the free NH_2 groups of **4** with aromatic aldehydes, *i.e.* 2-OH-5-NO_2-benzaldehyde and 4-NO_2-benzaldehyde, occurs at 45 °C in CH_2Cl_2 for 7 and 12 h, respectively, and brings about the formation of the platinum(II) complexes **5** and **6**, respectively, containing functionalized remote peripheral groups (Scheme 2, step III). These compounds gave satisfactory elemental analyses (C, H, N) and the expected FAB^+ mass spectra. IR spectra of **5** and **6**, in comparison with **4**, show the disappearance of the ν(N–H) stretching vibrations attributed to the remote NH_2 group of the hydrazone fragment and a new strong band of the ν(C=N) stretching vibration emerged at 1640 cm^{-1}. The Schiff condensation was also confirmed by NMR spectroscopy. In the ^{1}H NMR spectra of **5** and **6**, compared to that of **4**, the absence of protons from the NH_2 moiety was recognized and a new singlet from the azomethine proton appeared at 8.7 ppm. The $^{13}C\{^1H\}$ NMR spectra of **5** and **6** show new peaks at 165.8 and 161.3 ppm, correspondingly, from the azomethine H*C*=N fragment and the absence of the signal at 142.7 ppm from the C=NNH_2 group of the parent **4**.

The single-crystal X-ray diffraction study of **5** unambiguously confirmed the occurrence of the Schiff condensation (Fig. 4). In **5**, the H-bonding between the hydrogen of the aryl OH group and the N(4) atom of the hydrazone group was clearly observed (the distances O(2) ··· N(4), O(2)–H and O(2)–H ··· N(4) are 2.576(4), 0.98 and 1.75 Å; the angle O(2)–H ··· N(4) is 139.8°). The formation of this six-membered H-chelating ring is typical for the Schiff bases derived from salicylaldehyde[26] and this moiety is a good sequestering group for various metal centers.[27–29]

The formation of heteronuclear complexes

In **5**, the presence of the two chelate rings (Fig. 3) allowed the consideration of this complex as a potential Pt(II)-containing metallaligand potentially capable to form new heteropolynuclear species upon further complexation; the formation of such compounds, in particular Pt(II)-containing ones,[30] has been an area of rapt attention in the latest decade.

Various metal complexes, of both Cu(II)[27,28] and Co(II),[29] between the Schiff bases derived from salicylaldehyde and hydrazones are well-known and thoroughly structurally characterized. Accordingly, further metallization of **5** was achieved by its reaction with $M(OAc)_2{\cdot}nH_2O$ (M = Cu, n = 2; M = Co, n = 4) in a 1 : 1 molar ratio in CH_2Cl_2–CH_3OH at room temperature. In both cases, the C, H, and N elemental analysis data are in a good agreement with the formation of heteronuclear compounds with composition [Pt] : [M] = 1 : 1 suggesting a polymerization due to complexation. The IR spectra of **5** and

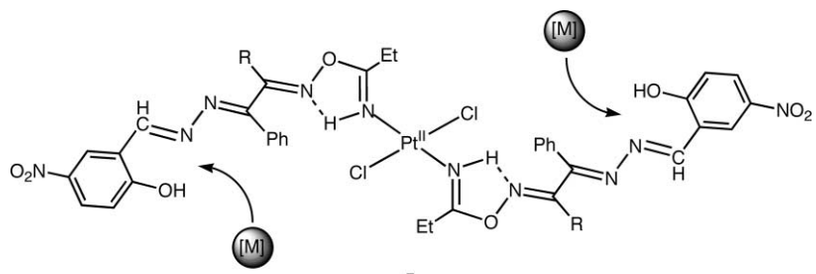


Fig. 3 Structure of the Pt(II)-based metallaligand **5** with indication of sites for metallation.

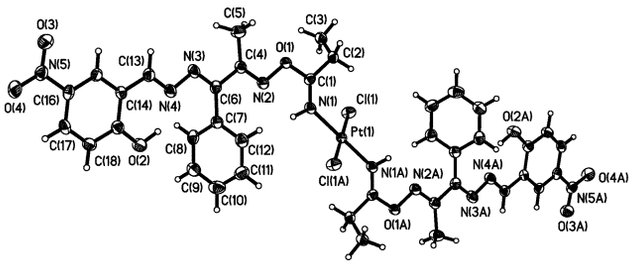


Fig. 4 Molecular structure of **5**. The thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt(1)–N(1): 2.009(3), Pt(1)–Cl(1): 2.3092(9), N(1)–C(1): 1.264(5), O(1)–C(1): 1.381(4), O(1)–N(2): 1.423(4), N(3)–N(4): 1.402(4), O(2)–C(19): 1.332(4), N(5)–C(16): 1.470(5), O(3)–N(5): 1.225(4), O(4)–N(5): 1.225(4); C(1)–N(1)–Pt(1): 133.0(2), N(1)–C(1)–O(1): 122.6(3), C(1)–O(1)–N(2): 111.5(3), C(6)–N(3)–N(4): 113.6(3), O(3)–N(5)–O(4): 123.6(3).

6 show a decrease of *ca.* 30 cm^{-1} of the ν(C=N) band of the azomethine group of the hydrazone fragment compared to **5** and this favors the formation of the six-membered metal chelating [M]*N*CCC*O* ring with the localization of the coordination bonds on the deprotonated OH group and the N azomethine atom.

Concluding remarks

It has been demonstrated that bifunctional hydrazone oximes react easily with Pt(IV)-complexed organonitriles to achieve, with high degree of regioselectivity, the product of HON-addition to the nitrile group. This reaction represents a novel type of reactivity for hydrazone oximes which are well-known ligands [31,32] for various metal-ions. We also established that the free NH_2 groups in the addition products provide an easy entry to a variety of metallaligands which can be obtained by Schiff condensation with aldehydes, *e.g.* salicylaldehyde. These metallaligands were used for further complexation with Cu(II) and Co(II) centers to give novel types of heterometallic systems.

Experimental

Materials and instrumentation

$Ph_3P{=}CHCO_2Me$ (Lancaster) and solvents were obtained from commercial sources and used as received. The hydrazone oximes were synthesized following the published procedure.[33] The complexes $[PtCl_4(RCN)_2]$ (R = Me, Et) were prepared as previously described.[34] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting (decomposition) points were determined on a Leica Galen III Kofler table. For TLC, Merck UV 254 SiO_2-plates have been used. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol (NBA) matrices of the samples with 8 keV (*ca.* 1.28 × 10^{15} J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. IR spectra (4000–400 cm^{-1}) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{195}Pt NMR spectra were measured on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are relative to $Na_2[PtCl_6]$ (by using aqueous $K_2[PtCl_4]$, δ −1630 ppm, as a standard), with half-height line width in parentheses.

Addition of hydrazone oximes to organonitriles in $[PtCl_4(RCN)_2]$

***trans*-[PtCl$_4${NH=C(Me)ON=C(Me)C(Ph)=NNH$_2$}$_2$] (1).** PhC(=NNH_2)C(Me)=NOH (17 mg, 0.10 mmol) was added to a suspension of *trans*-$[PtCl_4(MeCN)_2]$ (20 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) at 45 °C and the reaction mixture was left to stand for 50 min until complete homogenization, whereupon the solvent was evaporated in a flow of N_2 to *ca.* 0.5 mL followed by addition of Et_2O (5 mL) to precipitate **1**. Yield: 54%. Anal. Calc. for $C_{22}H_{28}N_8Cl_4O_2Pt$: C, 34.17; H, 3.65; N, 14.49%. Found: C, 34.28; H, 3.66; N, 14.56%. FAB$^+$-MS, *m*/*z*: 773 [M]$^+$, 724 [M − 2Cl + Na]$^+$, 702 [M − 2Cl]$^+$, 667 [M − 3Cl]$^+$; mp 180–182 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3426 mw ν(N–H), 3381 mw ν(N–H), 3252 mw ν(N–H), 1653 s and 1610 s ν(C=N), 1598 s ν(C=C), 1179 mw ν(C–O), 704 s δ(C–H). TLC (eluent chloroform–acetone = 10 : 1), R_f = 0.55. ^{1}H NMR in CD_2Cl_2, δ 2.36 (s, 3H), 2.63 (s, 3H), 6.24 (s, 2H, NH_2), 7.24–7.58 (m, 5H), 8.22 (s, br, 1H, NH). This compound is not sufficiently soluble in all common deuterated solvents to collect both ^{13}C and ^{195}Pt NMR spectra.

***trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(Me)=NNH$_2$}$_2$] (2).** MeC(=NNH_2)C(Me)=NOH (12 mg, 0.10 mmol) was added to a suspension of *trans*-$[PtCl_4(EtCN)_2]$ (22 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) at 45 °C and the reaction mixture was left to stand for 30 min, whereupon the solvent was evaporated in a flow of N_2 to dryness, the residue formed was washed with three 5-mL portions of Et_2O and dried *in vacuo* at room temperature. Yield: 62%. Anal. Calc. for $C_{14}H_{28}N_8Cl_4O_2Pt$: C, 24.83; H, 4.17; N, 16.54%. Found: C, 24.94; H, 4.09; N, 16.48%. FAB$^+$-MS, *m*/*z*: 677 [M]$^+$, 643 [M − Cl + H]$^+$, 606 [M − 2Cl]$^+$; mp 168–170 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3439 mw ν(N–H), 3309 mw ν(N–H), 3291 mw ν(N–H), 3227 mw ν(N–H), 1655 s and 1624 s ν(C=N), 1577 s ν(C=C), 1186 mw ν(C–O). TLC (eluent chloroform–acetone = 10 : 1), R_f = 0.62. ^{1}H NMR in CD_2Cl_2, δ 1.33 (t, *J* 7.5 Hz, 3H), 2.15 (s, 3H), 2.19 (s, 3H), 3.28 (q, *J* 7.5 Hz, 2H), 5.98 (s, 2H, NH_2), 8.80 (s, br, 1H, NH). The compound is too poorly soluble in all common deuterated solvents to obtain ^{13}C{^{1}H} NMR spectrum in a reasonable acquisition time. ^{195}Pt NMR spectrum in CD_2Cl_2, δ −141 (922 Hz).

***trans*-[PtCl$_4${NH=C(Et)ON=C(Me)C(Ph)=NNH$_2$}$_2$] (3).** PhC(=NNH_2)C(Me)=NOH (17 mg, 0.10 mmol) was added to a suspension of $[PtCl_4(EtCN)_2]$ (22 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) at 45 °C and the reaction mixture was left to stand for 10 min, whereupon the solvent was evaporated in a flow of N_2 to dryness, the obtained solid was washed with three 5-mL portions of Et_2O and dried *in vacuo* at room temperature. Yield: 87%. Anal. Calc. for $C_{24}H_{32}N_8Cl_4O_2Pt$: C, 35.96; H, 4.02; N, 13.98%. Found: C, 36.13; H, 4.04; N. 13.92%. FAB$^+$-MS, *m*/*z*: 802 [M + H]$^+$, 730 [M − 2Cl]$^+$, 695 [M − 3Cl]$^+$, 660 [M − 4Cl]$^+$; mp 172–174 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3379 mw ν(N–H), 3271 mw ν(N–H), 3221 mw ν(N–H), 1649 s ν(C=N), 1599 s ν(C=C), 1180 mw ν(C–O), 700 mw δ(C–H). TLC (eluent chloroform–acetone = 10 : 1), R_f = 0.58. ^{1}H NMR in CD_2Cl_2, δ 1.22 (t, *J* 7.5 Hz, 3H, CH_3CH_2), 3.08 (q, *J* 7.5 Hz, 2H, CH_3CH_2), 2.34 (s, 3H), 6.19 (s, 2H, NH_2), 7.21–7.54 (m, 5H, Ph) 8.22 (s, br, 1H, NH). ^{13}C{^{1}H} NMR in CD_2Cl_2, δ 10.7 and 25.3 (Et), 11.8 (Me), 129.1 and 130.1 ($CH_{ortho\ and\ meta}$), 132.3 (CH_{para}), 120.1 (C_{ipso}), 142.0 (C=NNH_2), 165.5 (C=NO) and 176.8 (C=NH). ^{195}Pt NMR spectrum in CD_2Cl_2, δ −129 (615 Hz).

***trans*-[PtCl$_2${NH=C(Et)ON=C(Me)C(Ph)=NNH$_2$}$_2$] (4).** The carbonyl-stabilized phosphorous ylide $Ph_3P{=}CHCO_2Me$ (10 mg, 0.03 mmol) was added at room temperature to a solution of **3** (15 mg, 0.02 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was vigorously stirred at 20–25 °C for 1 d and then was subject to column chromatography [silica gel type Merck 60 (70–230 mesh), eluent CH_2Cl_2–Et_2O = 5 : 1] to separate in the first fraction a rather intensively colored complex **2**. Then the eluent was evaporated in a flow of N_2 to dryness, the obtained solid was washed with three 5-mL portions of Et_2O and dried *in vacuo* at room temperature. Yield: 63%. Anal. Calc. for $C_{24}H_{32}N_8Cl_2O_2Pt$: C, 39.46; H, 4.42; N, 15.34%. Found: C, 39.74; H, 4.55; N. 15.58%. FAB$^+$-MS, *m*/*z*: 731 [M + H]$^+$, 695 [M − Cl]$^+$, 660 [M − 2Cl]$^+$, 625 [M − 3Cl]$^+$;

mp 147–148 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3460 mw ν(N–H), 3306 mw ν(N–H), 3206 mw ν(N–H), 1655 s ν(C=N), 1595 s ν(C=C), 1172 s ν(C–O), 704 mw δ(C–H). TLC (eluent chloroform–acetone = 15 : 1), $R_f = 0.54$. ^{1}H NMR in $CDCl_3$, δ 1.37 (t, J 7.5 Hz, 3H, CH_3CH_2), 3.09 (q, J 7.5 Hz, CH_3CH_2), 2.31 (s, 3H), 6.01 (s, 2H, NH_2), 7.17–7.52 (m, 6H, Ph + NH), NH is overlapped with the signals from the Ph group). ^{13}C{^{1}H} NMR in $CDCl_3$, δ 10.2 and 26.8 (Et), 11.6 (Me), 128.6 and 129.5 ($CH_{ortho\ and\ meta}$), 131.8 (CH_{para}), 119.8 (C_{ipso}), 142.7 (C=NNH_2), 164.0 (C=NO) and 173.1 (C=NH). ^{195}Pt NMR spectrum in $CDCl_3$, δ −2023 (505 Hz).

***trans*-[$PtCl_2${NH=C(Et)ON=C(Me)C(Ph)=NN=CH(C_6H_3-2-OH-5-NO_2}$_2$] (5).** 5-Nitrosalicylaldehyde (10 mg, 0.06 mmol) was added to a solution of **4** (22 mg, 0.03 mmol) in CH_2Cl_2 (3 mL) at 45 °C and the reaction mixture was left to stand for 7 h, whereupon the solvent was evaporated in a flow of N_2 to dryness, the obtained solid was washed with three 5-mL portions of Et_2O and dried *in vacuo* at room temperature. Yield: 59%. Anal. Calc. for $C_{38}H_{38}N_{10}Cl_2O_8Pt$: C, 44.36; H, 3.72; N, 13.62%. Found: C, 44.44; H, 3.63; N. 13.54%. FAB$^+$-MS, *m*/*z*: 752 [M − $2C_6H_3NO_3H$]$^+$, 682 [M − 2Cl − $2C_6H_3NO_3H$]$^+$, 647 [M − L]$^+$, 611 [M − Cl − L − H]$^+$, 576 [M − 2Cl − L]$^+$, where L is NH=C(Et)ON=C(Me)C(Ph)=NN=CH(C_6H_3-2-OH-5-NO_2); mp 164 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3287 mw ν(N–H), 1658 and 1612 s ν(C=N), 1595 s ν(C=C), 1522 mw $\nu_{as}(NO_2)$, 1340 s $\nu_s(NO_2)$, 1159 s ν(C–O), 706 mw δ(C–H). TLC (eluent chloroform–acetone = 10 : 1), R_f = 0.61. ^{1}H NMR in $CDCl_3$, δ 1.39 (t, J 7.5 Hz, 3H, CH_3CH_2), 3.12 (q, J 7.5 Hz, 2H, CH_3CH_2), 2.47 (s, 3H, Ph), 6.97–8.29 (m, 8H, Ph), 7.54 (s, 1H, NH), 8.78 (s, 1H, HC=N), 11.72 (s, 1H, OH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ 10.9 and 27.4 (Et), 13.3 (Me), 117.6 and 118.9 (C_{ipso}), 128.5–132.4 (m, C_{arom}), 164.6 (C=N), 165.8 (C=N) and 173.6 (C=NH). ^{195}Pt NMR spectrum in $CDCl_3$, δ −2041 (540 Hz).

***trans*-[$PtCl_2${NH=C(Et)ON=C(Me)C(Ph)=NN=CH(C_6H_4-4-NO_2}$_2$] (6).** 4-Nitrobenzaldehyde (9 mg, 0.06 mmol) was added to a solution of **4** (22 mg, 0.03 mmol) in CH_2Cl_2 (3 mL) at 45 °C and the reaction mixture was left to stand for 12 h, whereupon the solvent was evaporated in a flow of N_2 to dryness, the obtained oily residue was left to stand for 10 h in methanol (5 mL, 50 °C) until the yellow crystalline product formed. This product was washed with three 3-mL portions of Et_2O and dried *in vacuo* at room temperature. Yield: 27%. Anal. Calc. for $C_{38}H_{38}N_{10}Cl_2O_6Pt$: C, 45.78; H, 3.82; N, 14.06%. Found: C, 45.69; H, 3.74; N. 13.94%. FAB$^+$-MS, *m*/*z*: 998 [M + 2H]; mp 171–172 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3274 mw ν(N–H), 1661 and 1638 s ν(C=N), 1596 s ν(C=C), 1521 s $\nu_{as}(NO_2)$, 1344 s $\nu_s(NO_2)$, 1161 mw ν(C–O), 691 mw δ(C–H). TLC (eluent chloroform–acetone = 10 : 1), R_f = 0.64. ^{1}H NMR in $CDCl_3$, δ 1.47 (t, J 7.5 Hz, 3H, CH_3CH_2), 3.21 (q, J 7.5 Hz, 2H, CH_3CH_2), 2.38 (s, 3H, Ph), 7.51–8.35 (m, 10H, Ph), 8.64 s, 1H, HC=N), NH is overlapped with the signals of the Ph group. ^{13}C{^{1}H} NMR in $CDCl_3$, δ 10.2 and 27.0 (Et), 17.3 (Me), 118.4 and 119.9 (C_{ipso}), 128.5–132.4 (m, C_{arom}), 159.8 (C=N), 161.3 (HC=N), 163.4 (C=NH). ^{195}Pt NMR spectrum in $CDCl_3$, δ −1561 (580 Hz).

Liberation of the ligand from complex 4

Dppe (11 mg, 0.028 mmol) was added at room temperature to a solution of **4** (10 mg, 0.014 mmol) in chloroform (2 mL). A colorless crystalline precipitate of [$Pt(dppe)_2$]Cl_2 was removed by filtration after 30 min (14.2 mg, 98%) and the free ligand was characterized by NMR spectroscopy. ^{1}H NMR in $CDCl_3$, δ 1.20 (t, J 7.83, 3H, CH_3CH_2), 3.51 (q, J 7.08, 2H, CH_3CH_2), 2.30 (s, 3H, Me), 5.85 (s, 2H, NH_2), 7.22–7.52 (m, 6H, Ph), NH is overlapped with the signals of the Ph group. ^{13}C{^{1}H} NMR in $CDCl_3$, δ 9.4 and 26.5 (Et), 10.4 (Me), 127.3 and 128.1 ($CH_{ortho\ and\ meta}$), 131.5 (CH_{para}), 118.7 (C_{ipso}), 144.9 (C=N), 160.8 (C=NNH_2), and 168.1 (C=NH). The NMR data after *ca*. 20 h [^{1}H NMR ($CDCl_3$), δ 1.31 (t, 7.6 Hz, 3H, CH_2CH_3), 1.99 (s, 3H, CH_3C=N), 2.36 (q, 7.6 Hz, 2H, CH_2CH_3), 5.52 (s, 2H, NH_2), 7.13–7.46 (m, 5H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$), δ 9.35 (CH_3C=N), 10.41 (CH_2CH_3), 11.20 (CH_2CH_3), 120.62 (CH_3CH_2CN), 127.34–132.0 (m, C_{arom}), 146.94 (C=NNH_2), 161.97 (C=NO)]. The latter NMR data show that the liberated imine ligand decomposes to give the parent nitrile and the hydrazone oxime. In addition, the free hydrazone oxime was isolated as a solid after slow evaporation of $CDCl_3$. Complex [$Pt(dppe)_2$]Cl_2: Anal. Calc. for $C_{52}H_{48}Cl_2P_4Pt$: C, 58.76; H, 4.52%. Found: C, 58.69; H, 4.48%. IR spectrum in KBr, selected bands, cm^{-1}: 1482 mw ν(P–C_{Ph}), 1437 s ν(P–CH_2), 697 and 702s δ(C–H_{Ph}). ^{1}H NMR ($CDCl_3$), δ 3.39 (t, J 6.9 Hz, 4H, CH_2), 7.30–7.70 (m, 20H, Ph). ^{31}P{^{1}H} NMR ($CDCl_3$, rel. H_3PO_4), δ 47.9 (2368 Hz) [lit.[35] ^{31}P NMR spectrum in $CDCl_3$, δ 47.0 (2360 Hz)].

The synthesis of heteronuclear complexes

A solution of **5** (20 mg, 0.0195 mmol) in CH_2Cl_2 (2 mL) was added to a solution of $M(OAc)_2 \cdot nH_2O$ [M = Cu, n = 2; M = Co, n = 4] (0.0195 mmol) in CH_3OH (3 mL). The brown precipitate which formed immediately was isolated by filtration, washed three times with hot methanol and dichloromethane and dried in *vacuo*.

Yield: 74%. Anal. Calc. for $C_{38}H_{38}N_{10}Cl_2O_8CuPt \cdot CH_2Cl_2$: C, 39.79; H, 3.42; N, 11.89%. Found: C, 39.54; H, 3.11; N, 11.61%. The compound is stable on heating at least up to 250 °C. IR spectrum in KBr, selected bands, cm^{-1}: 3290 mw ν(N–H), 1660 s ν(C=N), 1604 s ν(C=N), 1546 mw $\nu_{as}(NO_2)$, 1316 s $\nu_s(NO_2)$.

Yield: 56%. Anal. Calc. for $C_{38}H_{38}N_{10}Cl_2O_8CoPt \cdot CH_2Cl_2$: C, 39.94; H, 3.44; N, 11.94% Found: C, 39.80; H, 3.03; N, 11.43%. The compound is stable on heating at least up to 250 °C. IR spectrum in KBr, selected bands, cm^{-1}: 3287 mw ν(N–H), 1653 s ν(C=N), 1605 s ν(C=N), 1545 mw $\nu_{as}(NO_2)$, 1315 s $\nu_s(NO_2)$.

X-Ray structure determinations

The X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Single crystals of **3**–**5** were mounted in inert oil within the cold gas stream of the diffractometer. The Denzo-Scalepack[36] program package was used for cell refinements and data reduction. Structures were solved by direct methods using the SHELXS-97 or SIR-97 programs.[37,38] A multiscan absorption correction based on equivalent reflections (XPREP in SHELXTL v. 6.12)[39] was applied to all data (T_{min}/T_{max} values were 0.24824/0.30984, 0.19314/0.26538, and 0.31969/0.37318, respectively, for **3**–**5**). All structures were refined with SHELXL-97[40] and WinGX graphical user interface.[41] In **3** and **4**, NH and NH_2 were located from the difference Fourier map and refined isotropically. In **5**, the OH hydrogen was also located from Fourier map but not refined. All other hydrogens were placed in idealized positions and constrained to ride on their parent atom. The crystallographic data are summarized in Table 1. Selected bond lengths and angles are shown in the figure captions.

CCDC reference numbers 231143–231145.

See http://www.rsc.org/suppdata/dt/b4/b402105c/ for crystallographic data in CIF or other electronic format.

Acknowledgements

D. A. G. expresses gratitude to the Foundation for Science and Technology (FCT) and the POCTI program (FEDER funded), Portugal (grant SFRH/BPD/11685/2002) for the fellowship. M. H. would like to thank the Academy of Finland for financial support. A. J. L. P. and V. Yu. K. are grateful to the FCT and the POCTI program (POCTI/QUI/43415/2001 project)

Table 1 Crystallographic data for **3**–**5**

	3	**4**	**5**
Empirical formula	$C_{24}H_{32}N_8Cl_4O_2Pt$	$C_{24}H_{32}N_8Cl_2O_2Pt$	$C_{38}H_{38}N_{10}Cl_2O_8Pt$
M_r	801.47	730.57	1028.77
T/K	150(2)	150(2)	150(2)
λ/Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	9.4035(1)	8.0753(2)	8.7209(2)
b/Å	9.5408(1)	8.6907(3)	10.9317(2)
c/Å	10.0344(2)	10.6485(4)	11.9651(2)
α/°	67.3988(6)	97.916(1)	109.488(1)
β/°	68.9532(6)	104.145(1)	101.502(1)
γ/°	82.598(1)	98.463(2)	100.261(1)
V/Å^3	775.63(2)	704.91(4)	1016.11(3)
Z	1	1	1
D_c/Mg m^{-3}	1.716	1.721	1.681
μ(Mo-Kα)/mm^{-1}	4.903	5.203	3.648
No. collected reflns.	11281	10837	16718
No. unique rflns.	3345	2761	3974
$R_{Int.}$	0.0249	0.0484	0.0576
$R1$ [a] ($I \geq 2\sigma$)	0.0173	0.0260	0.0300
$wR2$ [b] ($I \geq 2\sigma$)	0.0401	0.0518	0.0614

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

(FEDER funded) for financial support of these studies. The authors thank NATO for the Collaborative Linkage Grant PST.CLG.979289. V. Yu. K. is very much obliged to the Russian Fund for Basic Research for a grant (03–03–32363), the Royal Society of Chemistry for the Grant for International Authors and the Academy of Finland for support of the cooperation with the University of Joensuu. The authors express gratitude to Professor J. Vicente for valuable suggestions.

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