DALTON
FULL PAPER

First observation of metal-mediated nitrile–imine coupling giving ligated 1,3-diaza-1,3-dienes

Dmitrii A. Garnovskii,[a] Vadim Yu. Kukushkin,*[b] Matti Haukka,[c] Gabriele Wagner[a] and Armando J. L. Pombeiro*[a]

[a] *Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1049–001 Lisbon, Portugal. E-mail: pombeiro@ist.utl.pt*
[b] *Department of Chemistry, St. Petersburg State University, 198904 Stary Petergof, Russian Federation. E-mail: kukushkin@VK2100.spb.edu*
[c] *Department of Chemistry, PO Box 111, FIN-80101, Joensuu, Finland. E-mail: Matti.Haukka@Joensuu.Fi*

Received 10th October 2000, Accepted 20th December 2000
First published as an Advance Article on the web 16th February 2001

Coupling between benzophenone imine and coordinated organonitriles in the platinum(IV) complexes $[PtCl_4(RCN)_2]$ (R = Me or Et) proceeded rapidly under mild conditions to afford the 1,3-diaza-1,3-diene compounds $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ in good yield and this reaction is the first observation of metal-assisted nucleophilic addition of an imine to a ligated nitrile. $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ were reduced to the corresponding platinum(II) complexes $[PtCl_2\{NH{=}C(R)N{=}CPh_2\}_2]$ by the carbonyl-stabilized phosphorus ylide $Ph_3P{=}CHCO_2Me$. The $[PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2]$ complex was also detected in a mixture formed in the reaction between the platinum(II) nitrile complex $[PtCl_2(MeCN)_2]$ and $Ph_2C{=}NH$, but the selectivity of the platinum(II)-mediated nitrile–imine coupling was enhanced by employing for the reaction with benzophenone imine the phenyl cyanide complex $[PtCl_2(PhCN)_2]$ to give $[PtCl_2(NH{=}CPh_2)\{NH{=}C(Ph)N{=}CPh_2\}]$. Liberation of 1,3-diaza-1,3-dienes was exemplified by the reaction of $[PtCl_2\{NH{=}C(Et)N{=}CPh_2\}_2]$ with two equivalents of 1,2-bis(diphenylphosphino)ethane in $CHCl_3$ to give, along with free $NH{=}C(Et)N{=}CPh_2$ retained in solution, the solid complex $[Pt(dppe)_2]Cl_2$. All isolated metal complexes were characterized by elemental analyses, FAB mass spectrometry, IR, ^1H, ^{13}C-$\{^1H\}$ and ^{195}Pt NMR spectroscopies and *cis*-$[PtCl_4\{Z\text{-}NH{=}C(Et)N{=}CPh_2\}_2]$ also by X-ray single-crystal diffraction.

Introduction

In organic chemistry organonitriles RCN serve as synthons of great versatility for the formation of new C–O and C–N bonds due to nucleophilic addition of O- or N-donors, respectively, to the nitrile carbon.[1] The well recognized susceptibility of the C atom towards nucleophilic attack can be utilized by the application of organonitriles with a strong acceptor radical R. When activation by this way is insufficient another route to activate the nitriles can be applied, *i.e.* their coordination to a metal center, preferably in a rather high oxidation state, that promotes addition of nucleophiles to give new C–O,[2,3] C–N,[2,3] C–C,[4] C–P[5] or C–S[2,3] bonds. Many of these metal-promoted reactions were summarized in reviews on the subject[2,3] including the recent one by Michelin *et al.*[2]

As far as metal-mediated additions to give C–N bonds are concerned, reports on coupling between coordinated nitriles and ammonia, primary or secondary amines[2,3] became rather habitual although some new and interesting aspects of these reactions are still gradually appearing.[6] Among less usual and yet systematically unexplored additions of N-donors, attention should be drawn to: (*i*) the reaction between metal-bound[7,8] organonitriles and hydrazine or methylhydrazine to give amidrazone species; (*ii*) couplings between nitriles and potentially ambidentate *N*,*O*-nucleophiles such as alkylhydroxylamines giving, depending on the metal center, addition products with new C–N[9] or C–O[10] bonds; (*iii*) addition of azaheterocycles, *e.g.* pyrazole, containing a N–H bond to give iminoacylated rings.[11] In the context of the addition of N-donor nucleophiles to coordinated organonitriles a special case has recently been described by Kelly and Slawin[12] who discovered the addition, *via* the N atom, of sulfimide $Ph_2S{=}NH$ to acetonitrile ligand in the platinum(II) complex $[PtCl_2(MeCN)_2]$ to give $[PtCl(Ph_2S{=}NH)\{S,N\text{-}Ph_2S{=}NC(Me){=}NH\}]Cl$.

Owing to our interest in nucleophilic addition to metal-bound nitriles[13–16] and its application for organic synthesis[17] we have continued the search for new reagents for additions to ligated RCN molecules and focused our efforts on reactions with benzophenone imine, $Ph_2C{=}NH$. We report herein the first observation of a facile metal-induced nitrile–imine coupling to give ligated 1,3-diaza-1,3-dienes, although formation of the latter species as undetected intermediates, *via* zinc-mediated nucleophilic addition of imines to nitriles, was anticipated.[18] The previously known organic synthetic methods[19] for such diazadienes do not involve a direct reaction between a nitrile and an imine.

Results and discussion

Imines are known as good ligands for platinum[20] or other transition metals[21] and these species are coordinated either *via* the N atom or the C=N double bond. In addition, imine ligands that contain aromatic groups attached to the imine carbon, *e.g.* $Ph_2C{=}NH$, can easily undergo orthometallation giving very stable *N*,*C*-chelates.[20] Our interest in the exploration of benzophenone imine as a reagent for the nucleophilic addition to metal-bound organonitriles to obtain 1,3-diaza-1,3-dienes was recently sparked by intriguing data of Grøndahl *et al.*[20] who reported on the reaction between the platinum(II) complex $[PtCl_2(MeCN)_2]$ and two equivalents of $Ph_2C{=}NH$ in dichloromethane giving the substitution product $[PtCl_2(Ph_2C{=}NH)_2]$ as a solid in 20% yield, while "the mother liquor con-

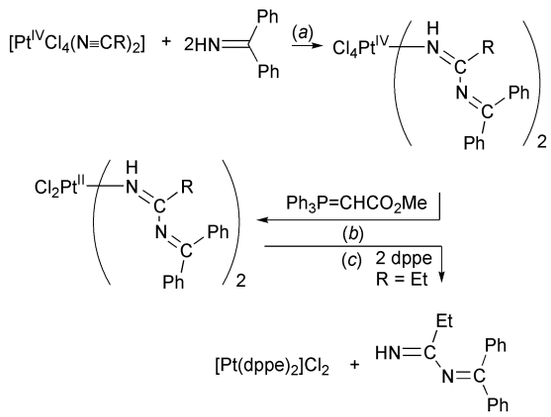
 DOI: 10.1039/b008154j

tained yet unidentified complexes".[20] Taking into account our previous experience of additions to coordinated organonitrile species,[13–16] we decided to try the extension to imines, as the nucleophiles, of nucleophile–nitrile coupling reactions and, concurrently, to investigate whether the low yield of $[PtCl_2(Ph_2C{=}NH)_2]$ is explained by the occurrence of an addition of imine to the coordinated nitriles. To perform the coupling we employed the same methodology as has previously been applied[13–15,17,18] to increase the selectivity of the addition and to enhance the reactivity of platinum-bound organonitriles: (*i*) to attempt the reaction between the imine and the platinum(IV) complexes $[PtCl_4(RCN)_2]$ (the latter proved to be highly reactive towards the addition of different nucleophiles[13,14,17,18]); (*ii*) if the coupling is successful, to reduce the compounds $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ to the corresponding platinum(II) complexes $[PtCl_2\{NH{=}C(R)N{=}CPh_2\}_2]$; (*iii*) to try to detect $[PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2]$ in the mother liquor from the synthesis of $[PtCl_2(Ph_2C{=}NH)_2]$[20] by application of both TLC and NMR methods, thus checking for the possible occurrence of coupling in $[PtCl_2(MeCN)_2]$; (*iv*) to activate nitriles in the platinum(II) complexes $[PtCl_2(RCN)_2]$ by introducing an acceptor substituent R, *e.g.* Ph, and to attempt coupling with benzophenone imine.

Platinum(IV)-mediated nitrile–imine coupling

In accord with the plan, we explored the reaction between the platinum(IV) complexes $[PtCl_4(RCN)_2]$ and two equivalents of $Ph_2C{=}NH$ in dichloromethane. We chose as starting materials for this part of the study the acetonitrile and propionitrile complexes $[PtCl_4(RCN)_2]$ (R = Me or Et). The former was prepared by chlorination of a mixture of *cis*- and *trans*-$[PtCl_2(MeCN)_2]$ (*ca.* 5:1 by NMR integration[22]) and presumably consists of an isomeric mixture of *cis*/*trans*-$[PtCl_4(MeCN)_2]$. However, the poor solubility of this compound does not allow one to confirm quantitatively this assumption. Isomeric forms of it were obtained by Cl_2 oxidation of (*i*) a mixture of *cis*- and *trans*-$[PtCl_2(EtCN)_2]$ (6:1 by NMR integration[23]) giving a mixture of *cis*/*trans*-$[PtCl_4(EtCN)_2]$ with almost the same isomeric ratio and (*ii*) pure *trans*-$[PtCl_2(EtCN)_2]$[23] to give the isomerically pure *trans*-$[PtCl_4(EtCN)_2]$ complex.

The heterogeneous reaction of *cis*/*trans*-$[PtCl_4(MeCN)_2]$ and the homogeneous reaction of *cis*/*trans*-$[PtCl_4(EtCN)_2]$ (containing mostly the *cis* isomer, see above) with the imine proceeds rather rapidly at room temperature, while for *trans*-$[PtCl_4(EtCN)_2]$ it is fast and selective even at −15 °C (but gives a broad spectrum of products at 20–25 °C). Subsequent evaporation of the solvent to dryness and treatment of the residue formed with Et_2O allowed isolation of $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ in *ca.* 80% yield (route (*a*) in Scheme 1). In



Scheme 1

the case of the isomeric mixtures as the starting materials appropriate mixtures of the geometrical isomers of $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ were isolated.

Reaction of *trans*-$[PtCl_4(EtCN)_2]$ with the imine led exclusively to *trans*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$, while treatment of the *cis*/*trans* mixture of $[PtCl_4(EtCN)_2]$ with $Ph_2C{=}NH$ results in the formation of *cis*/*trans*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$. Crystals of *cis*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ were separated mechanically from the latter mixture, after slow evaporation of its CH_2Cl_2–Et_2O solution, and fully characterized (see Experimental section). An X-ray single-crystal diffraction study of *cis*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ revealed an octahedral environment around the metal center and overall *cis* geometry with the newly formed $NH{=}C(Et)N{=}CPh_2$ ligands in the *Z* configuration (Fig. 1) with bond lengths and angles (Table 1) of normal values.[13,14,25,26] The 1,3-diaza-1,3-diene unit in the $NH{=}C(Et)N{=}CPh_2$ ligands is not planar but adopts a transoid conformation with torsion angles N=C–

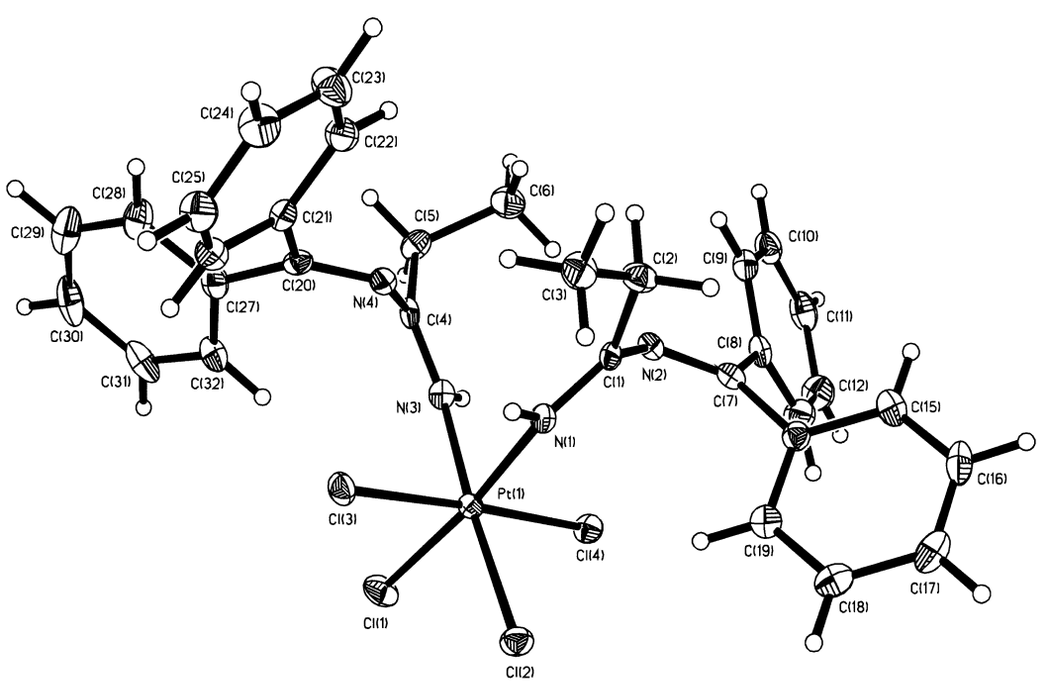


Fig. 1 PLATON[24] view of the structure of *cis*-$[PtCl_4\{Z\text{-}NH{=}C(Et)N{=}CPh_2\}_2]$ with the atomic numbering scheme.

Table 1 Bond lengths (Å) and angles (°) for $[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$

Pt(1)–Cl(1)	2.3149(7)	C(11)–C(12)	1.385(4)
Pt(1)–Cl(2)	2.3192(7)	C(12)–C(13)	1.376(4)
Pt(1)–Cl(3)	2.3159(8)	C(14)–C(19)	1.404(4)
Pt(1)–Cl(4)	2.3319(8)	C(14)–C(15)	1.398(4)
Pt(1)–N(1)	2.042(2)	C(15)–C(16)	1.385(4)
Pt(1)–N(3)	2.025(3)	C(16)–C(17)	1.386(4)
N(1)–C(1)	1.291(4)	C(17)–C(18)	1.387(4)
N(2)–C(1)	1.366(4)	C(18)–C(19)	1.391(4)
N(2)–C(7)	1.285(3)	C(20)–C(21)	1.493(4)
N(3)–C(4)	1.292(4)	C(20)–C(27)	1.486(4)
N(4)–C(4)	1.364(4)	C(21)–C(26)	1.390(4)
N(4)–C(20)	1.282(4)	C(21)–C(22)	1.388(4)
C(1)–C(2)	1.508(4)	C(22)–C(23)	1.390(4)
C(2)–C(3)	1.512(4)	C(23)–C(24)	1.391(5)
C(4)–C(5)	1.502(4)	C(24)–C(25)	1.379(4)
C(5)–C(6)	1.524(4)	C(25)–C(26)	1.394(4)
C(7)–C(14)	1.491(4)	C(27)–C(32)	1.397(4)
C(7)–C(8)	1.483(4)	C(27)–C(28)	1.409(4)
C(8)–C(9)	1.396(4)	C(28)–C(29)	1.381(4)
C(8)–C(13)	1.397(4)	C(29)–C(30)	1.383(6)
C(9)–C(10)	1.390(4)	C(30)–C(31)	1.390(5)
C(10)–C(11)	1.389(4)	C(31)–C(32)	1.384(4)
Cl(1)–Pt(1)–Cl(2)	93.68(2)	C(28)–C(29)–C(30)	120.0(3)
Cl(1)–Pt(1)–Cl(3)	90.36(3)	C(29)–C(30)–C(31)	120.1(3)
Cl(1)–Pt(1)–Cl(4)	87.22(2)	C(30)–C(31)–C(32)	120.4(3)
Cl(1)–Pt(1)–N(1)	174.39(7)	C(27)–C(32)–C(31)	120.3(3)
Cl(1)–Pt(1)–N(3)	87.87(7)	N(4)–C(4)–C(5)	117.4(2)
Cl(2)–Pt(1)–Cl(3)	87.48(2)	N(3)–C(4)–N(4)	122.2(3)
Cl(2)–Pt(1)–Cl(4)	91.25(2)	C(4)–C(5)–C(6)	109.5(2)
Cl(2)–Pt(1)–N(1)	89.34(7)	N(2)–C(7)–C(8)	117.1(2)
Cl(2)–Pt(1)–N(3)	175.92(7)	N(2)–C(7)–C(14)	124.9(2)
Cl(3)–Pt(1)–Cl(4)	177.19(2)	C(8)–C(7)–C(14)	117.9(2)
Cl(3)–Pt(1)–N(1)	85.05(7)	C(7)–C(8)–C(13)	120.2(2)
Cl(3)–Pt(1)–N(3)	96.29(7)	C(7)–C(8)–C(13)	120.2(2)
Cl(4)–Pt(1)–N(1)	97.45(7)	C(9)–C(8)–C(13)	119.2(3)
Cl(4)–Pt(1)–N(3)	85.05(7)	C(7)–C(8)–C(9)	120.6(2)
N(1)–Pt(1)–N(3)	89.43(10)	C(8)–C(9)–C(10)	120.3(3)
Pt(1)–N(1)–C(1)	133.1(2)	C(9)–C(10)–C(11)	119.7(3)
C(1)–N(2)–C(7)	125.8(2)	C(10)–C(11)–C(12)	119.9(3)
Pt(1)–N(3)–C(4)	133.3(2)	C(11)–C(12)–C(13)	120.6(3)
C(4)–N(4)–C(20)	126.4(3)	C(8)–C(13)–C(12)	120.1(3)
N(2)–C(1)–C(2)	114.6(2)	C(7)–C(14)–C(19)	122.2(2)
N(1)–C(1)–N(2)	122.7(2)	C(15)–C(14)–C(19)	119.5(2)
N(1)–C(1)–C(2)	122.1(3)	C(7)–C(14)–C(15)	118.3(2)
C(1)–C(2)–C(3)	116.5(2)	C(14)–C(15)–C(16)	120.3(3)
N(3)–C(4)–C(5)	119.5(3)	C(15)–C(16)–C(17)	120.2(3)
C(21)–C(22)–C(23)	119.7(3)	C(16)–C(17)–C(18)	119.8(3)
C(22)–C(23)–C(24)	120.3(3)	C(17)–C(18)–C(19)	120.8(3)
C(23)–C(24)–C(25)	120.1(3)	C(14)–C(19)–C(18)	119.3(3)
C(24)–C(25)–C(26)	119.8(3)	N(4)–C(20)–C(27)	124.8(2)
C(21)–C(26)–C(25)	120.2(3)	C(21)–C(20)–C(27)	118.9(2)
C(20)–C(27)–C(28)	118.3(2)	N(4)–C(20)–C(21)	116.3(2)
C(20)–C(27)–C(32)	123.0(2)	C(20)–C(21)–C(22)	120.0(2)
C(28)–C(27)–C(32)	118.6(2)	C(20)–C(21)–C(26)	120.0(2)
C(27)–C(28)–C(29)	120.7(3)	C(22)–C(21)–C(26)	119.9(3)

N=C of 104.4 and 111.8°, indicating a weak conjugation of the π system.

Spectroscopic data agree well with the proposed structure of the platinum(IV) complexes with 1,3-diaza-1,3-dienes (Scheme 1). IR spectra show the disappearance of the C≡N stretching vibrations and the appearance of the two strong ν(C=N) vibrations, a new strong and characteristic band due to δ(C–H) of the aromatics and appearance of N–H stretching vibrations. ^{13}C-{^1H} NMR spectra display, in particular, two signals from the two different carbons of the *C*=N bond (range δ 166–180) and signals in the ^{195}Pt NMR spectra emerge usually in the range of δ 100–186, which is *ca*. 300 ppm more positive than the characteristic values found for platinum(IV) $[PtCl_4(imine)_2]$ complexes.[13,14,17]

Reduction of $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ complexes

Recently some of us suggested a novel method for generation of a variety of platinum(II) complexes, including the difficult-to-obtain imine compounds, that involves reduction of the corresponding platinum(IV) complexes by carbonyl stabilized phosphorus ylides, $Ph_3P{=}CHCO_2R$, in non-aqueous media. The reaction now is extended to (1,3-diaza-1,3-diene)-platinum(IV) compounds and it is found that, similarly to other cases,[27] the reduction (route (*b*) in Scheme 1) with $Ph_3P{=}CHCO_2Me$ proceeds smoothly at room temperature. The products were purified by chromatography on silica gel and isolated in good yields. The main features of the spectroscopic data for the (1,3-diaza-1,3-diene)platinum(II) complexes are similar to those of the corresponding platinum(IV) complexes. The most significant difference is in their ^{195}Pt NMR spectra which display individual signals in a range from δ −2026 to −2143, which is in good argeement with the range found for other platinum(II) $[PtCl_2(imine)_2]$ compounds.[27]

Platinum(II)-mediated nitrile–imine coupling

A mixture of the geometrical isomers *cis*/*trans*-$[PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2]$ (which were also obtained as indicated above *via* reduction, by a phosphorus ylide, of the corresponding platinum(IV) species) was reliably detected, by TLC and NMR monitoring, in the mother liquor from the synthesis of $[PtCl_2(HN{=}CPh_2)_2]$ recently reported by Grøndahl and *et al*.[20] and reproduced by us (see Experimental section). However, these two by-products are formed along with two other unidentified species thus making difficult their isolation, from the reaction mixture, in an analytically pure form. Thus, the addition of benzophenone imine to the acetonitrile ligands in $[PtCl_2(MeCN)_2]$ occurs in accord with eqn. (1) but this is only a

$$[PtCl_2(MeCN)_2] + 2\ HN{=}CPh_2 \longrightarrow [PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2] \quad (1)$$

side-reaction accompanying the substitution and perhaps some other processes.

To enhance the selectivity of the nitrile–imine coupling at the platinum(II) centre we employed an (organonitrile)platinum(II) complex bearing an acceptor substituent attached to the nitrile group, *i.e. cis*/*trans*-$[PtCl_2(PhCN)_2]$. The latter is more reactive[18] towards nucleophilic addition than its acetonitrile analogue. The interaction is rather fast at 20–25 °C and gives two products. The first is a material so insoluble in the most common solvents that we were unable to obtain either its NMR (even at significant acquisition time) or FAB-MS spectra. However, based on elemental analyses and IR spectroscopy data we tentatively formulate this complex as the polymer $[PtCl_2\{\mu\text{-}N,N\text{-}NH{=}C(Ph)N{=}CPh_2\}]_\infty$. The alternative structure with the same empirical formula, *i.e.* $[PtCl_2(HN{=}CPh_2)(PhCN)]$, also cannot be ruled out but the absence of ν(C≡N) stretching vibrations and the low solubility favour the polymeric compound. The second product isolated from the mixture is formulated as $[PtCl_2(NH{=}CPh_2)\{NH{=}C(Ph)N{=}CPh_2\}]$ which is derived from both the addition and substitution reactions. Although we were unable to obtain crystals suitable for X-ray study, our main arguments confirming the formulation are based upon: (*i*) satisfactory elemental anlyses; (*ii*) observation of peaks due to the parent ion $[M]^+$ in FAB^+-MS; (*iii*) three different signals from carbons of the *C*=N bonds in ^{13}C-{^1H} NMR spectrum, while the ^{195}Pt NMR spectrum gives only one signal thus indicating isomeric purity of the compound.

Concluding remarks

In conclusion it is worthwhile to mention that (*i*) the nitrile–imine coupling is metal-mediated since it was demonstrated that benzophenone imine does not react with acetonitrile or propionitrile even under harsh conditions (50 °C, $CDCl_3$, 12 h).

The complexes are presumably formed by nucleophilic attack of the imine N atom on the electrophilically activated carbon atom of the organonitrile. (*ii*) In coordination chemistry, complexes containing the 1,3-diaza-1,3-diene linkage are known, although scarce, and all four reported examples are azametallacycles [M]–NH=C(R^1)–N=C(R^2)–NH.[28–31] None of these complexes was prepared by direct nitrile–imine coupling, being formed *e.g.* in an unusual reaction between $[Pt(PPh_3)_4]$ or $[RuCpCl(PPh_3)_2]$ and CF_3CN,[28,29] by metal-mediated reaction of cyanoguanidine with such nucleophiles as oximes or alcohols[30] or by the addition of $Li[(NH)_2CPh]$ to $[PtCl_2(PhCN)_2]$.[31] (*iii*) In organic chemistry 1,3-diaza-1,3-dienes are useful for syntheses of six-membered nitrogen containing heterocycles and their involvement in [4 + 2] cycloadditions to give these systems was a subject of rapt attention.[19,32] The known synthetic pathways[19] to achieve 1,3-diaza-1,3-dienes do not include direct interaction between organonitriles and imines. Our results indicate that, in the case of the platinum(II) species, liberation of 1,3-diaza-1,3-dienes can be achieved by the reaction of (1,3-diaza-1,3-diene)platinum(II) species and two equivalents of 1,2-bis(diphenylphosphino)ethane (dppe) in $CHCl_3$. This route [(*c*) in Scheme 1] was exemplified upon treatment of $[PtCl_2\{NH=C(Et)N=CPh_2\}_2]$ with dppe to give in a quantitative reaction, along with free NH=C(Et)N=CPh_2 retained in solution, the solid complex $[Pt(dppe)_2]Cl_2$ (see Experimental section).

Experimental

Materials and instrumentation

Benzophenone imine (Aldrich), $Ph_3P=CHCO_2Me$ (Lancaster) and solvents were obtained from commercial sources and used as received. The complexes $[PtCl_4(RCN)_2]$ (R = Me or Et) were prepared as previously described.[13] C, H and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Melting points were determined on a 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 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. Infrared spectra (4000–400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets, ^1H, ^{13}C-$\{^1H\}$, ^{31}P-$\{^1H\}$ and ^{195}Pt NMR spectra on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ (by using aqueous $K_2[PtCl_4]$, δ −1630, as a standard), with half height linewidths in parentheses.

Crystal structure determination of *cis*-$[PtCl_4\{NH=C(Et)N=CPh_2\}_2]$

Yellow blocks of the complex were grown by slow evaporation of a dichloromethane–diethyl ether mixture. X-Ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo-Kα radiation ($\lambda = 0.71073$ Å) and ϕ-scan data collection mode with a Collect[33] collection program. The Denzo/Scalepack[34] program pakage was used for cell refinements and data reduction. A multi-scan absorption correction, based on equivalent reflections (XPREP in SHELXTL v. 5.1[35]), was applied. The structure was solved by direct methods using SIR 97.[36] Structure refinements were carried out with SHELXL 97.[37] All non-hydrogen atoms were refined anisotropically. Aromatic hydrogens and CH_2 hydrogens were placed in idealized positions. Hydrogens in NH groups were refined with fixed $U_{iso} = 0.05$ Å^2. Crystallographic data are summarized in Table 2.

CCDC reference number 186/2310.

See http://www.rsc.org/suppdata/dt/b0/b008154j/ for crystallographic files in .cif format.

Table 2 Crystallographic data for *cis*-$[PtCl_4\{NH=C(Et)N=CPh_2\}_2]$

Empirical formula	$C_{32}H_{32}Cl_4N_4Pt$
M	809.50
T/K	120
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14)
a/Å	8.7930(2)
b/Å	25.2910(5)
c/Å	14.1000(3)
β/°	93.3360(10)
V/Å^3	3130.30(12)
Z	4
μ(Mo-Kα)/mm^{-1}	4.853
Collected reflections	31 459
Unique reflections	6453
Observed reflections	5796
*R*1	0.0218
*wR*2	0.0488

Addition of $Ph_2C=NH$ to organonitriles in $[PtCl_4(RCN)_2]$

***trans*- and *cis*-$[PtCl_4\{NH=C(Me)N=CPh_2\}_2]$.** $Ph_2C=NH$ (17 mg, 0.095 mmol) was added to a suspension of $[PtCl_4(MeCN)_2]$ (a mixture of *trans* and *cis* isomers; 20 mg, 0.048 mmol) in CH_2Cl_2 (5 mL) at 20–25 °C and the reaction mixture left to stand for 2 h until complete homogenization, whereafter 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 $[PtCl_4\{NH=C(Me)N=CPh_2\}_2]$. Yield 77%. In accord with ^1H and ^{195}Pt NMR data, the complex is a mixture of *trans* and *cis* isomers in an approximate ratio 3:2. Calc. for $C_{30}H_{28}Cl_4N_4Pt$: C, 46.11; H, 3.61; N, 7.17. Found: C, 46.21; H, 3.71; N, 6.73%. FAB$^+$-MS: *m*/*z* 803 $[M + H + Na]^+$; 781, $[M + H]^+$, 710, $[M - 2Cl]^+$; and 638, $[M - 4Cl]^+$. mp = 196–199 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3274m-w *ν*(N–H), 1633s and 1610s *ν*(C=N), 1597s *ν*(C=C) and 697s *δ*(C–H). ^1H NMR in DMSO-d_6: δ 1.95 (s, 3H, Me of *cis* isomer), 1.99 (s, 3H, Me of *trans* isomer), 7.50 ("t"), 7.57 (m), 7.67 ("d") and 7.73 (m)(10H of each isomer, Ph), 9.70 (s, br, J_{PtH} 18, NH of *cis* isomer) and 9.32 (s, br, J_{PtH} 29 Hz, NH of *trans* isomer). ^{13}C-$\{^1H\}$ NMR in DMSO-d_6: δ 22.4 (J_{PtC} 33, Me of *cis* isomer), 22.8 (J_{PtC} 28, Me of *trans* isomer), 128.4, 128.5, 128.6, 129.6 and 129.9 ($CH_{ortho,\ meta}$), 131.2, 131.6 and 132.7 (CH_{para}), 135.6, 136.0 and 137.0 (C_{ipso}), 168.2 (C=N of *cis* isomer), 175.5 (J_{PtC} 16, C=NH of *cis* isomer), 166.2 (C=N of *trans* isomer) and 176.5 (J_{PtC} 8 Hz, C=NH of *trans* isomer). ^{195}Pt NMR in DMSO-d_6: δ +184 (660)(*cis* isomer) and +100 (600 Hz)(*trans* isomer).

***trans*-$[PtCl_4\{NH=C(Et)N=CPh_2\}_2]$.** $Ph_2C=NH$ (16 mg, 0.089 mmol) was added to a solution of *trans*-$[PtCl_4(EtCN)_2]$ (20 mg, 0.045 mmol) in CH_2Cl_2 (3 mL) at −15 °C and the reaction mixture left to stand for 5 h, whereafter the solvent was evaporated to dryness in a flow of N_2, the residue washed with three 5 mL portions of Et_2O and dried *in vacuo* at room temperature. Yield 79%. Calc. for $C_{32}H_{32}Cl_4N_4Pt$: C, 47.48; H, 3.98; N, 6.92. Found: C, 47.33; H, 3.87; N, 6.47%. FAB$^+$-MS: *m*/*z* 809, $[M]^+$; 738, $[M - 2Cl]^+$ and 703, $[M - 3Cl]^+$. mp = 197–198 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3338m-w *ν*(N–H), 1651s and 1603s *ν*(C=N), 1587s *ν*(C=C) and 697s *δ*(C–H). TLC (eluent chloroform–acetone 30:1): $R_f = 0.63$. ^1H NMR in $CDCl_3$: δ 1.02 (t, *J* 7.2, 3H) and 2.24 (q, *J* 7.5, 2H)(Et), 7.46 (t, *J* 7.5, 4H), 7.53 (t, *J* 7.2, 2H) and 7.84 (d, *J* 7.5 Hz, 4H)(Ph); NH was not detected probably due to overlapping with the intense signals of the Ph groups. ^{13}C-$\{^1H\}$ NMR in $CDCl_3$: δ 9.8 and 30.8 (Et), 128.6 and 129.7 ($CH_{ortho\ and\ meta}$), 132.0 (CH_{para}), 136.2 (C_{ipso})(Ph), 170.2 (C=N) and 179.9 (C=NH). ^{195}Pt NMR in $CDCl_3$: δ +186 (500 Hz).

***cis*-$[PtCl_4\{NH=C(Et)N=CPh_2\}_2]$.** $Ph_2C=NH$ (16 mg, 0.089 mmol) was added to a solution of $[PtCl_4(EtCN)_2]$ (a mixture of *cis* and *trans* isomers in *ca.* 6:1 ratio; 20 mg, 0.045 mmol) in

CH_2Cl_2 (3 mL) at 20–25 °C and the reaction mixture left to stand for 2 h, whereafter the solvent was evaporated to dryness in a flow of N_2, the obtained solid washed with three 5 mL portions of Et_2O and dried *in vacuo* at room temperature. Yield of $[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ 81%. Found: C, 48.26; H, 3.92; N, 6.38%. FAB^+-MS: *m/z* 809, $[M]^+$; 774, $[M - Cl]^+$; 738, $[M - 2Cl]^+$; and 703, $[M - 4Cl]^+$. TLC (eluent chloroform–acetone = 30 : 1) displayed two spots with $R_f = 0.45$ (dominant in intensity) and 0.63 (specific for the *trans* isomer see above).

Pure *cis*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ was obtained by chromatographic separation of *cis*/*trans*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ on Merck silica gel 60 (70–230 mesh) (eluent: CH_2Cl_2–Et_2O 5 : 1, v/v). Found: C, 47.23; H, 3.82; N. 7.29%. FAB^+-MS: *m/z* 809, $[M]^+$; 761, $[M - 2Cl + Na]^+$; 738, $[M - 2Cl]^+$; and 667, $[M - 4Cl]^+$. mp = 207–208 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3327m-w *ν*(N–H), 1652s and 1604s *ν*(C=N), 699s *δ*(C–H). TLC (eluent chloroform–acetone = 30 : 1): $R_f = 0.45$. ^1H NMR in $CDCl_3$: *δ* 0.81 (t, *J* 7.2, 3H) and 2.10 (q, *J* 7.5, 2H)(Et), 7.44 (t, *J* 7.8, 4H), 7.55 (t, *J* 6.9, 2H) and 7.71 (d, *J* 8.4 Hz, 4H)(Ph); NH was not detected probably due to overlapping with the intense signals of the Ph groups. ^{13}C-$\{^1H\}$ NMR in $CDCl_3$: *δ* 9.8 and 30.8 (Et), 128.6 and 130.4 ($CH_{ortho\ and\ meta}$), 132.0 (CH_{para}), 136.2 (C_{ipso})(Ph), 170.3 (C=N) and 179.5 (C=NH). ^{195}Pt NMR in $CDCl_3$: *δ* −56 (600 Hz). Crystals of the *cis* isomer suitable for X-ray diffraction study were obtained by evaporation of a dichloromethane–diethyl ether solution of the isomeric mixture at room temperature.

Reaction of $Ph_2C{=}NH$ and $[PtCl_2(MeCN)_2]$

The previously described reaction[20] between $Ph_2C{=}NH$ and $[PtCl_2(MeCN)_2]$ (the authors reported the reaction with *trans*-$[PtCl_2(MeCN)_2]$ as the starting material although the complex is, in fact, a mixture of *cis* and *trans* isomers where the *trans* form is the minor component, *i.e.* 16%[22]) was reproduced. In our hands complete homogenization of the reaction mixture was reached after 3 d (10 d in Ref. 20) at 20–25 °C. However, the reaction mixture was stirred for 10 d and then the solvent was evaporated to dryness and the residue subjected to both TLC and NMR monitoring that allowed identification of the two isomers of $[PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2]$ obtained in the independent synthesis (see below).

Reaction of $Ph_2C{=}NH$ and $[PtCl_2(PhCN)_2]$

$Ph_2C{=}NH$ (30 mg, 0.170 mmol) was added to a solution of $[PtCl_2(PhCN)_2]$ (a mixture of *cis* and *trans* isomers;[38] 40 mg, 0.085 mmol) in $CHCl_3$ (5 mL) at 20–25 °C and the reaction mixture left to stand for 2 h, whereafter the yellow precipitate (22 mg) formed (complex **A**) was removed by filtration. The filtrate was subjected to column chromatography [Merck silica gel 60 (70–230 mesh), eluent CH_2Cl_2–Et_2O 5 : 1, v/v] to separate a rather intensively colored yellow complex **B** (TLC: $R_f = 0.68$, eluent chloroform–acetone 20 : 1, v/v).

Complex **A** is a highly insoluble material and we were unable to obtain its FAB^+-MS (3-nitrobenzyl alcohol and glycerol matrixes) and NMR spectra. However, its elemental analyses and IR spectrum give certain evidence in favor of the product of monosubstitution, *i.e.* $[PtCl_2(HN{=}CPh_2)(PhCN)]$ or, in view of its insolubility, of the polymeric coupled product $[PtCl_2\{\mu\text{-}N,N\text{-}NH{=}C(Ph)N{=}CPh_2\}]_\infty$ [Calc. for $C_{20}H_{16}Cl_2N_2Pt$: C, 43.63; H, 2.91; N, 5.10. Found: C, 44.40; H, 2.91; N, 5.10%. mp = 189–192 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3225m-w *ν*(N–H), 1652s *ν*(C=N), 1595s *ν*(C=C) and 695s *δ*(C–H)].

$[PtCl_2(HN{=}CPh_2)\{NH{=}C(Ph)N{=}CPh_2\}]$ **B**. Yield 27%. Calc. for $C_{33}H_{27}Cl_2N_3Pt{\cdot}\frac{1}{2}CH_2Cl_2$: C, 52.04; H, 3.62; N, 5.44. Found: C, 52.16; H, 3.53; N, 5.58%. FAB^+-MS: *m/z* 754, $[M + Na]^+$; 731, $[M]^+$; 695 $[M - HCl]^+$; and 661, $[M - 2HCl]^+$. mp = 169–171 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3225m-w *ν*(N–H), 1624s *ν*(C=N), 1598s *ν*(C=C) and 695s *δ*(C–H). ^1H NMR in $CDCl_3$: *δ* 6.90 (d, *J* 7.2, 2H), 7.10 (t, *J* 7.5, 2H), 7.18 (d, *J* 7.5, 2H), 7.28–7.56 (m, 12H), 7.76 (m, 6H), 8.28 (d, *J* 7.0 Hz, 2H) and 9.42 (s, br, NH). ^{13}C-$\{^1H\}$ NMR in $CDCl_3$: *δ* 128.5, 129.9 ($CH_{ortho,\ meta}$), 131.9 (CH_{para}) and 136.2 (C_{ipso})(CPh_2), signals of the other Ph groups in the range 126.4 to 137.7, 172.0, 174.6 and 179.4 (C=N). ^{195}Pt NMR in $CDCl_3$: *δ* −2018 (640 Hz).

Reduction of the (1,3-diaza-1,3-diene)platinum(IV) complexes

The platinum(IV) complexes $[PtCl_4\{NH{=}C(R)N{=}CPh_2\}_2]$ (R = Me or Et) were reduced by one equivalent of the carbonyl-stabilized phosphorus ylide $Ph_3P{=}CHCO_2Me$ in CH_2Cl_2 at 20–25 °C for *ca.* 3–4 h in accord with a recently suggested procedure.[27]

$[PtCl_2\{NH{=}C(Me)N{=}CPh_2\}_2]$. The complex was prepared from a mixture of *cis*- and *trans*-$[PtCl_4\{NH{=}C(Me)N{=}CPh_2\}_2]$. Yield 55%. Calc. for $C_{30}H_{28}Cl_2N_4Pt$: C, 50.71; H, 3.97; N, 7.89. Found: C, 50.88; H, 3.72; N, 7.18%. FAB^+-MS: *m/z* 733, $[M + Na]^+$; 710, $[M]^+$; and 638, $[M - 2Cl]^+$. mp = 199–201 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3244m-w *ν*(N–H), 1634s *ν*(C=N), 1598s *ν*(C=C) and 697s *δ*(C–H). TLC (eluent chloroform–acetone = 20 : 1) displayed two spots with $R_f = 0.49$ (dominant in intensity) and 0.30. NMR monitoring indicated that the compound is a mixture of two isomers in the approximate ratio 5 : 1. Major isomer: ^1H NMR in $CDCl_3$ *δ* 1.85 (s, 3H, Me), 7.46 (t, *J* 7.4, 4H), 7.54 (t, *J* 7.0, 2H), 7.82 (d, *J* 7.0 Hz, 4H)(Ph), NH not detected probably due to overlap with intense signals of the Ph groups; ^{13}C-$\{^1H\}$ NMR in $CDCl_3$ *δ* 24.1 (Me), 128.5 and 129.6 ($CH_{ortho\ and\ meta}$), 131.5 (CH_{para}), 135.9 (C_{ipso})(Ph), 168.2 (C=N) and 175.9 (C=NH); ^{195}Pt NMR in $CDCl_3$ *δ* −2119 (580 Hz). Minor isomer: ^1H NMR in $CDCl_3$ *δ* 1.93 (s, 3H, Me), 7.4–7.55 (6H, signal overlapped by the one due to the major isomer), 7.68 (d, *J* 7.5 Hz, 4H)(Ph), NH not detected probably due to overlap with intense signals of the Ph groups; ^{13}C-$\{^1H\}$ NMR in $CDCl_3$ *δ* 24.7 (Me), 128.1 and 129.4 ($CH_{ortho\ and\ meta}$), 130.8 (CH_{para}), (C_{ipso})(Ph), (C=N) and (C=NH) not detected; ^{195}Pt NMR not detected.

***trans*-$[PtCl_2\{NH{=}C(Et)N{=}CPh_2\}_2]$.** Yield 76%. Calc. for $C_{32}H_{32}Cl_2N_4Pt$: C, 52.04; H, 4.37; N, 7.59%. Found: C, 51.80; H, 4.27; N, 7.59. FAB^+-MS: *m/z* 761, $[M + Na]^+$; 738, $[M]^+$; and 667 $[M - 2Cl]^+$. mp = 207–208 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3239m-w *ν*(N–H), 1648s *ν*(C=N), 1596s *ν*(C=C) and 690s *δ*(C–H). TLC (eluent chloroform–acetone 15 : 1): $R_f = 0.65$. ^1H NMR in $CDCl_3$: *δ* 0.95 (t, *J* 7.5, 3H) and 2.14 (q., *J* 7.8, 2H)(Et), 7.28 (t, *J* 7.8, 4H), 7.40 (t, *J* 7.2, 2H) and 7.71 (d, *J* 8.1 Hz, 4H)(Ph), NH not detected (may be overlapped by intense signals of Ph groups). ^{13}C-$\{^1H\}$ NMR in $CDCl_3$: *δ* 9.7 and 30.5 (Et), 128.2 and 129.6 ($CH_{ortho\ and\ meta}$), 130.7 (CH_{para}), 136.0 (C_{ipso})(Ph), 166.4 (C=N) and 180.8 (C=NH). ^{195}Pt NMR in $CDCl_3$: *δ* −2026 (680 Hz).

***cis*- and *trans*-$[PtCl_2\{NH{=}C(Et)N{=}CPh_2\}_2]$.** The amount of the isolated platinum(IV) complex *cis*-$[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$ was insufficient to perform synthetic experiments. Therefore the reduction was carried out starting from the *cis*/*trans* isomeric mixture of $[PtCl_4\{NH{=}C(Et)N{=}CPh_2\}_2]$. Yield is 72%. Calc. for $C_{32}H_{32}Cl_2N_4Pt{\cdot}\frac{1}{4}CH_2Cl_2$: C, 50.98; H, 4.31; N, 7.37. Found: C, 51.23; H, 4.23; N, 7.20%. FAB^+-MS: *m/z* 761, $[M + Na]^+$; 738 $[M]^+$; and 667, $[M - 2Cl]^+$. mp = 201–203 °C (decomp.). IR spectrum in KBr, selected bands, cm^{-1}: 3246m-w *ν*(N–H), 1635s *ν*(C=N) and 699s *δ*(C–H). TLC (eluent chloroform–acetone = 15 : 1) displayed two spots with $R_f = 0.65$ and 0.47 (the latter is dominant in intensity). NMR characteristics of the *cis* isomer were obtained by comparison of spectra of *cis*/*trans*-$[PtCl_2\{NH{=}C(Et)N{=}CPh_2\}_2]$ with those of pure

trans-[$PtCl_2${NH=C{Et}N=CPh_2}$_2$] (see above). NMR monitoring indicated that the compound is a mixture of two isomers in an approximate ratio 20:10. *cis* Isomer (the major isomer): ^{1}H NMR in $CDCl_3$ δ 0.85 (t, *J* 7.5, 3H) and 2.10 (q, *J* 7.2 Hz, 2H)(Et), 7.47 (t, *J* 7.5, 4H), 7.52 (t, *J* 7.0, 2H) and 7.86 (d, *J* 7.8 Hz, 4H)(Ph), NH not detected (may be overlapped by intense signals of Ph groups); ^{13}C-{^{1}H} NMR in $CDCl_3$ δ 9.5 and 30.0 (Et), 128.5 and 129.7 ($CH_{ortho\ and\ meta}$), 131.5 (CH_{para}), 136.1 (C_{ipso})(Ph), 168.0 (C=N) and 179.9 (C=NH); ^{195}Pt NMR in $CDCl_3$ δ −2143 (620 Hz). The minor isomer is *trans*-[$PtCl_2${NH=C(Et)N=CPh_2}$_2$] (see above).

Liberation of the 1,3-diaza-1,3-diene from *trans*-[$PtCl_2${NH=C(Et)N=CPh_2}$_2$]

dppe (9.7 mg, 0.024 mmol) was added at room temperature to a solution of *trans*-[$PtCl_2${NH=C(Et)N=CPh_2}$_2$] (9.0 mg, 0.012 mmol) in chloroform (2 mL). A colorless crystalline precipitate of [Pt(dppe)$_2$]Cl_2 was filtered off after 30 min (11.5 mg, 98%), the filtrate was evaporated to dryness under a flow of dinitrogen at 20–25 °C, redissolved in $CDCl_3$ and the "free" ligand characterized by NMR spectroscopy. ^{1}H NMR in $CDCl_3$: δ 1.05 (t, *J* 7.4, 3H)(Me), 2.16 (q, *J* 7.3 Hz, 2H)(CH_2) and 7.30–7.50 (m, 10H)(Ph). ^{13}C-{^{1}H} NMR in $CDCl_3$: δ 9.9 (CH_3), 29.5 (CH_2), 126.6–137.0 (phenyl C), 138.3 (C_{ipso}) 165.2 (C=N) and 178.3 (C=NH).

Complex [Pt(dppe)$_2$]Cl_2. Calc. for $C_{52}H_{48}Cl_2P_4Pt\cdot\frac{1}{8}CDCl_3$: C, 58.09; H, 4.46. Found: C, 57.92; H, 4.36%. IR spectrum in KBr, selected bands, cm^{-1}: 1481m-w ν(P–C_{Ph}), 1435s ν(P–CH_2), 695 and 701s δ(C–H_{Ph}). ^{1}H NMR in $CDCl_3$: δ 3.38 (t, 6.90 Hz, 4H)(CH_2) and 7.30–7.70 (m, 20H)(Ph). ^{31}P-{^{1}H} NMR in $CDCl_3$ (relative to H_3PO_4): δ 47.7 (2364 Hz) [lit.[39] ^{31}P NMR spectrum in $CDCl_3$: δ 47.0 (2360 Hz)].

Acknowledgements

D. G. and G. W. are grateful to the PRAXIS XXI program for fellowships (BPD16368/98 and BPD11779/97). V. Yu. K. is very much obliged to INTAS (grant 97-0166) and the PRAXIS XXI program (grant BCC16428/98) for financial support of this study. V. Yu. K. and M. H. thank the Nordic Council of Ministers for a grant. A. J. L. P. thanks the FCT (Foundation for Science and Tecnology) and the PRAXIS XXI program (Portugal) for financial support. The authors thank Dr Irina A. Balova for valuable comments on the manuscript, Dr M. F. C. Guedes da Silva, Dr M. N. Kopylovich and Mrs N. A. Bokach for experimental assistance.

References

1 A. J. Fatiadi, in *The Chemistry of Triple-bonded Functional Groups*, Part 2, eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1983, p. 1066; E. N. Zilberman, *Reactions of Nitriles*, [in Russian], Khimia Publishers, Moscow, 1972, p. 166.
2 R. A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, 1996, **147**, 299.
3 B. N. Storhoff and H. C. Lewis, *Coord. Chem. Rev.*, 1977, **23**, 1; H. Endres, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, p. 261; A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals*, Academic Press, London, 1976; R. W. Hay, in *Reactions of Coordinated Ligands*, ed. P. S. Braterman, Plenum Press, New York, 1989, vol. 2, p. 280.
4 L. Knoll, *J. Organomet. Chem.*, 1978, **155**, C63; L. Knoll and H. Wolff, *Chem. Ber.*, 1979, **112**, 2709; L. Knoll, *J. Organomet. Chem.*, 1980, **186**, C42; J. Vicente, M. T. Chicote, M. A. Beswick and M. C. Ramirez de Arellano, *Inorg. Chem.*, 1996, **35**, 6592; J. Vicente, M. T. Chicote, J. Fernández-Baeza and F. Lahoz, *Inorg. Chem.*, 1991, **30**, 3617; J. Vicente, M. T. Chicote, J. Fernández-Baeza, A. Fernández-Baeza and P. G. Jones, *J. Am. Chem. Soc.*, 1993, **115**, 794; P. Braunstein, D. Matt, Y. Dusausoy and J. Protas, *J. Chem. Soc., Chem. Commun.*, 1979, 763; P. Braunstein, D. Matt, Y. Dusausoy and J. Fischer, *Organometallics*, 1983, **2**, 1410; A. J. Deeming, S. Donovan-Mtunzi, S. E. Kabir, A. J. Arce and Y. De Sanctis, *J. Chem. Soc., Dalton Trans.*, 1987, 1457; M. H. Chisholm, K. Folting, J. C. Huffman and N. S. Marchant, *Organometallics*, 1986, **5**, 602; M. H. Chisholm, J. C. Huffman and N. S. Marchant, *Polyhedron*, 1988, **7**, 919; B. Corain, M. Basato and A. C. Veronese, *J. Mol. Catal.*, 1993, **81**, 133.
5 H.-G. Ang, C.-H. Koh, L.-L. Koh, W.-L. Kwik, W.-K. Leong and W.-Y. Leong, *J. Chem. Soc., Dalton Trans.*, 1993, 847; F. A. Cotton, L. M. Daniels, C. A. Murillo and X. Wang, *Polyhedron*, 1998, **17**, 2781; F. A. Cotton and F. E. Kühn, *J. Am. Chem. Soc.*, 1996, **118**, 5826.
6 R. Bertani, D. Catanese, R. A. Michelin, M. Mozzon, G. Bandoli and A. Dolmella, *Inorg. Chem. Commun.*, 2000, **3**, 16; C. S. Chin, D. Chong, B. Lee, H. Jeong, G. Won, Y. Do and Y. J. Park, *Organometallics*, 2000, **19**, 638; A. Mommertz, R. Leo, W. Massa and K. Dehnicke, *Z. Naturforsch., Teil B*, 1998, **53**, 887.
7 G. Albertin, S. Antoniutti, A. Bacchi, M. Bergamo, E. Bordignon and G. Pelizzi, *Inorg. Chem.*, 1998, **37**, 479; G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon, P. M. Dolcetti and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1997, 4435; G. Albertin, S. Antoniutti, E. Bordignon and S. Pattaro, *J. Chem. Soc., Dalton Trans.*, 1997, 4445.
8 R. Mason, K. M. Thomas, A. R. Galbraith, B. L. Show and C. M. Elson, *J. Chem. Soc., Chem. Commun.*, 1973, 297; S. Du, N. Zhu and X. Wu, *Polyhedron*, 1994, **13**, 301.
9 K. Wieghardt, W. Holzbach, E. Hoffer and J. Weiss, *Chem. Ber.*, 1981, **114**, 2700; A. C. McDonell, S. G. Vasudevan, M. J. O'Connor and A. G. Wedd, *Aust. J. Chem.*, 1985, **38**, 1017.
10 G. Wagner, A. J. L. Pombeiro, Yu. N. Kukushkin, T. B. Pakhomova, A. D. Ryabov and V. Yu. Kukushkin, *Inorg. Chim. Acta*, 1999, **292**, 272.
11 A. Romero, A. Vegas and A. Santos, *J. Organomet. Chem.*, 1986, **310**, C8; J. Lopez, A. Santos, A. Romero and A. M. Echavarren, *J. Organomet. Chem.*, 1993, **443**, 221; C. J. Jones, J. A. McCleverty and A. S. Rothim, *J. Chem. Soc., Dalton Trans.*, 1986, 109; M. O. Albers, S. F. A. Crosby, D. C. Liles, D. J. Robinson, A. Shaver and E. Singleton, *Organometallics*, 1987, **6**, 2014; M. A. Cinellu, S. Stoccoro, G. Minghetti, A. L. Bandini, G. Banditelli and B. Bovio, *J. Organomet. Chem.*, 1989, **372**, 311; C. Pearson and A. L. Beauchamp, *Inorg. Chem.*, 1998, **37**, 1242; K. S.-Y. Leung and W.-T. Wong, *J. Chem. Soc., Dalton Trans.*, 1998, 1939.
12 P. F. Kelly and A. M. Z. Slawin, *J. Chem. Soc., Chem. Commun.*, 1999, 1081.
13 V. Yu. Kukushkin, T. B. Pakhomova, Yu. N. Kukushkin, R. Herrmann, G. Wagner and A. J. L. Pombeiro, *Inorg. Chem.*, 1998, **37**, 6511.
14 V. Yu. Kukushkin, T. B. Pakhomova, N. A. Bokach, G. Wagner, M. L. Kuznetsov, M. Galanski and A. J. L. Pombeiro, *Inorg. Chem.*, 2000, **39**, 216.
15 G. Wagner, A. J. L. Pombeiro, N. A. Bokach and V. Yu. Kukushkin, *J. Chem. Soc., Dalton Trans.*, 1999, 4083; V. Yu. Kukushkin, I. V. Ilichev, G. Wagner, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1999, 3047; V. Yu. Kukushkin, I. V. Ilichev, M. A. Zhdanova, G. Wagner and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 2000, 1567.
16 V. Yu. Kukushkin, T. Nishioka, S. Nakamura, I. Kinoshita and K. Isobe, *Chem. Lett.*, 1997, 189; Yu. N. Kukushkin, N. P. Kiseleva, E. Zangrando and V. Yu. Kukushkin, *Inorg. Chim. Acta*, 1999, **285**, 203; A. J. L. Pombeiro, D. L. Hughes and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1988, 1052; A. J. L. Pombeiro, *New J. Chem.*, 1994, **18**, 163; M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva and A. J. L. Pombeiro, *J. Chem. Soc., Dalton Trans.*, 1994, 3299; M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, C. Amatore and J.-N. Verpeaux, *Organometallics*, 1994, **13**, 3943; M. F. C. Guedes da Silva, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, C. Amatore and J.-N. Verpeaux, *Inorg. Chem.*, 1998, **37**, 2344; L. M. D. R. S. Martins, M. T. Duarte, A. M. Galvão, C. Resende, A. J. L. Pombeiro, R. A. Henderson and D. J. Evans, *J. Chem. Soc., Dalton Trans.*, 1998, 3311; V. Yu. Kukushkin, I. V. Ilichev, G. Wagner, M. D. Revenco, V. H. Kravtsov and K. Suwinska, *Eur. J. Inorg. Chem.*, 2000, 1315.
17 G. Wagner, A. J. L. Pombeiro and V. Yu. Kukushkin, *J. Am. Chem. Soc.*, 2000, **122**, 3106; G. Wagner, M. Haukka, J. J. R. Fraústo da Silva, A. J. L. Pombeiro and V. Yu. Kukushkin, *Inorg. Chem.*, in press.
18 J. L. Silver, M. Y. Al-Janabi, R. M. Johnson and J. L. Burmeister, *Inorg. Chem.*, 1971, **10**, 994.
19 A. Guzmán, M. Romero, F. X. Talamás, R. Villena, R. Greenhouse and J. M. Muchowski, *J. Org. Chem.*, 1996, **61**, 2470.
20 L. Grøndahl, J. Josephsen, R. M. Bruun and S. Larsen, *Acta Chem. Scand.*, 1999, **53**, 1069 and references therein.
21 M. A. Jiménez-Tenorio, M. Jiménez-Tenorio, M. C. Puerta and P. Valerga, *Inorg. Chim. Acta*, 2000, **300–302**, 869 and references therein.

22 F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 199.
23 V. Yu. Kukushkin, Å. Oskarsson and L. I. Elding, *Inorg. Synth.*, 1997, **31**, 279; P. Svensson, K. Lövqvist, V. Yu. Kukushkin and Å. Oskarsson, *Acta Chem. Scand.*, 1995, **49**, 72; V. Yu. Kukushkin, Å. Oskarsson and L. I. Elding, *Zh. Obshch. Khim.*, 1994, **64**, 881; *Russ. J. Gen. Chem.* (*Engl. Transl.*), 1994, **64**, 793.
24 A. L. Spek, PLATON, a Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, 2000; A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, C34.
25 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, S1.
26 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc.*, *Dalton Trans.*, 1989, S1.
27 G. Wagner, T. B. Pakhomova, N. A. Bokach, J. J. R. Fraústo da Silva, J. Vicente, A. J. L. Pombeiro and V. Yu. Kukushkin, in press.
28 W. J. Bland, R. D. W. Kemmitt and R. D. Moore, *J. Chem. Soc.*, *Dalton Trans.*, 1973, 1292.
29 V. Robinson, G. E. Taylor, P. Woodward, M. I. Bruce and R. C. Wallis, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1169.
30 M. F. C. Guedes da Silva, C. M. P. Ferreira, E. M. P. R. P. Branco, J. J. R. Fraústo da Silva, A. J. L. Pombeiro, R. A. Michelin, U. Belluco, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and V. Yu. Kukushkin, *Inorg. Chim. Acta* (*Topical Volume on Platinum Chemistry*), 1997, **265**, 267.
31 J. Baker, M. Kilner, M. M. Mahmoud and S. C. Wallwork, *J. Chem. Soc.*, *Dalton Trans.*, 1989, 837.
32 B. Sain, S. P. Singh and J. S. Sandhu, *Tetrahedron*, 1992, **48**, 4567; S. N. Muzumdar and M. P. Mahajan, *Synthesis*, 1990, 417; S. N. Muzumdar, S. Mukherjee, A. K. Sharma, D. Sengupta and M. P. Mahajan, *Tetrahedron*, 1994, **50**, 7579; S. N. Muzumdar and M. P. Mahajan, *Tetrahedron*, 1991, **47**, 1473.
33 Collect, Data collection software, Nonius, Delft, 1999.
34 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307.
35 G. M. Sheldrick, SHELXTL, Version 5.1, Bruker Analytical X-Ray Systems, Bruker AXS, Inc. Madison, WI, USA, 1998.
36 A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.
37 G. M. Sheldrick, SHELXL 97, University of Göttingen, 1997.
38 T. Uchiyama, Y. Toshiyasu, Y. Nakamura, T. Miwa and S. Kawaguchi, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 181l; H. H. Eysel, E. Guggolz, M. Kopp and M. L. Ziegler, *Z. Anorg. Allg. Chem.*, 1983, **499**, 31; L. Maresca, G. Natile, F. P. Intini, F. Gasparrini, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Am. Chem. Soc.*, 1986, **108**, 1180.
39 G. K. Anderson, J. A. Davies and D. J. Schoeck, *Inorg. Chim. Acta*, 1983, **76**, L251.