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Optically Active Mixed Unsymmetric Imine Platinum(II) Complexes – Utilization of the Liberated Imines for Further Syntheses of Mixed Imine-Diazadiene Complexes and of (*E*)-Cyanoalkenes

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Treatment of *trans*-[$PtCl_2(NCR)_2$] (**1**) {R = CH_2CO_2Me (**1a**), Ph (**1b**)} with (*R**)-camphor oxime (C_9H_{16})C=NOH (**2**) gives access to the optically active mixed imine-nitrile complexes *trans*-(*R**)-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}(NCR)] (**4**), which, on reaction with ketoximes R^1R^2C=NOH (**3**) {R^1 = R^2 = Me (**3a**), C_4H_8 (**3b**)}, give the chiral unsymmetric bis(imine) complexes *trans*-(*R**)-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}{NH=C(R)-ON=CR^1R^2}] (**6**) in moderate yields. An alternative route involves the reaction of the starting complexes **1** with ketoximes **3** to give the mixed imine-nitrile complexes *trans*-[$PtCl_2${NH=C(R)ON=CR^1R^2}(NCR)] (**5**), followed by reaction of the latter with (*R**)-camphor oxime (**2**) to afford products **6** in similar yields. Treatment of complexes **1** or **4** with two or one equivalent of **2**, respectively, gives the symmetrical bis-(imine) complexes *trans*-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}$_2$] (**7**). These reactions are accelerated by microwave irradiation to afford, in better yields (71–50 %), the same products. The new optically active diimine compounds NH=C(R)ON=C-(C_9H_{16}) (**8**) are quantitatively liberated upon reaction of complexes **7** with a diphosphane. The chiral diimino ester **8a** (R = CH_2CO_2Me) acts as a protic nucleophile and efficiently couples with the coordinated nitrile in **4** to give the new optically active, mixed, unsymmetric imine-1,3-diaza-1,3-diene complexes *trans*-(*R**,*R**)-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}{NH=C(R)N=C(CH_2CO_2Me)ON=C(C_9H_{16})}] (**9**). Diimino ester **8a** with an acidic α-methylene group also reacts with acyclic nitrones $^-O^+N(Me)$=C(H)R′ (**10**) to afford stereoselectively the (*E*)-cyanoalkenes (N≡C)C(CO_2Me)=C(H)R′ (**11**) {R′ = 4-MeC_6H_4 (**11a**), 2,4,6-$Me_3C_6H_2$ (**11b**)}. All of these compounds were characterized by IR and NMR (^1H, ^{13}C, and ^{195}Pt for metal complexes) spectroscopy, ESI-MS or FAB-MS, elemental analysis, and X-ray diffraction analysis (for **5c** and **7b**).

Introduction

Organonitrile–platinum complexes are precursors for a wide variety of N-containing Pt compounds.[1–5] It has been shown that, when coordinated to a suitable Pt^{II} or Pt^{IV} center, nitrile ligands can undergo coupling with different types of nucleophiles[6,7] or 1,3-dipoles.[8] The reactions of acyclic nitrones with *cis*-[$PtCl_2$(PhMeSO)(PhCN)], containing a chiral sulfoxide group, could be performed diastereoselectively, and the release of Δ^4-1,2,4-oxadiazoline ligands from the resulting complexes allowed the enantioselective synthesis of this class of heterocycles.[8h]

Recently, we reported the synthesis of new *trans*- and *cis*-mixed, unsymmetric oxadiazoline and/or imine complexes by treating *trans*- and *cis*-bis(methyl cyanoacetate)–Pt^{II} complexes with acetone oxime, *N*,*N*-diethylhydroxylamine, and cyclic or acyclic nitrones.[9] These reactions allowed the selective synthesis of the corresponding achiral, racemic, or 1:1 diastereoisomeric complexes, and these products are generally stable but not suitable to be applied in asymmetric chemistry. These observations stimulated our interest to extend the metal-mediated nitrile-oxime and/or nitrile-imine reactions to chiral Pt^{II} complexes. Further aims of this study are as follows: (i) To prepare optically active, mixed unsymmetric *trans*-Pt^{II} complexes by using (*R**)-camphor oxime as a chiral nucleophile towards the nitrile ligand. (ii) To synthesize bis(imine) platinum(II) complexes and use them as sources of chiral imines upon ligand liberation. (iii) To employ the released imines in situ for further syntheses. (iv) To apply focused microwave irradiation[10] in order to reduce the reaction time and to increase the yield, selectivity, and purity in comparison with traditional heating methods.[6b,8a,11]

We have synthesized new chiral, *trans* unsymmetric imine complexes of the types [$PtCl_2${(*R**)-imine}(nitrile)] and [$PtCl_2${(*R**)-imine}(imine)], bearing two different ligands, by undertaking the first examples of coupling an optically active oxime with a nitrile ligand coordinated to a platinum center. Further reactions that were also investigated pro-

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vided a facile metal-mediated route to new free chiral diimines, which can be used in situ for subsequent coupling with a coordinated nitrile to give *trans* mixed unsymmetric imine-diazadiene complexes. If the liberated imine bears the CH_2CO_2Me ester group with an acidic α-methylene, its reaction with acyclic nitrones affords (*E*)-cyanoalkenes stereoselectively.

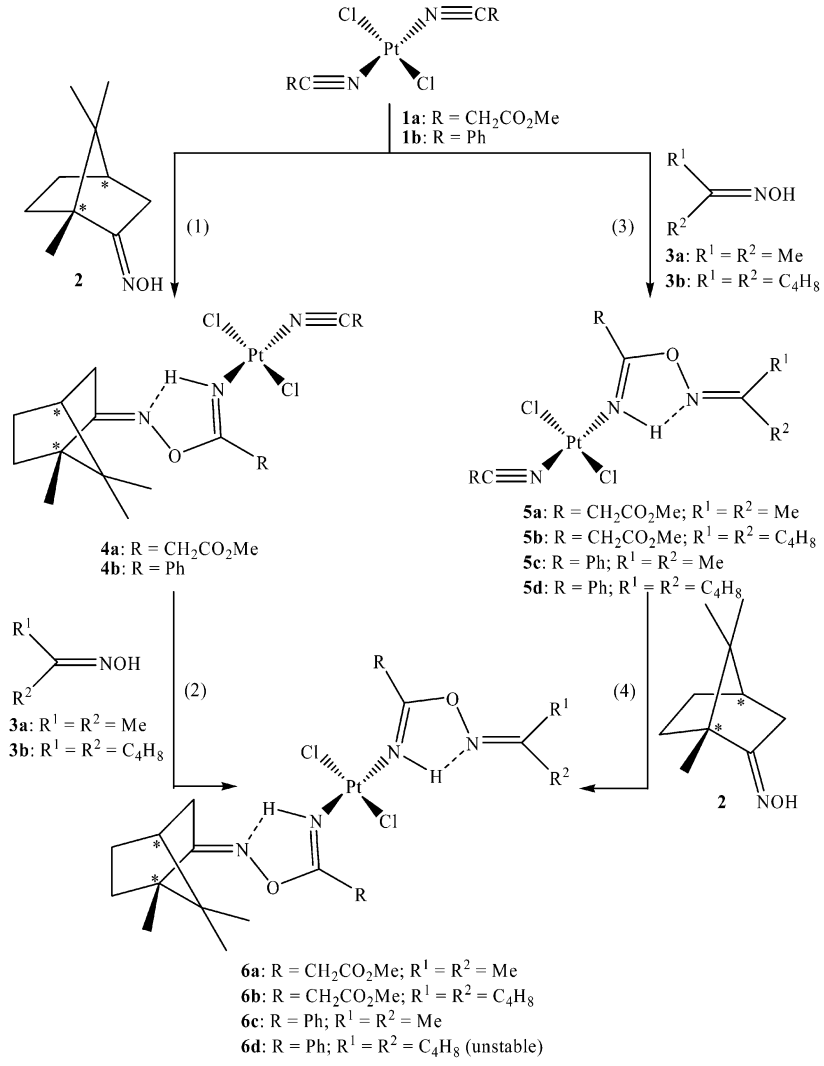
Results and Discussion

Optically Active Imine Complexes

In the first part of this work, we report the selective synthesis of new optically active, mixed unsymmetric platinum complexes of the general types *trans*-[$PtCl_2${(*R**)-imine}(nitrile)] **4** and *trans*-[$PtCl_2${(*R**)-imine}(imine)] **6** by using the bis(methyl cyanoacetate) *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] (**1a**) and the bis(benzonitrile) *trans*-[$PtCl_2(NCPh)_2$] (**1b**) as the starting dinitrile Pt^{II} complexes and (*R**)-camphor oxime (**2**), acetone oxime (**3a**), and cyclopentanone oxime (**3b**) as the reacting nucleophiles (Scheme 1). Complexes **6** were prepared by two different ways: (i) reaction (1) of the starting dinitrile Pt^{II} complexes **1** with the chiral oxime **2** to give the optically active complexes **4**, which were further converted to complexes **6** by treatment with oximes **3** [reaction (2)]; (ii) reaction (3) of complexes **1** with oximes **3** leading to complexes **5**, which, upon subsequent reaction (4) with oxime **2**, afford the same final products **6**.

All the obtained complexes, whose formation was monitored by TLC, were purified by column chromatography on silica gel and characterized by IR and NMR (^1H, ^{13}C, ^{195}Pt) spectroscopy, FAB-MS, and elemental analyses.

Treatment of *trans*-[$PtCl_2(NCR)_2$] (**1**) {R = CH_2CO_2Me (**1a**), Ph (**1b**)} with (*R**)-camphor oxime (**2**), in refluxing CH_2Cl_2 at 40 °C for 15 or 60 min (for **1a** or **1b**, respectively), gives access to the corresponding new, optically active monoimine complexes *trans*-(*R**)-[$PtCl_2${NH=C(R)-ON=C(C_9H_{16})}(NCR)] (**4**) {R = CH_2CO_2Me (**4a**), Ph (**4b**)} in moderate yields (55–50%). Further reaction of complexes **4a** or **4b** with acetone oxime **3a** or cyclopentanone



Scheme 1.

oxime **3b**, under the same experimental conditions, leads to the new, chiral, mixed unsymmetric bis(imine) complexes *trans*-(*R**)-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}{NH=C(R)ON=CR^1R^2}] (**6**) {R = CH_2CO_2Me; R^1 = R^2 = Me (**6a**), C_4H_8 (**6b**), R = Ph; R^1 = R^2 = Me (**6c**), C_4H_8(**6d**)} also in moderate yields (52–45%). All these reactions are accelerated by microwave (M.W.) irradiation (5 or 20 min, for **1a** and **4a** or **1b** and **4b**, respectively), giving the same products in better yields (70–52%) (Scheme 1).

An alternative route to obtain complexes **6a**–**6d** involves the reverse order of reactions, as follows: Firstly, the starting dinitrile–Pt^{II} complexes **1a** or **1b** react with acetone oxime **3a** or cyclopentanone oxime **3b** to give the monoimine complexes *trans*-[$PtCl_2${NH=C(R)ON=CR^1R^2}(NCR)] (**5**) {R = CH_2CO_2Me; R^1 = R^2 = Me (**5a**), C_4H_8 (**5b**), R = Ph; R^1 = R^2 = Me (**5c**), C_4H_8 (**5d**)} derived from a single iminoacylation in moderate yields (51–40%). Secondly, monoimine complexes **5a**–**5d** react with (*R**)-camphor oxime (**2**) to afford the final complexes **6a**–**6d** in comparable yields (52–44%). Also in these cases the reactions are accelerated by M.W. irradiation (5 or 20 min, for **1a** and **5a**–**5b** or **1b** and **5c**–**5d**, respectively), leading to the same products in better yields (71–50%) (Scheme 1).

Interestingly, the reaction of *trans*-[$PtCl_2$-($NCCH_2CO_2Me$)$_2$] (**1a**) with oximes **2** and **3** leads also to the formation of small amounts of the bis(imine) complexes *trans*-[$PtCl_2${NH=C(CH_2CO_2Me)ON=C(C_9H_{16})}$_2$] (6% yield) and the known[6b] *trans*-[$PtCl_2${NH=C(CH_2CO_2Me)-ON=CR^1R^2}$_2$] {R^1 = R^2 = Me (15% yield), C_4H_8 (10% yield)}, respectively, derived from nucleophilic additions to both nitrile ligands. Hence, the above-described reactions show a considerable selectivity towards the mixed ligand products derived from a single addition, which are the major ones. The use of M.W. irradiation is a convenient alternative way to the traditional refluxing method and provides a synthetic strategy for increasing the selectivity and the yield with reduction of the reaction time.[6b,8a,10,11]

Complexes **4** and **5** exhibit IR ν(N≡C) values (2339–2287 cm^{-1}) that are identical to those of the starting complexes **1**, and in their ^{1}H NMR spectra δ(N*H*) (8.01–8.15 ppm) reflects the hydrogen bond between the imine hydrogen and oxime nitrogen atoms, which stabilizes the *E* conformation of the iminoacyl ligand. The ^{13}C NMR spectra show the characteristic signals of the imine and nitrile ligands. The IR spectra of the bis(imine) complexes **6** exhibit ν(N=C) in the 1634–1654 cm^{-1} range. Both ^{1}H and ^{13}C NMR spectra show that the products contain two different imine ligands (e.g., two distinct ^{1}H NMR resonances of the hydrogen-bonded N*H* protons in the 8.06–8.36 ppm range).

The single-crystal X-ray diffraction structural analysis of the mono-iminoacylated Pt^{II} complex *trans*-[$PtCl_2${NH=C(Ph)ON=CMe_2}(NCPh)] (**5c**) confirms the formulation and its *trans* configuration (the molecular structure is depicted in Figure 1, crystal data and selected bond lengths and angles are given in Table 2 and Table 1, respectively). The values of the bond lengths, Pt–N [1.995(2) and 1.963(2) Å], Pt–Cl [2.2963(7) and 2.2998(8) Å], N1–C1 [1.283(3) Å], N2–C2 [1.137(4) Å], and

Table 1. Selected bond lengths [Å] and angles [°] for complexes **5c** and **7b**.

	5c	**7b**
Bond lengths		
Cl1–Pt1	2.2963(7)	2.2994(12)
Cl2–Pt1	2.2998(8)	2.3007(12)
N1–Pt1	1.995(2)	2.004(4)
N2–Pt1	1.963(2)	1.995(3)
N1–H1	0.85(4)	0.99(4)
C2–N2	1.137(4)	1.280(5)
C1–N1	1.283(3)	1.271(6)
N2–H2	–	0.95(3)
Bond angles		
Cl1–Pt1–Cl2	178.33(3)	179.74(4)
N1–Pt1–Cl2	89.52(6)	88.53(11)
N2–Pt1–Cl2	90.22(6)	91.13(13)
N1–Pt1–Cl1	89.43(6)	91.12 (11)
N2–Pt1–Cl1	90.85(6)	89.12(11)
N2–Pt1–N1	179.17(8)	179.07(15)
Pt1–N1–H1	120(3)	118(2)
Pt1–N2–H2	–	115.7(18)

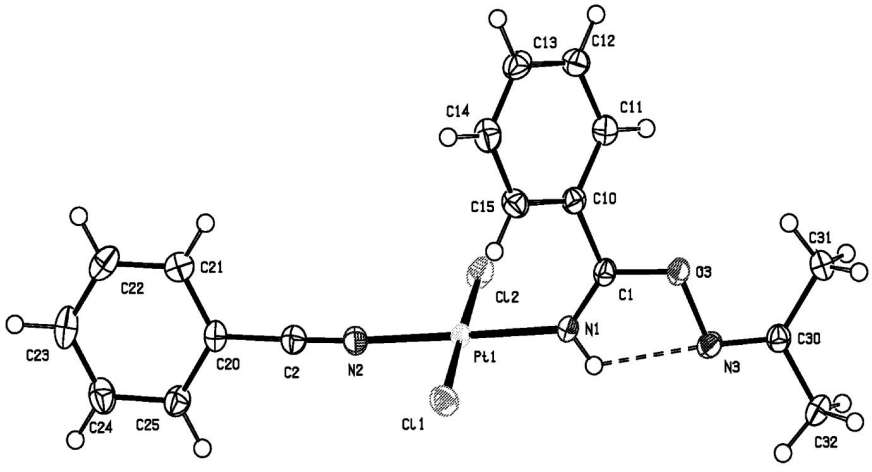


Figure 1. Molecular structure of the mono-iminoacylated Pt^{II} complex *trans*-[$PtCl_2${NH=C(Ph)ON=CMe_2}(NCPh)] (**5c**) with the atomic numbering scheme (ellipsoids are drawn at 50% probability).

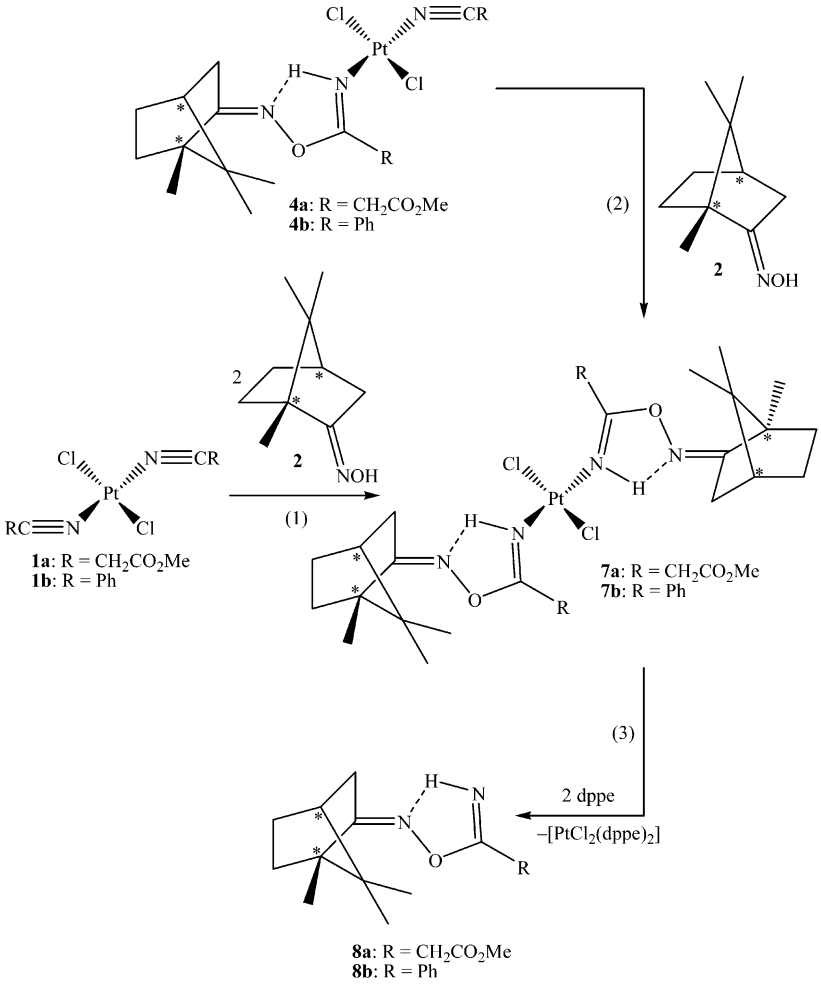
N1–H1 [0.85(4) Å], and the bond angles, Cl1–Pt1–N1 [89.43(6)°], Pt1–N1–H1 [120(3)°], and Cl1–Pt1–N2 [90.85(6)°], as well as those of the N1–H1···N3 hydrogen bond between the imine hydrogen and the oxime nitrogen atoms [*d*(H1···N3) is 2.13(4) Å, and the N1–H1···N3 angle is 115(3)°], which stabilizes the *E* conformation of the iminoacyl ligands, agree with those reported for other iminoacylated platinum(II) complexes.[6b,6j,9]

Symmetrical Imine Complexes

In the second part of this work, we report the synthesis of new symmetrical complexes of the general type *trans*-[$PtCl_2${(*R**)-imine}$_2$] **7** by reaction of complexes **1** or **4** with (*R**)-camphor oxime (**2**) (Scheme 2).

Treatment of *trans*-[$PtCl_2(NCR)_2$] (**1**) {R = CH_2CO_2Me (**1a**), Ph (**1b**)} or *trans*-(*R**)-[$PtCl_2${NH=C(R)ON=C-(C_9H_{16})}(NCR)] (**4**) {R = CH_2CO_2Me (**4a**), Ph (**4b**)} with two or one equivalent of (*R**)-camphor oxime (**2**), respectively, in refluxing CH_2Cl_2 (for 15 or 60 min, for **1a** and **4a** or **1b** and **4b**, respectively), gives the new bis(imine) complexes *trans*-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}$_2$] (**7**) {R = CH_2CO_2Me (**7a**), Ph (**7b**)} in moderate yields (50–48%) (Scheme 2, reactions 1 and 2, respectively). All these reactions are accelerated by M.W. irradiation (5 or 20 min, for **1a** and **4a** or **1b** and **4b**, respectively), giving the same products, **7a** and **7b**, in moderate to good yields (65–55%).

Both ^1H and ^{13}C NMR spectra of **7** are consistent with two equivalent imine ligands. The single-crystal X-ray diffraction structural analysis of *trans*-[$PtCl_2${NH=C(Ph)-ON=C(C_9H_{16})}$_2$] (**7b**) confirms the formulation and its *trans* geometry (the molecular structure is depicted in Figure 2, crystal data and selected bond lengths and angles are given in Table 2 and Table 1, respectively). The values of the bond lengths, Pt–N [2.004(4) and 1.995(3) Å], Pt–Cl [2.2994(12) and 2.3007(12) Å], N1–C1 [1.271(6) Å], and N2–C2 [1.280(5) Å], and the bond angles, Cl1–Pt1–N1 [91.23(11)°] and Pt1–N1–H1 [118(2)°], agree with those reported for other bis-iminoacylated platinum(II) complexes.[6b,6j] The stabilizing hydrogen bonds between the imine hydrogen atoms and the oxime nitrogen atoms (see above) are also confirmed by X-ray analysis [*d*(H1···N11) and *d*(H2···N22) are 1.99(4) and 2.05(3) Å, respectively; the N1–H1···N11 angle is 115(3)°, and the N2–H2···N22 angle is 114(2)°].



Scheme 2.

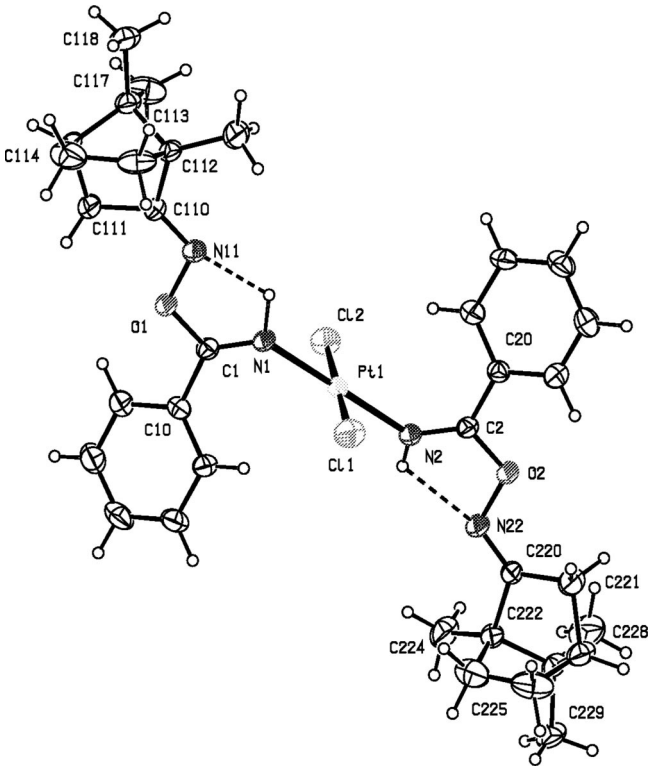
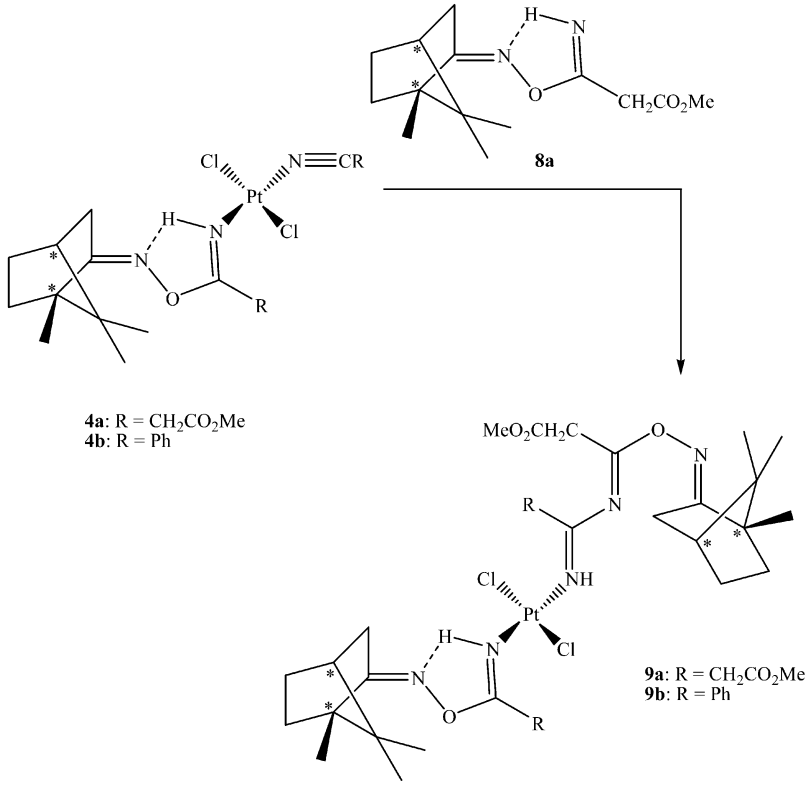


Figure 2. Molecular structure of the iminoacylated Pt^{II} complex *trans*-[$PtCl_2${NH=C(Ph)ON=C(C_9H_{16})}$_2$] (**7b**) with the atomic numbering scheme (ellipsoids are drawn at 50% probability).

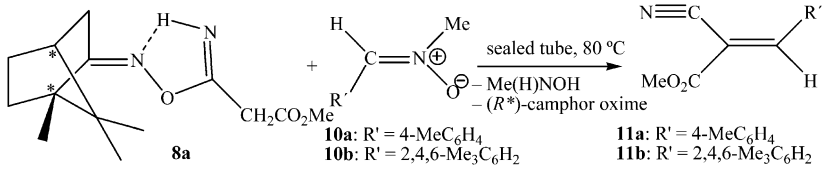
The liberation of the new optically active diimine ligands in complexes **7a** and **7b** was achieved upon addition of the diphosphane $Ph_2PCH_2CH_2PPh_2$ (dppe) to a $CDCl_3$ solution of any of those complexes at room temperature (Scheme 2, reaction 3). The free diimines NH=C(R)-ON=C(C_9H_{16}) (*R**-**8**) {R = CH_2CO_2Me (*R**-**8a**), Ph (*R**-**8b**)} are stable for at least one week at room temperature and were characterized by IR and NMR (^1H, ^{13}C) spectroscopy and FAB-MS. Their NMR resonances appear at higher fields than those of the corresponding complex precursors.

Optically Active Mixed Imine-Diazadiene Complexes

In pursuit of our interest[6g,6h,6k] in the reactivity of *free* imines, we have investigated the reaction between the liberated chiral diimino ester NH=C(CH_2CO_2Me)-ON=C(C_9H_{16}) (*R**-**8a**) and a Pt-coordinated nitrile. Hence, in the third part of this work, we found that this diimino ester efficiently couples with the nitrile ligand in *trans*-(*R**)-[$PtCl_2${NH=C(R)ON=C(C_9H_{16})}(NCR)] (**4**) {R = CH_2CO_2Me (**4a**), Ph (**4b**)}, in CH_2Cl_2 at room temperature, to give the new optically active, mixed unsymmetric imine-1,3-diaza-1,3-diene complexes *trans*-(*R**,*R**)-[$PtCl_2${NH=C(R)-ON=C(C_9H_{16})}{NH=C(R)N=C(CH_2CO_2Me)ON=C-(C_9H_{16})}] (**9**) {R = CH_2CO_2Me (**9a**), Ph (**9b**)} in moderate to good yields (65–49%) (Scheme 3). In these reactions, the diimino ester behaves as a protic nucleophile towards the ligated nitrile.



Scheme 3.



Scheme 4.

Both ^{1}H and ^{13}C NMR spectra of **9** confirm the presence of the two different ligands. To the best of our knowledge, these reactions represent the first examples of coupling a chiral imine with a nitrile ligand coordinated to a platinum center to give complexes bearing mixed chiral ligands of the general type [$PtCl_2${(*R**)-imine}{(*R**)-diazadiene}].

Synthesis of (*E*)-Cyanoalkenes

Apart from the protic nucleophile moiety, the chiral diimino ester **8a** also bears an acidic α-methylene group, and we investigated its reactivity towards acyclic nitrones $^-O^+N(Me)=C(H)R'$ (**10**). The corresponding (*E*)-cyanoalkenes ($N\equiv C)C(CO_2Me)=C(H)(R')$ (**11**) {R′ = 4-MeC_6H_4 (**11a**), 2,4,6-$Me_3C_6H_2$ (**11b**)} were obtained in moderate yields (ca. 52%) (Scheme 4).

The formation of products **11** involves the overall and formal removal of the two α-acidic methylene protons of the imino ester **8a** by the $\{NOMe\}^{2-}$ fragment of the nitrone $^-O^+N(Me)=C(H)R'$ which thus undergoes N=C bond cleavage, with coupling of the remaining imine- and oxime-derived fragments to afford $(N\equiv C)C(CO_2Me)=C(H)(R')$ and (*R**)-camphor oxime. This oxime could be isolated at the end of the reaction and characterized by ^{1}H and ^{13}C NMR spectroscopy. The final step conceivably is the C–O bond cleavage of the $HN=C[ON=C(C_9H_{16})]C(CO_2Me)=C(H)(R')$ species, affording products **11**. We recently reported a similar mechanism involving the synthesis of (*E*)-cyanoalkenes starting from free nitriles.[8a]

Concluding Remarks

The results of this work show that bis(nitrile)–Pt^{II} complexes of the type *trans*-[$PtCl_2$(nitrile)$_2$] (nitrile = $NCCH_2CO_2Me$ or NCPh) can act as convenient starting materials for the syntheses of a variety of optically active mixed-ligand complexes of the types *trans*-[$PtCl_2${(*R**)-imine}(nitrile)] **4** and *trans*-[$PtCl_2${(*R**)-imine}(imine)] **6**, and the reactions represent the first examples of coupling a chiral oxime with a nitrile ligand coordinated to a platinum center. This methodology could also introduce optical activity into achiral mixed-ligand complexes of the type *trans*-[$PtCl_2$(imine)(nitrile)] **5** by nucleophilic addition of (*R**)-camphor oxime to the nitrile ligand.

Microwave irradiation generally enhances the reaction rates and yields, and also the selectivity of the reaction of the starting complex with (*R**)-camphor oxime, because the first nucleophilic addition appears to be accelerated to a higher extent than the second one.

The association of those reactions with the subsequent ligand liberation from the metal provides a facile metal-mediated route to the syntheses of previously unknown optically active diimine compounds **8**, which are inaccessible directly by pure organic chemistry. They can thus be generated and used in situ,[6a,6g] namely for further coupling with the coordinated nitrile in **4** to give the new optically active, mixed unsymmetric imine-diazadiene complexes [$PtCl_2$-{(*R**)-imine}{(*R**)-diazadiene}] **9**. In the case of the generated free diimino ester **8a** (bearing an acidic α-methylene group), its reaction with acyclic nitrones affords (*E*)-cyanoalkenes stereoselectively. Imino esters are useful intermediates in organic synthesis, and their coordination to a metal can stabilize them, allowing their storage for a prolonged time. When required, their liberation can be easily undertaken and used in situ.

Further potential interests of these studies include the eventual use of the chiral imines as precursors of lactam heterocycles[12] (which could be applied in enantioselective catalysis[13]) and the possible pharmacological significance of the Pt complexes, since enantiomerically pure platinum compounds with N-ligands can display enhanced antitumor activity.[14] Further reactions are under study in our laboratory towards the synthesis of chiral heterocyclic compounds.

Experimental Section

Materials and Instrumentation

Reagents and solvents were purchased from Aldrich and dried by usual procedures. Complexes *trans*-[$PtCl_2(NCCH_2CO_2Me)_2$] (**1a**),[6b] *trans*-[$PtCl_2(NCPh)_2$] (**1b**),[15] and acyclic nitrones $^-O^+N(Me)=C(H)R'$ (**10**)[16] were prepared according to published methods. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. ^{1}H, ^{13}C, and ^{195}Pt NMR spectra (in $CDCl_3$) were measured with a Varian Unity 300 spectrometer at ambient temperature. Positive-ion FAB mass spectra were obtained with a Trio 2000 instrument by bombarding the samples in 3-nitrobenzyl alcohol (NBA) matrixes with 8 keV (ca. 1.28×10^{15} J) Xe atoms. Electrospray mass spectra were recorded with an ion-trap instrument (Varian 500-MS LC Ion Trap Mass Spectrometer) equipped with an electrospray (ESI) ion source. ^{1}H and ^{13}C chemical shifts (δ) are expressed in ppm relative to $Si(Me)_4$, and ^{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. *J* values are in Hz. Infrared spectra (4000–400 cm^{-1}) were recorded with a Bio-Rad FTS 3000MX and a Jasco FT/IR-430 instrument by using KBr pellets, and the wavenumbers are in cm^{-1}. Optical rotations were measured with a Perkin–Elmer 241 polarimeter by using a 0.5-dm cell. Concentrations (*c*) are given in mg mL^{-1}. The microwave irradiation experi-

ments were undertaken in a focused microwave CEM Discover reactor (10 mL, 13-mm diameter, 300 W) which was fitted with a rotational system and an IR detector of temperature.

Heating Methods

(i) The Conventional Method: The reactions were carried out in refluxing CH_2Cl_2 with stirring, and their progress was monitored by TLC (CH_2Cl_2/Et_2O as eluent). After concentration of the solution in vacuo to dryness, the crude residue was purified by column chromatography on silica (CH_2Cl_2 or CH_2Cl_2/Et_2O as eluent) followed by evaporation of the solvent in vacuo to give the final products.

(ii) Focused Microwave Irradiation: The reagents and solvent (CH_2Cl_2) were added to a cylindrical Pyrex tube, which was then placed in a focused microwave reactor. After the reaction, the mixture was cooled down, the solvent was removed in vacuo, and the crude residue was purified as indicated in (i).

Reactions of *trans*-[PtCl$_2$(NCR)$_2$] (1) {R = CH$_2$CO$_2$Me (1a), Ph (1b)} with (*R)-Camphor Oxime (2), Acetone Oxime (3a), or Cyclopentanone Oxime (3b)**

(i) By the Conventional Method: A solution of **1a** (50.0 mg, 0.108 mmol) or **1b** (51.0 mg, 0.108 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the appropriate oxime **2** or **3** (0.108 mmol), and the mixture was heated with stirring at 40 °C for 15 or 60 min (for **1a** or **1b**, respectively).

(ii) By Focused Microwave Irradiation: A CH_2Cl_2 solution of the reagents in the above amounts was subjected to focused microwave irradiation at 40 °C for 5 or 20 min (for **1a** or **1b**, respectively). In both cases, the corresponding mono-iminoacylated products **4** or **5** were isolated and purified as indicated above.

***trans*-(*R**)-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}(NCCH$_2$CO$_2$Me)] (4a):** Method (i) (37.5 mg, 55% yield), method (ii) (47.7 mg, 70% yield). $[\alpha]_D^{20}$ = –7.1 (*c* = 0.59 in $CHCl_3$). IR: $\tilde{\nu}$ = 3479 (NH), 2339 (N≡C), 1749 (CO_2Me), 1656 (C=N) cm^{-1}. ^{1}H NMR: δ = 0.76, 0.90, and 1.01 (three s, 3 H each, Me groups), 1.19–1.27 (m, 1 H), 1.41–1.50 (m, 1 H), 1.65–2.09 (m, 4 H), 2.51–2.60 (m, 1 H), 3.74 and 3.82 (two s, 3 H each, MeO), 4.00 and 4.13 (two s, 2 H each, CH_2), 8.01 (br. s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR: δ = 11.4, 18.9, 20.0 (Me), 26.8, 27.3, 32.7, 35.6, 40.2 (CH_2), 43.8 (CH), 49.6 (*C*Me), 53.3 (*C*Me$_2$), 53.4 and 54.4 (MeO), 112.6 (N≡C), 162.1 and 166.6 (*C*O$_2$Me), 168.9 [C(O)=N], 180.5 [(O)N=*C*CH$_2$] ppm. ^{195}Pt NMR: δ = –2228 (*J* = 812 Hz) ppm. FAB$^+$-MS: *m*/*z* = 631 [M]$^+$. $C_{18}H_{27}Cl_2N_3O_5Pt$ (631.41): calcd. C 34.24, H 4.31, N 6.66; found C 34.12, H 4.37, N 6.55.

***trans*-(*R**)-[PtCl$_2${NH=C(Ph)ON=C(C$_9$H$_{16}$)}(NCPh)] (4b):** Method (i) (34.5 mg, 50% yield), method (ii) (46.2 mg, 67% yield). $[\alpha]_D^{20}$ = –9.4 (*c* = 0.65 in $CHCl_3$). IR: $\tilde{\nu}$ = 3464 (NH), 2287 (N≡C), 1641 (C=N) cm^{-1}. ^{1}H NMR: δ = 0.81, 0.94, and 1.01 (three s, 3 H each, Me groups), 1.23–1.27 (m, 1 H), 1.47–1.54 (m, 1 H), 1.76–1.97 (m, 3 H), 2.16–2.22 (m, 1 H), 2.66–2.72 (m, 1 H), 7.48–7.69 (m, 8 H), 8.15 (br. s, 1 H, NH), 8.64 (d, J_{HH} = 7.2 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR: δ = 11.5, 18.9, 20.1 (Me), 27.5, 32.8, 35.9 (CH_2), 43.9 (CH), 49.6 (*C*Me), 54.5 (*C*Me$_2$), 110.5 (C$_q$, N≡C*Ph*), 116.8 (N≡C), 128.7, 129.5, 130.1, 130.2, 133.4, 133.9, and 135.2 (C$_{aromatic}$), 169.0 [C(O)=N], 179.9 [(O)N=*C*CH$_2$] ppm. ^{195}Pt NMR: δ = –2176 (*J* = 886 Hz) ppm. FAB$^+$-MS: *m*/*z* = 639 [M]$^+$. $C_{24}H_{27}Cl_2N_3OPt$ (639.47): calcd. C 45.08, H 4.26, N 6.57; found C 45.30, H 4.30, N 6.50.

***trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}(NCCH$_2$CO$_2$Me)] (5a):** Method (i) (29.6 mg, 51% yield), method (ii) (41.2 mg, 71% yield). All the spectroscopic, FAB-MS, and elemental analytical data are in agreement with those reported earlier.[9]

***trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_4$H$_8$)}(NCCH$_2$CO$_2$Me)] (5b):** Method (i) (30.4 mg, 50% yield), method (ii) (39.5 mg, 65% yield). IR: $\tilde{\nu}$ = 3444 (NH), 2338 (N≡C), 1743 (CO_2Me), 1648 (C=N) cm^{-1}. ^{1}H NMR: δ = 1.81 (m, 4 H), 2.53 (m, 4 H) [=C(C$_4$*H*$_8$)], 3.76 and 3.83 (two s, 3 H each, MeO), 4.01 and 4.13 (two s, 2 H each, CH_2), 8.05 (br. s, 1 H, NH) ppm. ^{13}C{^{1}H} NMR: δ = 24.9, 25.6, 30.5, 32.1 [=C(*C*$_4$H$_8$)], 26.9 and 40.0 (CH_2), 53.4 and 54.7 (MeO), 112.6 (N≡C), 162.1 and 166.6 (*C*O$_2$Me), 168.7 [N=*C*(C$_4$H$_8$)], 178.5 [*C*(O)=N] ppm. ^{195}Pt NMR: δ = –2230 (*J* = 805 Hz) ppm. FAB$^+$-MS: *m*/*z* = 563 [M]$^+$. $C_{13}H_{19}Cl_2N_3O_5Pt$ (563.29): calcd. C 27.72, H 3.40, N 7.46; found C 27.67, H 3.50, N 7.60.

***trans*-[PtCl$_2${NH=C(Ph)ON=CMe$_2$}(NCPh)] (5c):** Method (i) (28.2 mg, 48% yield), method (ii) (32.3 mg, 55% yield). IR: $\tilde{\nu}$ = 3436 (NH), 2288 (N≡C), 1646 (C=N) cm^{-1}. ^{1}H NMR: δ = 2.11 and 2.12 (two s, 3 H each, =CMe$_2$), 7.49–7.73 (m, 8 H), 8.29 (br. s, 1 H, NH), 8.67 (d, J_{HH} = 8.0 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR: δ = 17.5 and 21.9 (Me groups), 109.9 (C$_{ipso}$, N≡C*Ph*), 116.3 (N≡C), 128.2, 128.6, 129.2, 129.6, 132.9, 133.4, and 134.6 (C$_{aromatic}$), 165.5 (=*C*Me$_2$), 168.1 [C(O)=N] ppm. ^{195}Pt NMR: δ = –2186 (*J* = 806 Hz) ppm. FAB$^+$-MS: *m*/*z* = 545 [M]$^+$. $C_{17}H_{17}Cl_2N_3OPt$ (545.32): calcd. C 37.44, H 3.14, N 7.71; found C 37.74, H 3.25, N 7.33.

***trans*-[PtCl$_2${NH=C(Ph)ON=C(C$_4$H$_8$)}(NCPh)] (5d):** Method (i) (24.7 mg, 40% yield), method (ii) (30.8 mg, 50% yield). IR: $\tilde{\nu}$ = 3448 (NH), 2289 (N≡C), 1638 (C=N) cm^{-1}. ^{1}H NMR: δ = 1.85–1.87 (m, 4 H) and 2.55–2.66 (m, 4 H) [=C(C$_4$H$_8$)], 7.47–7.79 (m, 8 H), 8.22 (br. s, 1 H, NH), 8.66 (d, J_{HH} = 7.1 Hz, 2 H) ppm. ^{13}C{^{1}H} NMR: δ = 24.4, 25.0, 29.9, and 31.5 (C$_4$H$_8$), 109.8 (C$_{ipso}$, N≡C*Ph*), 116.2 (N≡C), 128.1, 128.5, 129.1, 129.4, 132.7, 133.3, and 134.5 (C$_{aromatic}$), 168.2 [=*C*(C$_4$H$_8$)], 176.9 [C(O)=N] ppm. ^{195}Pt NMR: δ = –2181 (*J* = 876 Hz) ppm. FAB$^+$-MS: *m*/*z* = 571 [M]$^+$. $C_{19}H_{19}Cl_2N_3OPt$ (571.36): calcd. C 39.94, H 3.35, N 7.35; found C 39.90, H 3.40, N 7.42.

Reactions of Mono-Iminoacylated Pt^{II} Complexes *trans*-(*R)-[PtCl$_2${NH=C(R)ON=C(C$_9$H$_{16}$)}(NCR)] (4) {R = CH$_2$CO$_2$Me (4a), Ph (4b)} or *trans*-[PtCl$_2${NH=C(R)ON=CR^{1}R^2}(NCR)] (5) {R = CH$_2$CO$_2$Me; R^1 = R^2 = Me (5a), C$_4$H$_8$ (5b), R = Ph; R^1 = R^2 = Me (5c), C$_4$H$_8$ (5d)} with (*R**)-Camphor Oxime (2), Acetone Oxime (3a), or Cyclopentanone Oxime (3b)**

(i) By the Conventional Method: A solution of **4a** (58.7 mg, 0.093 mmol), **4b** (59.5 mg, 0.093 mmol), **5a** (50.0 mg, 0.093 mmol), **5b** (52.4 mg, 0.093 mmol), **5c** (50.7 mg, 0.093 mmol), or **5d** (53.1 mg, 0.093 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to the appropriate oxime **2** or **3** (0.093 mmol). The mixture was heated with stirring at 40 °C for 15 or 60 min (for **4a** and **5a**–**b** or **4b** and **5c**–**d**, respectively).

(ii) By Focused Microwave Irradiation: A CH_2Cl_2 solution of the reagents in the above amounts was subjected to focused microwave irradiation at 40 °C for 5 or 20 min (for **4a** and **5a**–**b** or **4b** and **5c**–**d**, respectively). In both cases, the corresponding products **6** were isolated and purified as indicated above.

***trans*-(*R**)-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}{NH=C(CH$_2$CO$_2$Me)ON=CMe$_2$}] (6a):** Method (i) (34.1 mg, 52% yield), method (ii) (39.3 mg, 60% yield). $[\alpha]_D^{20}$ = –1.4 (*c* = 0.40 in $CHCl_3$). IR: $\tilde{\nu}$ = 3448 (NH), 1749 (CO_2Me), 1654 (C=N) cm^{-1}. ^{1}H NMR: δ = 0.79, 0.94, and 1.06 (three s, 3 H each, Me groups), 1.21–1.27 (m, 2 H), 1.46–1.52 (m, 2 H), 1.91–1.95 (m, 1 H), 2.02 and 2.04 (two s, 3 H each, =CMe$_2$), 2.53–2.65 (m, 2 H), 3.79 (s, 6 H, MeO),

4.20 (s, 4 H, CH_2CO_2Me), 8.06 and 8.19 (two s, br, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.5, 19.0, 20.1 (Me), 17.9 and 22.4 (=C*Me*$_2$), 27.5, 32.8, 35.7 (CH_2), 39.9 and 40.2 (*C*H_2CO_2Me), 44.0 (CH), 49.7 (*C*Me), 53.3 (*C*Me$_2$), 54.4 (MeO), 166.2 (*C*O_2Me), 167.1 (=*C*Me$_2$), 167.7 and 168.1 [C(O)=N], 179.9 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2058 (J = 886 Hz) ppm. FAB^+-MS: m/z = 704 $[M]^+$. $C_{21}H_{34}Cl_2N_4O_6Pt$ (704.50): calcd. C 35.80, H 4.86, N 7.95; found C 35.75, H 4.80, N 7.86.

***trans*-(*R**)-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}{NH=C-(CH$_2$CO$_2$Me)ON=C(C$_4$H$_8$)}] (6b):** Method (i) (33.3 mg, 49% yield), method (ii) (37.3 mg, 55% yield). $[\alpha]_D^{20}$ = –36.8 (c = 0.49 in $CHCl_3$). IR: $\tilde{\nu}$ = 3432 (NH), 1749 (CO_2Me), 1652 (C=N) cm^{-1}. ^1H NMR: δ = 0.81, 0.95, and 1.07 (three s, 3 H each, Me groups), 1.26–2.55 (m, 15 H) [CH_2, CH, and =C(C_4H_8)], 3.80 (s, 6 H, MeO), 4.19 and 4.20 (two s, 2 H each, C*H*$_2CO_2Me$), 8.07 and 8.14 (two s, br, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.5, 19.0, 20.1 (Me), 25.1, 25.7, 30.4, 32.1 [=C(*C*$_4H_8$)], 27.5, 32.9, 35.7 (CH_2), 40.0 and 40.2 (*C*H_2CO_2Me), 44.0 (CH), 49.6 (*C*Me), 53.4 (*C*Me$_2$), 54.4 (MeO), 167.2 (*C*O_2Me), 167.9 [N=*C*(C_4H_8)], 168.1 and 177.8 [*C*(O)=N], 179.9 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2059 (J = 874 Hz) ppm. FAB^+-MS: m/z = 730 $[M]^+$. $C_{23}H_{36}Cl_2N_4O_6Pt$ (730.54): calcd. C 37.81, H 4.97, N 7.67; found C 37.90, H 4.80, N 7.77.

***trans*-(*R**)-[PtCl$_2${NH=C(Ph)ON=C(C$_9$H$_{16}$)}{NH=C(Ph)-ON=CMe$_2$}] (6c):** Method (i) (29.8 mg, 45% yield), method (ii) (34.4 mg, 52% yield). $[\alpha]_D^{20}$ = –8.8 (c = 0.25 in $CHCl_3$). IR: $\tilde{\nu}$ = 1634 (C=N) cm^{-1}. ^1H NMR: δ = 0.82, 0.96, and 1.12 (three s, 3 H each, Me groups), 1.20–1.28 (m, 2 H), 1.50–1.56 (m, 2 H), 1.86–1.96 (m, 1 H), 2.07 and 2.08 (two s, 3 H each, =C*Me*$_2$), 2.57–2.71 (m, 2 H), 7.46–7.64 (m, 6 H), 8.22 and 8.36 (two s, br, 2 H, NH), 8.66 (t, J_{HH} = 8.1 Hz, 4 H) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.9, 18.3, 19.4 (Me), 17.3 and 21.8 (=C*Me*$_2$), 26.8, 32.2, 35.2 (CH_2), 43.4 (CH), 49.0 (*C*Me), 53.6 (*C*Me$_2$), 127.9, 128.1, 129.1, 129.2, 129.4, 132.1, 133.4, and 134.5 ($C_{aromatic}$), 164.6 (=*C*Me$_2$), 167.3 and 168.4 [C(O)=N], 179.3 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2177 (J = 876 Hz) ppm. FAB^+-MS: m/z = 712 $[M]^+$. $C_{27}H_{34}Cl_2N_4O_2Pt$ (712.57): calcd. C 45.51, H 4.81, N 7.86; found C 45.72, H 5.01, N 8.21.

***trans*-(*R**)-[PtCl$_2${NH=C(Ph)ON=C(C$_9$H$_{16}$)}{NH=C(Ph)ON=C-(C$_4$H$_8$)}] (6d):** Upon evaporation of the solvent, the initially yellow solution transformed into a dark oil, with product decomposition, precluding the possibility of recording reliable characterization data.

Reaction of *trans*-[PtCl$_2$(NCR)$_2$] (1) {R = CH$_2$CO$_2$Me (1a), Ph (1b)} or *trans*-(*R)-[PtCl$_2${NH=C(R)ON=C(C$_9$H$_{16}$)}(NCR)] (4) {R = CH$_2$CO$_2$Me (4a), Ph (4b)} with (*R**)-Camphor Oxime (2)**

(i) By the Conventional Method: A solution of **1a** (50.0 mg, 0.108 mmol), **1b** (51.0 mg, 0.108 mmol), **4a** (58.7 mg, 0.093 mmol), or **4b** (59.5 mg, 0.093 mmol) in dry CH_2Cl_2 (3 mL) was added at room temperature to (*R**)-camphor oxime (**2**) (2 equiv. for **1a**–**b** or 1 equiv. for **4a**–**b**). The mixture was heated with stirring at 40 °C for 15 or 60 min (for **1a** and **4a** or **1b** and **4b**, respectively).

(ii) By Focused Microwave Irradiation: A CH_2Cl_2 solution of the reagents in the above amounts was subjected to focused microwave irradiation at 40 °C for 5 or 20 min (for **1a** and **4a** or **1b** and **4b**, respectively). In both cases, the corresponding symmetric bis-iminoacylated products **7** were isolated and purified as indicated above.

***trans*-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}$_2$] (7a):** Method (i) (41.4 mg, 48% yield), method (ii) (56.0 mg, 65% yield). IR: $\tilde{\nu}$ = 3437 (NH), 1755 (CO_2Me), 1651 (C=N) cm^{-1}. ^1H NMR: δ = 0.79, 0.94, and 1.06 (three s, 3 H each, Me groups), 1.21–1.29 (m, 1 H), 1.43–1.54 (m, 1 H), 1.64–2.13 (m, 4 H), 2.59–2.65 (m, 1 H), 3.79 (s, 3 H, MeO), 4.17 and 4.21 (two s, 2 H, CH_2), 8.06 (br. s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.5, 19.0, 20.1 (Me), 27.5, 32.8, 35.7 (CH_2), 40.1 (*C*H_2CO_2Me), 44.0 (CH), 49.6 (*C*Me), 53.3 (*C*Me$_2$), 54.4 (MeO), 167.2 (*C*O_2Me), 168.0 [C(O)=N], 179.8 [(O)-N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2060 (J = 846 Hz) ppm. FAB^+-MS: m/z = 798 $[M]^+$. $C_{28}H_{44}Cl_2N_4O_6Pt$ (798.66): calcd. C 42.11, H 5.55, N 7.02; found C 42.54, H 5.77, N 6.95.

***trans*-[PtCl$_2${NH=C(Ph)ON=C(C$_9$H$_{16}$)}$_2$] (7b):** Method (i) (43.5 mg, 50% yield), method (ii) (47.8 mg, 55% yield). IR: $\tilde{\nu}$ = 3463 (NH), 1637 (C=N) cm^{-1}. ^1H NMR: δ = 0.82, 0.95, and 1.11 (three s, 3 H each, Me groups), 1.18–1.27 (m, 1 H), 1.49–1.61 (m, 1 H), 1.76–1.96 (m, 3 H), 2.14–2.20 (m, 1 H), 2.64–2.71 (m, 1 H), 7.46–7.63 (m, 3 H), 8.24 (br. s, 1 H, NH), 8.64 (d, J_{HH} = 7.2 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.9, 18.3, 19.4 (Me), 26.8, 32.2, 35.1 (CH_2), 43.3 (CH), 48.9 (*C*Me), 53.6 (*C*Me$_2$), 127.9, 129.2, 129.4, 132.1 ($C_{aromatic}$), 167.2 [C(O)=N], 178.4 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –1947 (J = 750 Hz) ppm. FAB^+-MS: m/z = 806 $[M]^+$. $C_{34}H_{44}Cl_2N_4O_2Pt$ (806.72): calcd. C 50.62, H 5.50, N 6.95; found C 50.94, H 5.25, N 6.56.

Liberation of the Iminoacylated Oxime 8: The ligand dppe (39.5 mg, 0.099 mmol) was added to a solution of *trans*-[PtCl$_2${NH=C(R)-ON=C(C$_9$H$_{16}$)}$_2$] (**7**) {R = CH$_2$CO$_2$Me (**7a**), Ph (**7b**)} (0.049 mmol) in $CDCl_3$ (1 mL, 99.8% D), and the mixture was left to stand for 30 min, with the release of a colorless precipitate of $[Pt(dppe)_2]Cl_2$. This solid was removed by filtration, and the filtrate was characterized by NMR and, after being taken to dryness, by IR and FAB-MS.

NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$) (*R-8a):** $[\alpha]_D^{20}$ = –32.7 (c = 0.40 in $CHCl_3$). IR: $\tilde{\nu}$ = 1749 (CO_2Me), 1611 and 1672 (C=N) cm^{-1}. ^1H NMR: δ = 0.81, 0.92, and 1.05 (three s, 3 H each, Me groups), 1.21–1.26 (m, 1 H), 1.44–1.47 (m, 1 H), 1.75–1.94 (m, 3 H), 2.10–2.18 (m, 1 H), 2.59–2.65 (m, 1 H), 3.65 (s, 3 H, MeO), 3.72 and 4.38 (two s, 2 H, CH_2), 7.67 (br. s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.9, 18.4, 19.4 (Me), 27.0, 32.5, 34.6 (CH_2), 43.5 (CH), 48.6 (*C*Me), 50.2 (MeO), 53.0 (*C*Me$_2$), 64.3 (*C*H_2CO_2Me), 168.8 [C(O)=N], 171.8 (*C*O_2Me), 175.2 [(O)N=*C*CH_2] ppm. FAB^+-MS: m/z = 266 $[M]^+$.

NH=C(Ph)ON=C(C$_9$H$_{16}$) (*R-8b):** $[\alpha]_D^{20}$ = –15.2 (c = 0.37 in $CHCl_3$). IR: $\tilde{\nu}$ = 1650 (C=N) cm^{-1}. ^1H NMR: δ = 0.85, 0.97, and 1.14 (three s, 3 H each, Me groups), 1.27–1.34 (m, 1 H), 1.48–1.62 (m, 1 H), 1.77–2.00 (m, 3 H), 2.24–2.30 (m, 1 H), 2.71–2.79 (m, 1 H), 7.30 (d, J_{HH} = 6.0 Hz, 2 H), 7.38–7.48 (m, 2 H), 7.69 (br. s, 1 H, NH), 8.01 (d, J_{HH} = 6.0 Hz, 1 H) ppm. $^{13}C\{^1H\}$ NMR: δ = 11.0, 18.5, 19.5 (Me), 27.1, 32.6, 34.8 (CH_2), 43.6 (CH), 48.6 (*C*Me), 53.0 (*C*Me$_2$), 127.6, 128.1, 129.1, 131.9 ($C_{aromatic}$), 162.7 [C(O)=N], 176.0 [(O)N=*C*CH_2] ppm. FAB^+-MS: m/z = 270 $[M]^+$.

Reactions of the Mono-Iminoacylated Pt^{II} Complexes *trans*-(*R)-[PtCl$_2${NH=C(R)ON=C(C$_9$H$_{16}$)}(NCR)] (4) {R = CH$_2$CO$_2$Me (4a), Ph (4b)} with the Diimino Ester NH=C(CH$_2$CO$_2$Me)ON=C-(C$_9$H$_{16}$) (*R**-8a)**

Diimino ester **8a** (35.6 mg, 0.134 mmol) was added to a solution of **4a** (50.0 mg, 0.079 mmol) or **4b** (50.0 mg, 0.078 mmol) in dry CH_2Cl_2 at room temperature, and the reaction solution was stirred for 2 h. The progress of the reaction was monitored by TLC (CH_2Cl_2 as eluent). After concentration of the solution in vacuo to dryness, the crude residue was purified by column chromatography on silica (CH_2Cl_2 as eluent) followed by evaporation of the solvent in vacuo to give the corresponding complexes **9**.

***trans*-(*R**,*R**)-[PtCl$_2${NH=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}{NH=C-(CH$_2$CO$_2$Me)N=C(CH$_2$CO$_2$Me)ON=C(C$_9$H$_{16}$)}] (9a):** 46.0 mg,

65% yield. $[\alpha]_D^{20}$ = –20.3 (*c* = 0.40 in $CHCl_3$). IR: $\tilde{\nu}$ = 3443 (NH), 1749 (CO_2Me), 1655 (C=N) cm^{-1}. ^1H NMR: δ = 0.78–1.04 (m, 18 H, Me groups), 1.19–2.60 (m, 14 H), 3.77 (s, 9 H, MeO), 4.10–4.23 (m, 6 H, CH_2CO_2), 8.04 (br. s, 1 H, NH), 8.40 (br. s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.8, 11.0, 18.3, 18.4, 19.3, 19.4 (Me), 26.8, 27.2, 32.1, 32.6, 32.9, 34.9 (CH_2), 39.4 (CH_2CO_2Me), 43.3, 43.6 (CH), 48.1, 48.9 (*C*Me), 51.7, 52.6 (MeO), 53.7 (CMe_2), 166.4 [C(O)=N], 167.3 (CO_2Me), 169.9 [C(N)=N], 179.1 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2011 (*J* = 850 Hz) ppm. ESI-MS: *m*/*z* = 896 $[M]^+$. $C_{32}H_{49}Cl_2N_5O_8Pt$ (896.26): calcd. C 42.81, H 5.50, N 7.80; found C 42.94, H 5.27, N 7.96.

***trans*-(*R**,*R**)-[$PtCl_2${NH=C(Ph)ON=C(C_9H_{16})}{NH=C(Ph)-N=C(CH_2CO_2Me)ON=C(C_9H_{16})}] (9b):** 34.6 mg, 49% yield. $[\alpha]_D^{20}$ = –25.4 (*c* = 0.37 in $CHCl_3$). IR: $\tilde{\nu}$ = 3437 (NH), 1725 (CO_2Me), 1638 (C=N) cm^{-1}. ^1H NMR: δ = 0.83–1.12 (m, 18 H, Me groups), 1.61–2.40 (m, 14 H), 3.78 (s, 3 H, MeO), 4.62 (s, 2 H, CH_2CO_2), 7.47–7.61 (m, 8 H), 8.25 (br. s, 1 H, NH), 8.65 (d, J_{HH} = 6.0 Hz, 2 H) ppm. $^{13}C\{^1H\}$ NMR: δ = 10.9, 12.5, 17.9, 18.0, 18.3, 19.5 (Me), 25.6, 26.9, 32.2, 35.2, 35.4 (CH_2), 39.5 (CH_2CO_2), 43.4 (CH), 46.0, 46.8 (*C*Me), 48.9 (MeO), 53.7 (CMe_2), 119.7, 120.9, 128.0, 129.3, 129.5, 132.2, 147.7 ($C_{aromatic}$), 167.2 [C(O)=N], 168.9 [C(N)=N], 171.7 (CO_2Me), 178.5 [(O)N=*C*CH_2] ppm. ^{195}Pt NMR: δ = –2013 (*J* = 825 Hz) ppm. ESI-MS: *m*/*z* = 905 $[M]^+$. $C_{38}H_{49}Cl_2N_5O_4Pt$ (905.81): calcd. C 50.39, H 5.45, N 7.73; found C 50.55, H 5.85, N 7.82.

Reactions of the Diimino Ester (*R-8a) with the Acyclic Nitrones $^-O^+N(Me)=C(H)R'$ (10) {R′ = 4-MeC_6H_4 (10a), 2,4,6-$Me_3C_6H_4$ (10b)}**

A solution of **8a** (30.0 mg, 0.113 mmol) in dry CH_2Cl_2 (3.0 mL) was added at room temperature to the appropriate nitrone **10** (1.2 equiv.), and the mixture was heated in a sealed stainless steel tube (20 mL) at 80 °C for 2 h. The progress of the reaction was monitored by TLC (CH_2Cl_2 as eluent). After concentration of the solution in vacuo to dryness, the crude residue was purified by column chromatography on silica (CH_2Cl_2 as eluent) followed by evaporation of the solvent in vacuo to give the corresponding (*E*)-cyanoalkenes **11**.

(N≡C)C(CO_2Me)=C(H)(4-MeC_6H_4) (11a): 11.6 mg, 51% yield. All the spectroscopic, FAB-MS, and elemental analytical data are in agreement with those reported earlier.[8a]

(N≡C)C(CO_2Me)=C(H)(2,4,6-$Me_3C_6H_2$) (11b): 13.5 mg, 52% yield. All the spectroscopic, FAB-MS, and elemental analytical data are in agreement with those reported earlier.[8a]

X-ray Crystal Structure Determinations for 5c and 7b: Single crystals of **5c** were obtained by diffusing diethyl ether in a dichloromethane solution of the complex. Diffusion of toluene in an acetone solution of **7b** yielded single crystals of this complex. Intensity data were collected by using a Bruker AXS-KAPPA APEX II diffractometer with graphite-monochromated Mo-K_α radiation. Data were collected at 150 K for **5c** and **7b** by using omega scans of 0.5° per frame, and a full sphere of data was obtained. Cell parameters were retrieved with Bruker SMART software and refined with Bruker SAINT on all the observed reflections. Absorption corrections were applied by using SADABS.[17] The structure was solved by direct methods with the SHELXS-97 package[18] and refined with SHELXL-97[19] with the WinGX graphical user interface.[20] All hydrogen atoms were inserted in calculated positions, except H1 and H2. Least-squares refinement with anisotropic thermal motion parameters for all the non-hydrogen atoms and isotropic parameters for the remaining was employed. Crystallographic parameters and residuals are given in Table 2. CCDC-657057 and -657056 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 2. Relevant crystal data for *trans*-[$PtCl_2${NH=C(Ph)-ON=CMe_2}(NCPh)] (**5c**) and *trans*-[$PtCl_2${NH=C(Ph)ON=C-(C_9H_{16})}$_2$] (**7b**).

	5c	**7b**
Empirical formula	$C_{17}H_{17}Cl_2N_3OPt$	$C_{34}H_{44}Cl_2N_4O_2Pt$
Formula weight	545.32	806.71
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$
T [K]	150(2)	150(2)
a [Å]	9.2541(10)	11.7513(4)
b [Å]	9.8917(11)	14.2981(4)
c [Å]	11.3966(13)	20.7949(7)
α [°]	109.041(6)	90
β [°]	91.674(6)	90
γ [°]	110.700(5)	90
V [$Å^3$]	910.08(18)	3493.99(19)
Z	2	4
$\rho_{calcd.}$ [$g\,cm^{-3}$]	1.990	1.534
F(000)	520	1616
$R_{Int.}$	0.0412	0.0404
*R*1[a] ($I \geq 2\sigma$)	0.0163	0.0285
*wR*2[b] ($I \geq 2\sigma$)	0.0375	0.0515
GoF	1.051	0.965

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

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