Reduction of (imine)Pt(IV) to (imine)Pt(II) Complexes with Carbonyl-Stabilized Phosphorus Ylides

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Received July 12, 2000

A novel method is reported for generation of the difficult-to-obtain (imine)Pt(II) compounds that involves reduction of the corresponding readily available Pt(IV)-based imines by carbonyl-stabilized phosphorus ylides, $Ph_3P{=}CHCO_2R$, in nonaqueous media. The reaction between *neutral* (imino)Pt(IV) compounds $[PtCl_4\{NH{=}C(Me)ON{=}CR^1R^2\}_2]$ [$R^1R^2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$, (Me)C(Me)=NOH], $[PtCl_4\{NH{=}C(Me)ONR_2\}_2]$ (R = Me, Et, CH_2Ph), $[PtCl_4\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$ (R^1 = H; R^2 = Ph or C_6H_4Me; R^3 = Me) as well as *anionic*-type platinum(IV) complexes $(Ph_3PCH_2Ph)[PtCl_5\{NH{=}C(Me)ON{=}CR_2\}]$ [$R_2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$] and 1 equiv of $Ph_3P{=}CHCO_2R$ (R = Me, Et) proceeds under mild conditions (ca. 4 h, room temperature) to give selectively the platinum(II) products (in good to excellent isolated yields) without further reduction of the platinum center. All thus prepared compounds (excluding previously described Δ^4-1,2,4-oxadiazoline complexes) were characterized by elemental analyses, FAB mass spectrometry, IR and ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ and ^{195}Pt NMR spectroscopies, and X-ray single-crystal diffractometry, the latter for $[PtCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]$ [crystal system tetragonal, space group $P4_2/n$ (No. 86), $a = b = 10.5050(10)$ Å, $c = 15.916(3)$ Å] and $(Ph_3PCH_2CO_2Me)[PtCl_3(NCMe)]$ [crystal system orthorhombic, space group $Pna2_1$ (No. 33), $a = 19.661(7)$ Å, $b = 12.486(4)$ Å, $c = 10.149(3)$ Å]. The reaction is also extended to a variety of other Pt(II)/Pt(IV) couples, and the ylides $Ph_3P{=}CHCO_2R$ are introduced as mild and selective reducing agents of wide applicability for the conversion of Pt(IV) to Pt(II) species *in nonaqueous media*, a route that is especially useful in the case of compounds that cannot be prepared directly from Pt(II) precursors, and for the generation of systematic series of Pt(II)/Pt(IV) complexes for biological studies.

Introduction

Alteration of reactivity of organic species upon their coordination to a metal center opens up a possibility for metal-mediated reactions that are not feasible for the substrates in the noncoordinated state, and this area, i.e., ligand reactions, has been a subject of rapt attention in the last two decades.[1−4] It is not unusual when the reactivity of substrates is different for a different oxidation state of a particular metal ion. Our recent comparative reactivity studies of (organonitrile)platinum(IV) compounds vs the corresponding platinum(II) complexes are illustrative in that respect. First, we have observed the reaction between the platinum(IV) complexes $[PtCl_4(RCN)_2]$ (R = Me, CH_2Ph, Ph) and oximes, $R^1R^2C{=}NOH$, or dioximes, HON=C{spacer}C=NOH, which led to the isolation of the imino compounds $[PtCl_4\{NH{=}C(R)ON{=}CR^1R^2\}_2]$[5] and $[PtCl_4\{NH{=}C(R)ON{=}C\{spacer\}C{=}NOH\}_2]$,[6] respectively. It was also found that the iminoacylation of oximes[5,6] occurs *only at the Pt(IV) center* (or at other metal centers in a relatively high oxidation state[7−9]) and the reaction does not proceed at all—even under harsh conditions—at either (organonitrile)Pt(II) complexes or at free RCN. These observations were rationalized by a mechanistic theoretical study[10] that suggested both lower activation energy and higher stability of products in the case of platinum(IV) systems compared with the platinum(II) ones.

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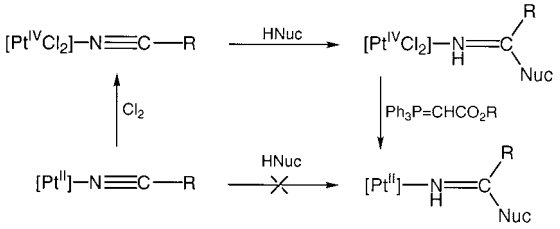
10.1021/ic000769c CCC: $20.00
Published on Web 03/02/2001

Second, we discovered an unusual coupling between nitriles bound to the platinum(IV) center in $[PtCl_4(RCN)_2]$ and nitrones $^{-}ON^{+}(R^3)=CR^1R^2$ [11,12] (the latter can be viewed as the "frozen", by alkylation, form of the other oxime tautomer) to give, in the course of [2 + 3] cycloaddition, Δ^4-1,2,4-oxadiazoline compounds $[PtCl_4\{N=C(Me)O-N(R^3)-C(R^1)(R^2)\}_2]$.[11,12] The role of the metal oxidation state on the control of the reactivity was verified when it was found that the highly reactive *platinum(IV) complexes* $[PtCl_4(RCN)_2]$ exhibit such a leveling effect on the cycloaddition that it might be performed under mild reaction conditions starting even from a very unreactive organonitrile bearing an electron-donor substituent, while for the much less reactive organonitriles in *platinum(II) complexes* $[PtCl_2(RCN)_2]$ a differentiating effect is recognized in such a way that the cycloaddition occurs only in the case of organonitriles with an electron-acceptor substituent.[12]

These two reactions, which proceed at a quadruply charged platinum center and are limited or even totally unreachable by use of (organonitrile)Pt(II) precursors, allow the isolation of Pt(IV)-bound imino species that cannot be prepared in so-called pure organic chemistry. Furthermore, imines $NH=C(Me)ON=CR^1R^2$ with two donor substituents at the carbon, prepared in the course of the reactions with oximes,[5-9] represent a distinctive subclass of unusually *stable* imines, and their preparation could be useful both for coordination chemistry in modeling elusive monodentate imine ligands[13-15] and for organic chemistry as models of unstable intermediates in a nitrilium ion catalyzed Beckmann rearrangement.[16,17]

As a continuation of our project on the reactivity of organonitrile platinum compounds[5-12] and preparation and biological investigation[18] of metal-stabilized imino species, we focused our attention on (imine)Pt(II) compounds. Complexes of this type are rather scarce,[19-30] and their chemistry is very little explored despite intrinsic antitumor activity of some of them.[31-33] Previously (imine)Pt(II) species were prepared either by base-catalyzed alcohol addition,[19-25] by hydrolysis[26] or ammonia addition[27] to nitrile platinum(II) complexes, or by direct reaction of some stable organic imines and Pt(II) precursors.[28-30] We report herein on a novel method for generation of (imine)Pt(II) compounds that involves reduction of the corresponding readily available Pt(IV)-based imines by carbonyl-stabilized phosphorus ylides, $Ph_3P=CHCO_2R$, in nonaqueous media (Scheme 1). The easy-to-obtain[34] ylides $Ph_3P=CHCO_2R$ (R = Me, Et) and in particular the former one that is commercially available are now introduced as mild and selective reducing agents for conversion of Pt(IV) to Pt(II) species, a route that is especially useful in the case of compounds that cannot be prepared directly from Pt(II) precursors. In this way we take advantage of the stronger activation power of a Pt(IV) center toward nucleophilic addition to organonitrile ligands to form, upon addition followed by reduction, final (imine)Pt(II) complexes which otherwise would not be accessible.

Scheme 1



Results and Discussion

Reduction of (imine)Pt(IV) Compounds with $Ph_3P=CHCO_2R$ and Characterization of Products. A systematic approach to investigations of chemical reactivity[1-4] and biological activity[35-40] of platinum compounds often involves comparative studies for platinum(II) complexes vs the corresponding platinum(IV)-based compounds. The most common route for preparation of these couples is oxidation of platinum(II) complexes with Cl_2 (or its so-called "solid chlorine equivalents", e.g., PCl_5[41-43] or $PhICl_2$[44-46]) or other halogens in aqueous or

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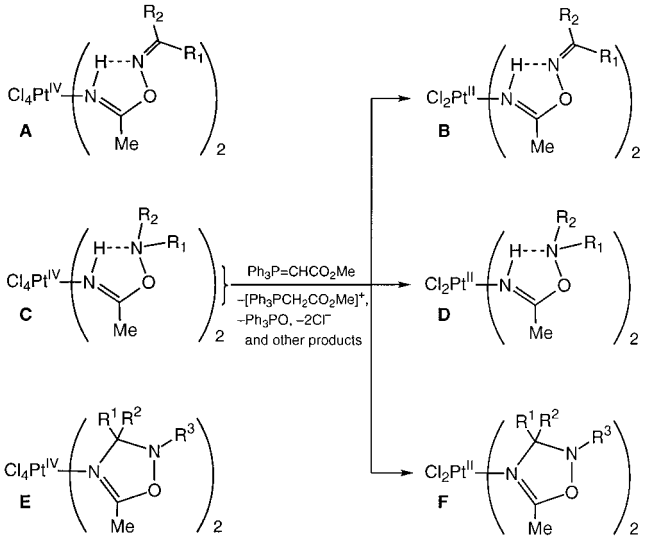
nonaqueous media to give $[PtX_4LL']$ complexes or reaction with hydrogen peroxide[47−50] in water to generate $[PtX_2(OH)_2LL']$ species. The opposite way, i.e., reduction of platinum(IV) complexes, although known, is much less common, being applied mostly for syntheses performed in *aqueous media* due to better solubilities of the typical reducing agents,[4] e.g., $N_2H_4 \cdot H_2SO_4$, $NH_2OH \cdot HCl$, oxalate, or ascorbate, in water. To the best of our knowledge a reagent that effectively reduces in nonaqueous media a variety of platinum(IV) centers to platinum(II) ones has not yet been devised although applications of SO_2, ethanol, olefins, or formaldehyde[4] for the reduction of some narrow classes of platinum(IV) compounds were reported in the literature.

During attempts to extend to $[PtCl_4(MeCN)_2]$ the previous studies on the nucleophilic attack of carbonyl-stabilized phosphorus ylides to organonitriles coordinated to Pt(II),[51−53] we observed a facile reduction of the platinum center that proceeded under mild conditions (see below). This result prompted us to explore further the potential of the phosphorus ylides for the reduction of platinum(IV) complexes other than the nitrile-based compounds. For this study we addressed (imine)Pt(IV) complexes[5,6] including (Δ^4-1,2,4-oxadiazoline)Pt(IV) compounds[11] due to (i) the general interest in this class of complexes justified in the Introduction and (ii) the necessity to develop a route to (imine)Pt(II) species especially those that cannot be prepared directly from Pt(II) precursors.

The reaction between $[PtCl_4\{NH{=}C(Me)ON{=}CR^1R^2\}_2]$ ($R^1R^2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$, and (Me)C(Me)=NOH) and 1 equiv of $Ph_3P{=}CHCO_2Me$ ($Ph_3P{=}CHCO_2Et$ can be used instead) proceeds under mild conditions (ca. 4 h, room temperature) to give a mixture of one platinum-containing product along with phosphorus-containing species (**A** → **B** in Scheme 2). The latter can be easily separated from the platinum material by washing the mixture with ethanol and diethyl ether. Alternatively, column chromatography is useful for the separation (see Experimental Section). Independently of the method applied for the purification, the isolated yields of the platinum compounds range from good to excellent (80−95%). The same method of reduction was used for the conversion of other *neutral* (imine)Pt(IV) compounds, i.e., $[PtCl_4\{NH{=}C(Me)ONR_2\}_2]$ (R = Me, Et, CH_2Ph)[54] (**C** → **D** in Scheme 2) and $[PtCl_4\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$ ($R^1 = H$; R^2 = Ph or C_6H_4-Me; $R^3 = Me$[11,12]) (**E** → **F** in Scheme 2). In addition, the ylides reduce readily the *anionic-type* compounds $(Ph_3PCH_2Ph)[PtCl_5\{NH{=}C(Me)ON{=}CR_2\}]$ [$R_2 = Me_2$, $(CH_2)_4$, $(CH_2)_5$] to give the appropriate platinum(II) complexes $(Ph_3PCH_2Ph)[PtCl_3\{NH{=}C(Me)ON{=}CR_2\}]$, which were isolated in individual form in 60−70% yields after chromatography on silica gel. In the latter case, some other platinum-containing species were also detected in the reaction mixtures but only as minor components and were not isolated and identified.

Scheme 2



All thus prepared compounds (excluding previously described Δ^4-1,2,4-oxadiazoline complexes[12]) were characterized by elemental analyses, FAB mass spectrometry and IR and ^1H, $^{13}C\{^1H\}$, and ^{195}Pt NMR spectroscopies. The X-ray structure determination of $[PtCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]$ (**1**) (Figure 1) revealed its trans configuration, and, similarly to the corresponding platinum(IV) complex,[5] the imine ligands exhibit the one-end rather than the *N*,*N*-bidentate coordination mode. The iminoacyl species are in the *E* conformation which is held by a N−H···N hydrogen bond [N(1)···N(2), N(1)−H, N(1)H···N(2) are 2.66, 0.9641, and 2.2640 Å; N(1)−H···N(2) 103.788°] between the imine =N*H* atom and the oxime nitrogen. No evidence for the *Z* conformation in solution was obtained by NMR spectroscopy.

General features of the IR and ^1H and $^{13}C\{^1H\}$ NMR spectra of $[PtCl_2\{NH{=}C(Me)ON{=}CR^1R^2\}_2]$, $[PtCl_2\{NH{=}C(Me)ONR_2\}_2]$, and $[PtCl_2\{N{=}C(Me)O{-}N(R^3){-}C(R^1)(R^2)\}_2]$ are similar to those observed for the appropriate platinum(IV) complexes.[5,6,11,54] The most significant difference between the two types of complexes is their ^{195}Pt NMR spectra which show the disappearance of the Pt(IV) signal in the range from −156 to −194 ppm [from 0.8 to 2.6 for anionic Pt(IV) complexes], while a new resonance emerges in the range from −2033 to −2210 ppm [from −1807 to −1811 for the anionic-type Pt(II) complexes].

Plausible Mechanism of Reducing Action of the Ylides. In coordination chemistry, the carbonyl-stabilized phosphorus ylides display two principal reactivity modes, i.e., they act as *C*-donor ligands displacing poorer ligands[55−64] and as nucleophiles in the addition to metal-activated organonitriles[51−53] and

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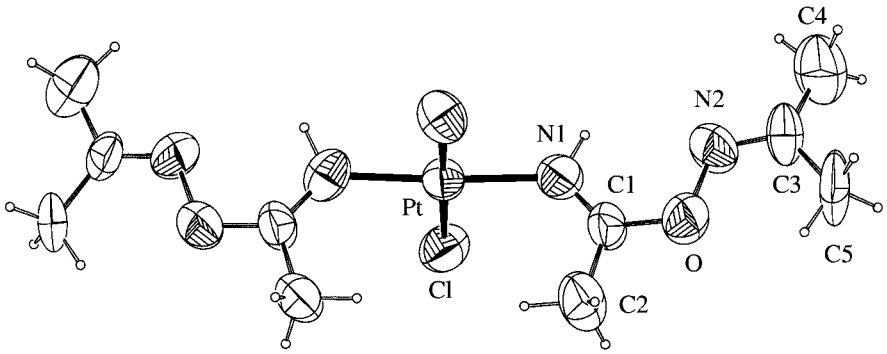

Figure 1. PLATON drawing of *trans*-[$PtCl_2${NH═C(Me)ON═CMe_2}$_2$] with atomic numbering scheme. Selected bond distances (Å): Pt−Cl 2.296(8), Pt−N(1) 1.98(2), N(1)−C(1) 1.27(4), O−C(1) 1.34(3), O−N(2) 1.43(3), N(2)−C(3) 1.25(3).

alkenes.[65] Reducing properties of the ylides are totally unexplored in coordination chemistry although they are known from *organic* chemistry.[66−69] It was shown that chlorination of Ph_3P═$CHCO_2Me$ gives ($Ph_3PCHClCO_2Me$)Cl, which immediately reacts, by transylidation, with yet unreacted Ph_3P═$CHCO_2$-Me to give ($Ph_3PCH_2CO_2Me$)Cl and Ph_3P═$CClCO_2Me$.[66] Further chlorination of Ph_3P═$CClCO_2Me$ gives ($Ph_3PCCl_2CO_2$-Me)Cl and Ph_3P═O. The latter presumably forms via hydrolytic cleavage of ($Ph_3PCCl_2CO_2Me$)Cl and/or Ph_3P═$CClCO_2Me$.[67,68] In our systems, in accord with these findings, we observed the formation of ($Ph_3PCH_2CO_2Me$)Cl which was isolated from the synthesis of [$PtCl_2${NH═C(Me)ON═CMe_2}$_2$] and characterized. Triphenylphosphine oxide was also isolated after chromatography on silica gel, and its appearance agrees with the previous report indicating that Ph_3P═$CClCO_2Et$ decomposes during chromatography on Al_2O_3 to give Ph_3P═O.[68]

The reaction between [$PtCl_4(MeCN)_2$] and Ph_3P═$CHCO_2$-Me in acetonitrile is remarkable from the viewpoint of understanding the reducing action of the ylides. Treatment of the complex with 1 equiv of Ph_3P═$CHCO_2Me$ results in precipitation of the platinum(II) complex [$PtCl_2(MeCN)_2$]. The filtrate, after removal of the insoluble material, was shown by TLC and $^{31}P\{^1H\}$ NMR monitoring to contain Ph_3P═O. Subsequent removal of the solvent and recrystallization of the residue from EtOH allowed the isolation of pure ($Ph_3PCH_2CO_2Me$)[$PtCl_3$-(MeCN)], where the phosphonium cation, formed in the course of the process, was unambiguously identified by X-ray crystallography (Figure 2, Table 1).

Although the addition of ylides to coordinated nitrile species should be easier in the case of [$PtCl_4(MeCN)_2$], as compared to [$PtCl_2(MeCN)_2$],[51−53] the reduction is conceivably faster and becomes the dominant reaction path. It is reasonable to assume that the reduction of [$PtCl_4(MeCN)_2$] leads to [$PtCl_2(MeCN)_2$] and ($Ph_3PCH_2CO_2Me$)Cl followed by replacement of the weakly bonded acetonitrile ligand in nonaqueous media by the halide to generate the anionic complex, a process that is known from the chemistry of platinum(II)-based nitrile compounds.[70]

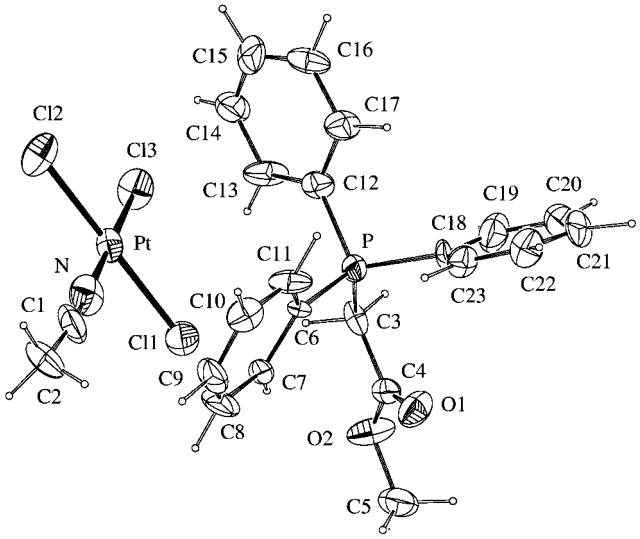

Figure 2. PLATON drawing of ($Ph_3PCH_2CO_2Me$)[$PtCl_3$(NCMe)] with atomic numbering scheme. Bond distances in the anion (Å): Pt−Cl(1) 2.329(5), Pt−Cl(2) 2.296(5), Pt−Cl(3) 2.260(6), Pt−N 1.951(18), C(1)−N1.14(3), C(1)−C(2) 1.46(3).

Table 1. Crystal Data and Structure Refinement for *trans*-[$PtCl_2${NH═C(Me)ON═CMe_2}$_2$] and ($Ph_3PCH_2CO_2Me$)[$PtCl_3$(NCMe)]

empirical formula	$C_{10}H_{20}N_4Cl_2O_2Pt$	$C_{23}H_{23}NCl_3O_2PPt$
fw	494.29	677.82
T, °C	20(2)	20(2)
space group	$P4_2/n$ (No. 86)	$Pna2_1$ (No. 33)
a/Å	10.5050(10)	19.661(7)
b/Å	10.5050(10)	12.486(4)
c/Å	15.916(3)	10.149(3)
α/deg	90	90
β/deg	90	90
γ/deg	90	90
V/Å^3	1756.4(4)	2491.4(14)
Z	4	4
D_c, Mg/m^3	1.869	1.807
μ(Mo Kα), mm^{-1}	8.296	6.33
R^a	0.0394	0.0379
$R_w{}^b$	0.0982	0.0410

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

Reduction of Other Platinum(IV) Complexes. Facile reduction of (imine)Pt(IV) compounds with the ylides Ph_3P═$CHCO_2R$ in nonaqueous media opens up a route to such (imine)-Pt(II) complexes which are unaccessible by direct synthesis from platinum(II) precursors. Moreover, despite the fact that this study

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was mostly focused around the reduction of (imine)Pt(IV) species, the method is more general and it was also successfully applied in this work to some other systems (see Experimental Section) involving $[PtCl_4L_2]$ (L = Me_2S, Me_2SO, pyridine, 2-propanone oxime), $[PtCl_4(py)(Me_2S)]$, $[PtCl_4(Me_2SO)(NHEt_2)]$, and the anionic complex $(Ph_3PCH_2Ph)[PtCl_5(Me_2SO)]$. It is worthwhile to mention that (i) dimethyl sulfoxide ligands remain intact upon the reduction in spite of the fact that deoxygention of the sulfinyl group with other phosphorus ylides,[71] although more reactive than $Ph_3P{=}CHCO_2Me$, is known; (ii) despite the fact that *coordinated* 2-propanone oxime exhibits a significant OH acidity,[72] the reaction between $[PtCl_4(Me_2C{=}NOH)_2]$ and $Ph_3P{=}CHCO_2Me$, which is a base, led to the reduction products rather than to those derived from neutralization; and (iii) chlorides which liberated upon the reduction in nonaqueous media can displace the weakly bound ligands[73−78] (such as, for example, MeCN or Me_2SO) in $[PtCl_2L_2]$ to form the anionic complexes $[PtCl_3L]^-$. The substitution of either acetonitrile or dimethyl sulfoxide in $[PtCl_2L_2]$ by Cl^- in organic solvents has previously been described.[70,80]

Concluding Remarks. It is anticipated that reduction with ylides represents a very convenient method for generation of imine and other platinum(II) compounds in a nonaqueous phase. Indeed, the readily available ylides are highly soluble in the most common organic solvents, and this allows the performance of the syntheses in a homogeneous liquid phase. The reduction proceeds rapidly and under mild conditions with 1 equiv of the ylide to form selectively the platinum(II) products without further reduction of the platinum center which—in the case of reduction to the platinum black—would result in decomposition. Moreover, the products of oxidation of the ylides can be easily separated from the platinum products, and after workup the platinum(II) compounds were isolated in good yields. The only disadvantage we see so far is the case of anionic complexes, since the generated phosphonium cation can compete with other cations giving mixtures where the anionic platinum complex is linked to two different counterions.

The recommended procedure was proved to be efficient for the reduction of different platinum(IV) complexes containing N-donor ligands with sp^3, sp^2, and sp configurations of the N atoms, and this implies that the method can be useful for the generation of systematic series of Pt(II)/Pt(IV) complexes for biological studies which most often involve complexes with ligated N donors. Thus, the reduction gives the platinum(II) members in Pt(II)/Pt(IV) couples, and reoxidation of the Pt(II) complexes with, for instance, H_2O_2 should give the corresponding dihydroxo species, thus forming the homologous sets of complexes.

Experimental Section

Materials and Instrumentation. Solvents were obtained from commercial sources and used as received. $Ph_3P{=}CHCO_2Me$ was purchased from Lancaster while other ylides were prepared in accord with the published method.[79] Imino compounds[5,6,11,54] (except $[PtCl_4\{NH{=}C(Me)ON{=}CMeEt\}_2]$, whose synthesis is given below) and other complexes *trans*-$[PtCl_4L_2]$ (L = Me_2SO,[80,81] Me_2S,[80] py,[82] 2-propanone oxime,[83] MeCN[81]), $[PtCl_4(py)(Me_2S)]$,[84,85] $[PtCl_4(Me_2SO)(NHEt_2)]$,[80,81] and $(Ph_3PCH_2Ph)[PtCl_5(Me_2SO)]$[80,81] were prepared in accord with the published methods. 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 (NBA) matrixes 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 were measured on a Varian UNITY 300 spectrometer at ambient temperature. ^{195}Pt chemical shifts are given relative to $Na_2[PtCl_6]$ (by using aqueous $K_2[PtCl_4]$ = −1630 ppm as a standard), and half-height line widths are shown in parentheses.

$[PtCl_4\{NH{=}C(Me)ON{=}CMeEt\}_2]$. This platinum(IV) compound for the reduction experiments was prepared accordingly to the published method[5] and used as the starting material for the reduction experiments (see below). Anal. Calcd for $C_{12}H_{24}N_4Cl_4O_2Pt$: C, 24.30; H, 4.08; N, 9.44. Found: C, 23.95; H, 4.28; N, 9.56. FAB^+-MS, *m*/*z*: 615 $[M + Na]^+$, 593 $[M + H]^+$, 557 $[M - HCl]^+$, 522 $[M - 2Cl]^+$. IR spectrum (selected bands), cm^{-1}: 3273 m ν(N−H), 1655 sh and 1634 s ν(C=N), 1183 m ν(C−O). ^1H NMR in $CDCl_3$, δ: 1.12 (t, 7.8 Hz, major signal), 1.10 (t, 7.8 Hz, minor signal), 2.37 (quart., 7.8 Hz, major signal) and 2.49 (quart., 7.8 Hz, minor signal) (Et), 2.06 (s, major signal) and 2.03 (s, minor signal) (Me), 2.62 (s, major signal) and 2.61 (minor signal) (HN=C(*Me*)), 8.45 (br, NH). $^{13}C\{^1H\}$ NMR in $CDCl_3$, δ: 18.0 (major signal) and 18.2 (minor signal) (HN=C*Me*), 10.2 (major signal), 10.1 (minor signal), 29.2 (major signal) and 24.3 (minor signal) (Et), 16.0 (major signal) and 19.3 (minor signal) (Me), 170.4 (major signal) and 170.2 (minor signal) (N=C), 174.4 (major signal) and 174.2 (minor signal) (HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −160 (825 Hz). EtMeC=NOH exists as an equilibrium mixture of ca. 75% *E* and 25% *Z* isomer; therefore two sets of signals for the ligand in an approximate ratio of 4:1 were expected and observed.

Reduction of Pt(IV) Complexes to the Corresponding Pt(II) Complexes with $Ph_3P{=}CHCO_2Me$. The solid phosphorus ylide $Ph_3P{=}CHCO_2Me$ (17 mg, 0.050 mmol) was added to a solution of the corresponding Pt(IV) complex (0.050 mmol) in CH_2Cl_2 (3 mL) whereupon the color of the solution changed from deep yellow to pale yellow within ca. 1 h. The reaction mixture was kept at room temperature for 3 h, then the solvent was evaporated and the residue subjected to chromatography on silica gel. Elution with CH_2Cl_2/Et_2O (9:1, v/v) afforded the pure Pt(II) complex with yields ranges from 85% to 90% for neutral compounds and from 60% to 70% for anionic complexes; subsequent elution with CH_2Cl_2/MeOH gave an approximate 1:1 mixture of two phosphorus-containing compounds, from which the $(Ph_3PCH_2CO_2Me)Cl$ was crystallized as a colorless solid using CH_2Cl_2/Et_2O as solvent of crystallization and Ph_3PO was obtained from the mother liquor. Identification of $(Ph_3PCH_2CO_2Me)Cl$ and Ph_3PO was done by comparison of their ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR and IR spectra with those of commercial samples. Reduction of the anionic complexes followed the same procedure and occurred without color change. Completeness of the reaction was checked by TLC, and the product was isolated by chromatography on silica gel, eluent CH_2Cl_2/acetone (3:1, v/v).

$[PtCl_2\{NH{=}C(Me)ON{=}CMe_2\}_2]$. Anal. Calcd for $C_{10}H_{20}N_4Cl_2O_2Pt$: C, 24.30; H, 4.08; N, 11.34. Found: C, 24.35; H, 4.00; N, 11.19.

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FAB$^+$-MS, *m/z*: 517 [M + Na]$^+$, 494 [M]$^+$, 458 [M − HCl]$^+$, 421 [M − HON=CMe_2]$^+$, 385 [M − HON=CMe_2 − HCl]$^+$, 348 [M − 2HON=CMe_2 − HCl]$^+$. IR spectrum (selected bands), cm^{-1}: 3222 m ν(N−H), 1666 and 1646 s ν(C=N), 1173 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 2.02 and 2.03 (two s, 3H each, (=C*Me*$_2$), 2.64 (s, 3H, N=C*Me*), 7.92 (br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 17.1 and 21.8 (=C*Me*$_2$), 19.4 (N=C*Me*), 164.1 (N=*C*Me$_2$), 170.5 (HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −2040 (770 Hz).

[PtCl$_2${NH=C(Me)ON=CMeEt}$_2$]. Anal. Calcd for $C_{12}H_{24}N_4Cl_2O_2Pt$: C, 27.59; H, 4.63; N, 10.73. Found: C, 28.01; H, 4.69; N, 10.70. FAB$^+$-MS, *m/z*: 522 [M]$^+$, 486 [M − HCl]$^+$, 450 [M − HCl − Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3210 m ν(N−H), 1659 and 1643 s ν(C=N), 1177 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.13 (t, 7.5 Hz, major signal), 1.09 (t, 7.5 Hz, minor signal), 2.34 (quart., 7.8 Hz, major signal) and 2.42 (quart., 7.8 Hz, minor signal) (Et), 1.99 (s, major signal) and 2.00 (s, minor signal) (Me), 2.57 (s, major signal) and 2.56 (minor signal) (HN=C(*Me*)), 7.91 (br, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 19.3 (major signal) and 19.5 (minor signal) (HN=C*Me*), 10.3 (major signal), 9.9 (minor signal), 29.2 (major signal) and 24.0 (minor signal) (Et), 15.6 (major signal) and 19.4 (minor signal) (Me), 168.7 (major signal) and 169.5 (minor signal) (N=C), 170.9 (HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −2088 (800 Hz). EtMeC=NOH exists as an equilibrium mixture of ca. 75% *E* and 25% *Z* isomer; therefore two sets of signals for the ligand in an approximate ratio of 4:1 were expected and observed.

[PtCl$_2${NH=C(Me)ON=C(CH$_2$)$_4$}$_2$]. Anal. Calcd for $C_{14}H_{24}N_4Cl_2O_2Pt$: C, 30.78; H, 4.43; N, 10.25. Found: C, 30.96; H, 4.82; N, 10.05. FAB$^+$-MS, *m/z*: 546 [M]$^+$, 510 [M − Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3220 m ν(N−H), 1651 s ν(C=N), 1170 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.82 (m, 4H) and 2.47 (m, 4H) (=C(CH$_2$)$_4$), 2.54 (s, 3H, N=C*Me*), 7.83 (br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 19.4 (N=C*Me*), 24.4, 24.9, 29.6 and 31.4 ((CH$_2$)$_4$), 176.6 (N=*C*(CH$_2$)$_4$), 171.0 (HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −2088 (840 Hz).

[PtCl$_2${NH=C(Me)ON=C(CH$_2$)$_5$}$_2$]. Anal. Calcd for $C_{16}H_{28}N_4Cl_2O_2Pt$: C, 33.46; H, 4.91; N, 9.75. Found: C, 33.42; H, 5.05; N, 9.79. FAB$^+$-MS, *m/z*: 597 [M + Na]$^+$, 575 [M + H]$^+$, 539 [M − Cl]$^+$, 539 [M − Cl − HCl]$^+$. IR spectrum (selected bands), cm^{-1}: 3209 m ν(N−H), 1663 and 1643 s ν(C=N), 1180 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 1.67 (m, 4H), 1.77 (m, 2H), 2.34 (t, 6.6 Hz, 2H) and 2.54 (t, 6.6 Hz, 2H) (=C(CH$_2$)$_5$), 2.59 (s, 3H, N=C*Me*), 7.92 (br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 19.6 (N=C*Me*), 25.1, 25.7, 26.7, 27.1 and 31.9 ((CH$_2$)$_5$), 169.8 (N=*C*(CH$_2$)$_5$ and HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −2091 (680 Hz).

[PtCl$_2${NH=C(Me)ON=C(Me)C(Me)=NOH}$_2$]. Anal. Calcd for $C_{12}H_{22}N_6Cl_2O_4Pt$: C, 24.84; H, 3.82; N, 12.22. Found: C, 25.12; H, 4.10; N, 12.13. FAB$^+$-MS, *m/z*: 603 [M + Na]$^+$, 580 [M]$^+$, 545 [M − Cl]$^+$. IR spectrum (selected bands), cm^{-1}: 3241 m ν(N−H), 1670 s ν(C=N), 1189 m ν(C−O). ^{1}H NMR in acetone-d_6, δ: 2.09 and 2.18 (two s, 3H each, (=C(*Me*)C(*Me*)), 2.67 (s, 3H, N=C*Me*), 8.50 (br, 1H, NH). ^{13}C{^{1}H} NMR in acetone-d_6, δ: 9.7 and 11.6 (=C(*Me*)C(*Me*)), 19.6 (N=C*Me*), 153.0 and 163.7 (two ON=*C*), 170.7 (HN=C). ^{195}Pt NMR in acetone-d_6, δ: −2055 (400 Hz).

[PtCl$_2${NH=C(Me)ONMe$_2$}$_2$]. Anal. Calcd for $C_8H_{20}N_4Cl_2O_2Pt$: C, 20.43; H, 4.29; N, 11.91. Found: C, 20.58; H, 4.18; N, 11.77. FAB$^+$-MS, *m/z*: 469 [M]$^+$, 433 [M − Cl]$^+$, 398 [M − 2Cl]$^+$. IR spectrum in KBr, selected bands, cm $^{-1}$: 3247 m ν(N−H), 1665 s ν(C=N). ^{1}H NMR in $CDCl_3$, δ: 2.48 (s, 3H, =CMe), 2.73 (s, 6H, NMe_2) 8.05 (s, br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 18.8 (Me), 47.5 (NMe_2), 170.7 (C=N). ^{195}Pt NMR in $CDCl_3$, δ: −2047 (800 Hz).

[PtCl$_2${NH=C(Me)ONEt$_2$}$_2$]. Anal. Calcd for $C_{12}H_{28}N_4Cl_2O_2Pt$: C, 27.38; H, 5.35; N, 10.64. Found: C, 27.57; H, 5.28; N, 10.55. FAB$^+$-MS, *m/z*: 526 [M]$^+$, 454 [M − 2HCl]$^+$. IR spectrum in KBr, selected bands, cm $^{-1}$: 3256 m−w ν(N−H), 1665 s ν(C=N). ^{1}H NMR in $CDCl_3$, δ: 2.51 (s, 3H, =CMe), 1.09 (t, 7.2 Hz, 6H), 2.90 (quart., 6.6 Hz, 2H) and 2.91 (quart., 7.2 Hz, 2H) (NEt_2) 8.15 (s, br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 18.4 (Me), 11.6 and 52.7 (NEt_2), 172.3 (C=N). ^{195}Pt NMR in $CDCl_3$, δ: −2028 (700 Hz).

[PtCl$_2${NH=C(Me)ON(CH$_2$Ph)$_2$}$_2$]. Anal. Calcd for $C_{32}H_{36}N_4Cl_2O_2Pt$: C, 49.62; H, 4.68; N, 7.23. Found: C, 49.80; H, 4.57; N, 7.14. FAB$^+$-MS, *m/z*: 797 [M + Na]$^+$, 774 [M]$^+$, 738 [M − HCl]$^+$. IR spectrum (selected bands), cm^{-1}: 3271 m ν(N−H), 1655 s ν(C=N), 1157 m ν(C−O). ^{1}H NMR in $CDCl_3$, δ: 2.30 (s, 3H, N=C*Me*), 3.98 and 4.05 (two d, 13.2 Hz, 2H each, (C*H*$_2$Ph), 7.29 (m, 4H) and 7.36 (m, 6H) (CH$_2$*Ph*), 8.14 (br, 1H, NH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 18.4 (N=C*Me*), 61.5 (*C*H$_2$Ph), 128.3, 128.8, 129.6 and 133.9 (CH$_2$*Ph*), 171.1 (HN=C). ^{195}Pt NMR in $CDCl_3$, δ: −2033 (580 Hz).

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ON=CMe$_2$}]. Anal. Calcd for $C_{31}H_{34}N_2Cl_3OPPt$: C, 47.55; H, 4.38; N, 3.58. Found: C, 46.38; H, 4.12; N, 3.41. FAB$^-$-MS, *m/z*: 429 [M$_{anion}$]$^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3308 m−w ν(N−H), 3056 m−w and 2927 m ν(C−H), 1643 s ν(C=N), 1110 s−m ν(P−C). ^{1}H NMR in $CDCl_3$, δ: 7.7 (m, 15H, Ph), 7.1 (m, 5H, CH$_2$*Ph*), 5.17 (d, J_{PH} 14.0 Hz, 2H, C*H*$_2$-Ph), 3.11 (quart, J_{HH} 7.6 Hz, 2H, Et), 1.24 (t, J_{HH} 7.6 Hz, 3H, Et), 1.94 (s, 6H, =C*Me*$_2$). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 30.7 ($^1J_{PC}$ 51.1 Hz, *C*H$_2$-Ph), 117.5 ($^1J_{PC}$ 84.6 Hz, C_{ipso} from Ph), 127.1 ($^2J_{PC}$ 8.4 Hz, C_{ipso} from CH$_2$Ph),128.3 (J_{PC} 3.7 Hz, CH_p from Ph), 128.7 (J_{PC} 2.9 Hz, CH_m from Ph), 130.2 (J_{PC} 12.7 Hz, CH from Ph), 131.5 (J_{PC} 5.3 Hz, CH_o from CH$_2$Ph), 134.3 (J_{PC} 10.1 Hz, CH from Ph), 134.9 (J_{PC} 2.7 Hz, CH_p from Ph), 163.4 (C=N from ON=CMe_2), 172.6 (C=N from HN=C(Et)), 26.7 (CH$_2$ from Et), 10.1 (CH$_3$ from Et), 16.9 and 21.8 (=C*Me*$_2$). ^{31}P{^{1}H} in $CDCl_3$, δ: 23.6. ^{195}Pt NMR in $CDCl_3$, δ: −1811 (660 Hz).

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ON=C(C$_4$H$_8$)}]. Anal. Calcd for $C_{33}H_{36}N_2Cl_3OPPt$: C, 48.99; H, 4.48; N, 3.46. Found: C, 48,43; H, 4.51; N, 3.36. FAB$^-$-MS, *m/z*: 454 [M$_{anion}$ − H]$^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3311 m−w ν(N−H), 3057 m−w and 2927 m ν(C−H), 1646 s ν(C=N), 1110 s−m ν(P−C). ^{1}H NMR in $CDCl_3$, δ: 7.7 (m, 15H, Ph), 7.1 (m, 5H, CH$_2$*Ph*), 5.21 (d, J_{PH} 14.0 Hz, 2H, C*H*$_2$-Ph), 3.11 (quart, J_{HH} 7.6 Hz, 2H, Et), 1.25 (t, J_{HH} 7.6 Hz, 3H, Et), 2.42 (m, 4H, α-CH$_2$ from =C(C$_4$H$_8$)), 1.78 (m, 4H, β-CH$_2$ from =C(C$_4$H$_8$)). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 30.7 ($^1J_{PC}$ 45.0 Hz, *C*H$_2$Ph), 117.5 ($^1J_{PC}$ 84.6 Hz, C_{ipso} from Ph), 127.1 ($^2J_{PC}$ 8.4 Hz, C_{ipso} from CH$_2$Ph), 128.3 (J_{PC} 3.7 Hz, CH_p from Ph), 128.7 (J_{PC} 2.9 Hz, CH_m from Ph), 130.2 (J_{PC} 12.7 Hz, CH from Ph), 131.5 (J_{PC} 5.3 Hz, CH_o from CH$_2$Ph), 134.3 (J_{PC} 10.1 Hz, CH from Ph), 134.9 (J_{PC} 2.7 Hz, CH_p from Ph), 174.9 (C=N from ON=C(C$_4$H$_8$)$_2$), 172.8 (C=N from HN=C(Et)), 26.6 (CH$_2$ from Et), 10.2 (CH$_3$ from Et), 31.2 and 29.2 (α-CH$_2$ from =C(C$_4$H$_8$)), 24.9 and 24.4 (β-CH$_2$ from =C(C$_4$H$_8$)). ^{31}P{^{1}H} in $CDCl_3$, δ: 23.6. ^{195}Pt NMR in $CDCl_3$, δ: −1808 (625 Hz).

[Ph$_3$PCH$_2$Ph][PtCl$_3${NH=C(Et)ON=C(C$_5$H$_{10}$)}]. Anal. Calcd for $C_{34}H_{38}N_2Cl_3OPPt$: C, 49.61; H, 4.65; N, 3.40. Found: C, 49.06; H, 4.64; N, 3.30. FAB$^+$-MS, *m/z*: 468 [M$_{anion}$ − H]$^+$. IR spectrum in KBr, selected bands, cm^{-1}: 3307 m−w ν(N−H), 3057 m−w, 2932 and 2859 m−w ν(C−H), 1639 s ν(C=N), 1109 s−m ν(P−C). ^{1}H NMR in $CDCl_3$, δ: 7.7 (m, 15H, Ph), 7.1 (m, 5H, CH$_2$*Ph*), 5.15 (d, J_{PH} 14.3 Hz, 2H, C*H*$_2$Ph), 3.10 (quart, J_{HH} 8.3 Hz, 2H, Et), 1.24 (t, J_{HH} 8.3 Hz, 3H, Et), 2.46 (t, J_{HH} 5 Hz, 2H, CH$_2$ from =C(C$_5$H$_{10}$)), 2.23 (t, J_{HH} 5.6 Hz, 2H, CH$_2$ from =C(C$_5$H$_{10}$)) 1.64 (m, 6H, CH$_2$ from =C(C$_5$H$_{10}$)). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 30.7 ($^1J_{PC}$ 53 Hz, *C*H$_2$Ph), 117.5 ($^1J_{PC}$ 86.7 Hz, C_{ipso} from Ph), 127.0 ($^2J_{PC}$ 8.4 Hz, C_{ipso} from CH$_2$Ph), 128.3 (J_{PC} 3.7 Hz, CH_p from Ph), 128.7 (J_{PC} 2.8 Hz, CH_m from Ph), 130.2 (J_{PC} 12.8 Hz, CH from Ph), 131.5 (J_{PC} 5.4 Hz, CH_o from CH$_2$Ph), 134.3 (J_{PC} 9.2 Hz, CH from Ph), 134.9 (J_{PC} 2.8 Hz, CH_p from Ph), 168.0 (C=N from ON=CMe_2), 172.8 (C=N from HN=CEt), 10.1 (CH$_3$ from Et), 26.8 (CH$_2$ from Et), 31.9 and 26.7 (α-CH$_2$ from =C(C$_5$H$_{10}$)), 26.6, 25.6 and 25.2 (β- and γ-CH$_2$ from =C(C$_5$H$_{10}$)). ^{31}P{^{1}H} NMR in $CDCl_3$, δ: 23.6. ^{195}Pt NMR in $CDCl_3$, δ: −1807 (700 Hz).

[PtCl$_2${NH=C(Me)ON(Me)CHR}$_2$] (R = Ph, C$_6$H$_4$Me). Isolated yield is 99% (R = Ph) and 87% (R = C$_6$H$_4$Me). ^{1}H, ^{13}C{^{1}H}, and ^{195}Pt NMR are identical to those already described.[12]

Reduction of Other Platinum(IV) Complexes. The reduction proceeds similarly to the reduction of imine complexes, and NMR yields are almost quantitative. All platinum(II) products from the reaction are known, and their formation was confirmed by NMR spectroscopy (data obtained are given below) and when possible by comparison of other characteristics with those of known compounds.

***trans*-[PtCl$_2$(HON=CMe$_2$)$_2$]:**[83] from the reduction of *trans*-[PtCl$_4$-(HON=CMe_2)$_2$]. ^{1}H NMR in $CDCl_3$, δ: 2.15 and 2.61 (two s, 3H each, J_{PtH} not observed, N=C*Me*$_2$), 9.80 (1H, OH). ^{13}C{^{1}H} NMR in $CDCl_3$, δ: 19.2 and 26.8 (N=C*Me*$_2$), 164.0 (N=C). ^{195}Pt NMR in $CDCl_3$, δ: −1998 (480 Hz).

***trans*-[PtCl$_2$py$_2$]:**[86] from the reduction of *trans*-[PtCl$_4$py$_2$]. ^{1}H NMR in CDCl$_3$, δ: 7.13 (t, 7.5 Hz, 2H), 7.61 ("t", 7.8 Hz, 1H), 8.62 (m, J_{PtH} 31 Hz, 2H). ^{195}Pt in CDCl$_3$, δ: −1944 (600 Hz). The solubility of the complex in CDCl$_3$ is insufficient to measure the ^{13}C{^{1}H} NMR spectrum even at high acquisition time.

***trans*-[PtCl$_2$(py)(Me$_2$S)]:**[87] from the reduction of *trans*-[PtCl$_4$(py)(Me$_2$S)]. ^{1}H NMR in CDCl$_3$, δ: 2.44 (J_{PtH} 40.5 Hz, Me$_2$S), 7.38 (m, 2H), 7.87 (m, 1H), 8.83 (m, 2H) (Py). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 22.9 (J_{PtC} 11.5 Hz), 125.4 (J_{PtC} 34.7 Hz), 138.8, 152.2 (Py). ^{195}Pt NMR in CDCl$_3$, δ: −2821 (500 Hz).

***trans*-[PtCl$_2$(Me$_2$S)$_2$]:**[88] from the reduction of *trans*-[PtCl$_4$(Me$_2$S)$_2$]. ^{1}H NMR in CDCl$_3$, δ: 2.48 (J_{PtH} 41.4 Hz). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 22.3 (J_{PtC} 11.9 Hz). ^{195}Pt NMR in CDCl$_3$, δ: −3409.

***trans*-[PtCl$_2$(Me$_2$SO)(NHEt$_2$)]:**[80,81] from the reduction of *trans*-[PtCl$_4$(Me$_2$SO)(NHEt$_2$)]. ^{1}H NMR in CDCl$_3$, δ: 1.48 (t, 7.2 Hz, 6H), 2.68 (m, 2H) and 3.18 (m, 2H) (Et), 3.37 (s + d, J_{PtH} 19 Hz, 6H, DMSO), 3.88 (br, 1H, NH). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 14.7 and 48.8 (Et), 44.0 (J_{PtC} 55 Hz, DMSO). ^{195}Pt NMR in CDCl$_3$, δ: −3139 (480 Hz).

[PtCl$_3$(Me$_2$SO)]$^-$.[80] The complex is formed upon reduction of either (Ph$_3$PCH$_2$Ph)[PtCl$_5$(Me$_2$SO)] or [PtCl$_4$(Me$_2$SO)$_2$]. In the latter case liberation of a dimethyl sulfoxide molecule is observed along with the formation of (Ph$_3$PCH$_2$CO$_2$Me)[PtCl$_3$(Me$_2$S═O)]. For anion: ^{1}H NMR in CDCl$_3$, δ: 3.39 (s + d, J_{PtH} 20.7 Hz); ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 44.1 (J_{PtC} 62.6 Hz); ^{195}Pt NMR in CDCl$_3$, δ: −3000. For free DMSO: ^{1}H NMR in CDCl$_3$, δ: 2.64 (s); ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 40.9.

The reduction of [PtCl$_4$(MeCN)$_2$] with 1 equiv of Ph$_3$P═CHCO$_2$Me in MeCN results in release of the solid [PtCl$_2$(MeCN)$_2$] (8%). Subsequent removal of the solvent from the filtrate and recrystallization of a precipitate formed from hot EtOH gives analytically pure [Ph$_3$PCH$_2$CO$_2$Me][PtCl$_3$(MeCN)] (37%). **[Ph$_3$PCH$_2$CO$_2$Me][PtCl$_3$(MeCN)].** Anal. Calcd for C$_{23}$H$_{23}$NCl$_3$O$_2$PPt: C, 40.75; H, 3.42; N, 2.07. Found: C, 40.98; H, 3.52; N, 1.81. FAB$^-$-MS, *m*/*z*: 342 [M$_{anion}$]$^-$, 299 [M$_{anion}$ − MeCN]$^-$, 266 [M$_{anion}$ − MeCN − Cl]$^-$; FAB$^+$-MS, *m*/*z*: 335 [M$_{cation}$]$^+$. IR spectrum (selected bands), cm^{-1}: 2909 and 2874 m ν(C−H), 1728 vs ν(C═O), 1437 vs ν(C═C), 1107 s ν(P−C); the band due to ν(C≡N) was not observed. ^{1}H NMR in CDCl$_3$, δ: 2.18 (s, 3H, MeCN), 3.42 (s, 3H, OMe), 4.92 (d, J_{PH} 13.8 Hz, 2H, PCH$_2$), 7.50−7.64 (m, 15H, Ph). ^{13}C{^{1}H} NMR in CDCl$_3$, δ: 4.0 (*Me*CN), 31.6 (J_{PC} 58 Hz, PCH$_2$), 53.4 (OMe), 112.4 (Me*C*N), 117.4 (J_{PC} 89 Hz, C$_{ipso}$), 130.1 (J_{PC} 12.8 Hz, CH), 133.6 (J_{PC} 10.9 Hz, CH), 135.1 (J_{PC} 3.6 Hz, CH$_{para}$) (Ph), 164.7 (C═O). ^{31}P{^{1}H} NMR in CDCl$_3$, δ: 20.8. ^{195}Pt NMR in CDCl$_3$, δ: −2022 (355 Hz).

X-ray Structure Determination of [PtCl$_2${NH═C(Me)ON═CMe$_2$}$_2$]. Colorless plates of the complex were grown from dichloromethane solution upon addition of diethyl ether. Diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer. Cell parameters were obtained from 24 centered reflections with Θ between 11° and 13°. Range of *hkl*: h = 0−12, k = 0−11, l = 0−19. Standard reflections were measured every 100 min and showed practically no change with time (±1%). Diffractometer data were processed by the program PROFIT[89] with profile analysis of reflections. The structures were solved by means of Fourier synthesis based upon the Pt-atom coordinates obtained from the Patterson synthesis using the SHELXTL package.[90] After that, all reflections with $I < 2\sigma(I)$ were excluded from calculations. Refinement was done by full-matrix least squares based on F^2 using the SHELX-97 package.[91] All non-H atoms were treated anisotropically. H atoms were located in a difference Fourier map and refined isotropically. An extinction correction has been applied. Lorentz, polarization, and absorption corrections were made.[92] Scattering factors are from *International Tables for X-ray Crystallography*.[93] Crystal data are given in Table 1.

X-ray Structure Determination of (Ph$_3$PCH$_2$CO$_2$Me)[PtCl$_3$(MeCN)]. Yellow plates were obtained on slow evaporation of ethanol solution. The cell dimensions and symmetry of crystals were defined in the Weissenberg camera. Diffraction data were collected on a Syntex P2$_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å), ω-scan method with variable scan rate (2−29.3°/min). Weak reflections were neglected. The intensity of one standard reflection was measured every 50 reflections and showed practically no change with time (±1%). After Lorentz and polarization correction, the structure was solved by means of the Patterson technique (heavy atom method) and following Fourier synthesis and was refined by a full-matrix (anisotropic for all non-hydrogen atoms and isotropic for hydrogen atoms) least-squares method based on F. No extinction correction was made. Before anisotropic refinement an absorption correction was made using the DIFABS[94] program. The contribution of hydrogen atoms was included at fixed calculated positions, based on geometrical reqiurement. All experimental data processing, solving and refinement were performed using CSD[92] program.

Acknowledgment. G.W. is grateful to the PRAXIS XXI program for a fellowship (BPD11779/97). V.Yu.K. is very much obliged to the PRAXIS XXI program (Grant BCC16428/98) for financial support of this study. J.V. and V.Yu.K. are indebted to INTAS for Grant 97-0166. N.A.B. thanks the Soros Foundation for a fellowship. A.J.L.P. thanks the FCT (Foundation for Science and Tecnology) and the PRAXIS XXI program for financial support. We thank Dr. M. Galanski for valuable comments on the manuscript, Profs. V. K. Belsky and V. S. Fundamensky for the X-ray analyses, and Dr. Z. A. Khromenkova for providing us some platinum(IV) complexes for the reduction studies.

Supporting Information Available: X-ray crystallographic files in CIF format for the complexes *trans*-[PtCl$_2${NH═C(Me)ON═CMe$_2$}$_2$] and (Ph$_3$PCH$_2$CO$_2$Me)[PtCl$_3$(NCMe)]. This material is available free of charge via the Internet at http://pubs.acs.org.

IC000769C

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