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# Synthesis of the First Family of Platinum(IV) Complexes with Phosphorus Ylide Ligands

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The reactions of  $(PPN)[PtCl_5(NH_2R')]$  [ $PPN = Ph_2P=N=PPh_2$ ;  $R' = H$  (**1**),  $Me$  (**2**)], prepared by treatment of  $[PtCl_4(NH_2R')(Me_2SO)]$  with  $[PPN]Cl$ , with 1 equiv of the carbonyl-stabilized phosphorus ylides  $Ph_3P=CHC(O)R$  ( $R = OMe, OEt, Me$ ) lead to the substitution of one chloride to afford the first Pt(IV) complexes containing phosphorus ylides, *cis*- $[PtCl_4(NH_2R')\{CH(PPh_3)C(O)R\}]$  [ $R = OMe, R' = H$  (**4**),  $Me$  (**5**);  $R = OEt, R' = H$  (**6**),  $Me$  (**7**);  $R = Me, R' = H$  (**8**),  $Me$  (**9**)]. Their electrochemical behavior was investigated by cyclic voltammetry and controlled potential electrolysis, and the crystal structure of complex **4** was determined by X-ray diffraction studies.

## Introduction

Complexes of phosphorus ylides have attracted much attention in synthetic and theoretical chemistry<sup>1</sup> and also have some useful practical implications, e.g., as polymerization catalysts.<sup>2</sup> Phosphorus ylides form complexes with virtually every metal of the periodic table.<sup>1</sup> In particular, many platinum(II) complexes with phosphorus ylides have been prepared, for instance, containing the carbonyl-stabilized ylides,  $Ph_3P=CHC(O)R$  [ $R = Me, Ph, OMe, OEt$ ].<sup>3,4</sup> These platinum(II) compounds were obtained by replacing  $Me_2S$ , chloride, nitriles, or ethylene or by bridge-splitting of dimeric chloro-platinum(II) complexes with the corresponding ylides. Complexes with nonstabilized ylides have also been de-

scribed,<sup>5</sup> and many of them were synthesized by reacting chloromethylene complexes,  $[Pt]-CH_2Cl$ , with phosphines. The abundance of (ylide)Pt(II) complexes dramatically contrasts with the few reported fruitless attempts to synthesize complexes of platinum(IV). Indeed, to the best of our knowledge, there is one report<sup>6</sup> describing the insufficiently characterized platinum(IV) compound “ $\{(Me_2N)_3PCH_2\}_4PtCl_4$ ” (only C and H elemental analyses were given and no other data presented<sup>6</sup>) and an account on several unsuccessful attempts to prepare Pt(IV) complexes with the phosphorus diylide  $Ph_3P=C=PPh_3$  by reacting it with  $[PtMe_3X]$  ( $X = PF_6^-, CF_3SO_3^-, I^-$ ). From these reactions only one Pt(II) species was isolated and characterized.<sup>7</sup>

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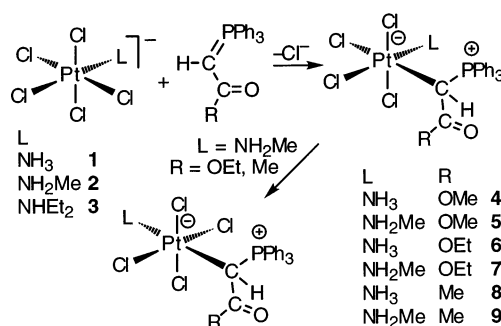
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In recent years, our group has been involved in investigations of the reactivity of metal-activated nitriles,<sup>8,9</sup> a topic that we recently reviewed.<sup>10</sup> In particular, one of us has been investigating the nucleophilic attack of phosphorus ylides<sup>11</sup> to nitriles coordinated to platinum(II) and observed that *trans*-[PtCl<sub>2</sub>(NCR)<sub>2</sub>] (R = Me, Ph, C<sub>6</sub>F<sub>5</sub>) react with the carbonyl-stabilized ylides to give complexes containing ylidoimino or/and iminophosphorano ligands. To ascertain the influence of the oxidation state of the metal in these reactions, we planned to study the reactivity of [PtCl<sub>4</sub>(NCR)<sub>2</sub>] with the carbonyl-stabilized ylides. We also realized the interest of the reaction products if simple substitution reactions would occur to give the first Pt(IV) complexes with phosphorus ylides.

Disappointingly, the reaction of [PtCl<sub>4</sub>(NCMe)<sub>2</sub>] with Ph<sub>3</sub>P=CHCO<sub>2</sub>Me led to a mixture of the platinum(II) complexes (Ph<sub>3</sub>PCH<sub>2</sub>CO<sub>2</sub>Me)[PtCl<sub>3</sub>(NCMe)] and [PtCl<sub>2</sub>(NCMe)<sub>2</sub>].<sup>12</sup> However, this reduction was the starting point to study and describe a general, selective, and high yield method for the synthesis of difficult-to-obtain imine Pt(II) complexes by reducing the corresponding readily available Pt(IV)-based imines with carbonyl-stabilized ylides.<sup>12</sup> Moreover, from the latter results, we concluded that to prepare Pt(IV) complexes with phosphorus ylides via the substitution route, the Pt(IV) precursor must be a weaker oxidant than the previously studied<sup>12</sup> complexes containing nitriles, imines, sulfoxides, or thioethers. We hypothesized that anionic complexes with efficient electron-donor ligands, such as [PtCl<sub>5</sub>(amine)]<sup>-</sup>, would be promising candidates, and in accord with our expectations, it was observed that the ylides Ph<sub>3</sub>P=CHC(O)R (R = OMe, OEt, Me) react with [PPN][PtCl<sub>5</sub>(NH<sub>2</sub>R')] (PPN = Ph<sub>2</sub>P=N=PPh<sub>2</sub>, R' = H, Me) displacing the chloride, in a nonredox process, to give the first family of Pt(IV) complexes with phosphorus ylides. These results are reported herein.

Scheme 1



## Results and Discussion

**Synthetic Part.** All anionic complexes [PPN][PtCl<sub>5</sub>(amine)] [PPN = Ph<sub>2</sub>P=N=PPh<sub>2</sub>; amine = NH<sub>3</sub> (1), NH<sub>2</sub>Me (2), NH<sub>2</sub>Et (3)] were prepared by substitution of dimethyl sulfoxide in the platinum(IV) complex [PtCl<sub>4</sub>(amine)(Me<sub>2</sub>SO)], in accord with the method published for a similar compound, i.e., [Ph<sub>3</sub>PCH<sub>2</sub>Ph][PtCl<sub>5</sub>(NH<sub>3</sub>)].<sup>9c</sup> The choice of the PPN<sup>+</sup> counterion is determined by its high lipophilicity, which provides good solubility in the most common organic solvents.

Treatment of [PPN][PtCl<sub>5</sub>(NH<sub>2</sub>R')] (R' = H, Me) with 1 equiv of the carbonyl-stabilized phosphorus ylide Ph<sub>3</sub>P=CHC(O)R (R = OMe, OEt) in chloroform leads to substitution of one chloride to afford the neutral complexes *cis*-[PtCl<sub>4</sub>(NH<sub>2</sub>R'){CH(PPh<sub>3</sub>)C(O)R}] [R = OMe, R' = H (4), Me (5); R = OEt, R' = H (6), Me (7)] and [PPN]Cl (Scheme 1).

Complexes 4 and 5 were released as yellow crystalline products directly from the reaction mixture and isolated in 50–65% yields, while 6 and 7, which exhibit much higher solubilities, were isolated by removal of the solvent followed by their purification by column chromatography on silica gel. These four complexes have been characterized by elemental analyses, FAB-mass spectrometry, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}, and <sup>195</sup>Pt{<sup>1</sup>H} NMR (including the inverse detection HMQC method), and IR spectroscopies and 4 by X-ray crystallography also. The reactions of ylides Ph<sub>3</sub>P=CHC(O)R with [PPN][PtCl<sub>5</sub>(NH<sub>2</sub>Et)] gave a broad mixture of compounds, among which the substitution products were not detected by NMR spectroscopy.

The reactions of [PPN][PtCl<sub>5</sub>(NH<sub>2</sub>R')] (R' = H, Me) with Ph<sub>3</sub>P=CHC(O)Me lead to the unstable substitution products [PtCl<sub>4</sub>(NH<sub>2</sub>R'){CH(PPh<sub>3</sub>)C(O)Me}] [R' = H (8), Me (9)]. All our attempts to isolate 8 or 9 as pure compounds were unsuccessful since they rapidly decomposed either on SiO<sub>2</sub> or upon washing with Et<sub>2</sub>O after removal of the solvent in a vacuum. However, they were characterized by FAB-MS from their CDCl<sub>3</sub> solutions and the reactions monitored by NMR spectroscopy. The greater relative stability of complexes 4–7 could be due to the more basic character of the ylides with R = OMe, OEt than that with R = Me. However, when the Pt(IV) complexes 4–7 were heated in solution and also in the solid phase, an overall degradation with no dominant compound was observed.

For the most sterically hindered compounds of the series, i.e., [PtCl<sub>4</sub>(NH<sub>2</sub>Me){CH(PPh<sub>3</sub>)CO<sub>2</sub>Et}] (7) and [PtCl<sub>4</sub>(NH<sub>2</sub>Me){CH(PPh<sub>3</sub>)C(O)Me}] (9), *cis*-to-*trans* isomerization in solution was detected, thus indicating that the substitution in [PtCl<sub>5</sub>(NH<sub>2</sub>R')] occurs at the

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*cis* position to the amine, in accord with higher *trans*-effect of Cl<sup>−</sup> ligand versus amine,<sup>13</sup> and that the isomerization occurs due to steric reasons.

**NMR and IR Characterization of the (Ylide)Pt(IV) Complexes.** NMR spectra for the stable complexes **4–7** were measured in dms-*d*<sub>6</sub> due to their low solubility in the most common deuterated organic solvents. For the two unstable species **8** and **9**, NMR data were obtained by <sup>1</sup>H NMR monitoring of the reaction in CDCl<sub>3</sub>. All complexes exhibit a doublet with satellites due to the CH proton coupled with <sup>31</sup>P and <sup>195</sup>Pt. This resonance appears in the range 6.21–6.34 (in dms-*d*<sub>6</sub>) and 6.34–6.55 (in CDCl<sub>3</sub>) ppm, which is, as expected, low field shifted with respect to the corresponding resonance in similar Pt(II) complexes (3.82–5.60 ppm).<sup>3</sup> The values of <sup>2</sup>J<sub>P–H</sub> (6.5–9.8 Hz) and <sup>2</sup>J<sub>Pt–H</sub> (89.0–97.5 Hz) are not significantly different from those previously reported for Pt(II) complexes.<sup>3</sup> The corresponding CH carbon gives a doublet in the <sup>13</sup>C{<sup>1</sup>H} NMR at 15.17–15.37 ppm (<sup>1</sup>J<sub>P–C</sub> 44.5–48.2 Hz) with <sup>195</sup>Pt satellites (<sup>1</sup>J<sub>Pt–C</sub> 569.0–573.6 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR spectra display a singlet in the range 31.36–33.28 ppm (for *cis*-isomers in dms-*d*<sub>6</sub>) flanked by <sup>195</sup>Pt satellites with <sup>2</sup>J<sub>PPt</sub> ca. 60 Hz. The chemical shift of the <sup>195</sup>Pt resonance is mainly dependent on the nature of the ylide, although the difference in solvents also should be taken into account. Thus, complexes with R = OMe, OEt, **4–7**, show such resonance at lower field (−579 to −657 ppm) than the others with R = Me (**8**, −749.7 ppm; **9**, −729, −813 ppm). One of the two resonances observed in **9**, that at lower frequency, could be assigned to the *trans*-isomer in good agreement with the data reported in the literature for *cis*- and *trans*-isomers of platinum(IV) complexes [PtCl<sub>4</sub>L<sub>2</sub>].<sup>8a,d,9b,14</sup> This assignment allows the *trans* geometry to be attributed to the only isomer of **7** detected in solution after data acquisition of the <sup>195</sup>Pt{<sup>1</sup>H} NMR spectrum. The chemical shift of this resonance (−657 ppm) is abnormally lower than the corresponding one in their *cis* homologous **4–6** appearing in the range from −579 to −584 ppm.

The frequency of the band assigned to the ν(C=O) stretching mode in free carbonyl-stabilized ylides is unusually low for a carbonyl group [R = Me (1540 cm<sup>−1</sup>), OEt (1610 cm<sup>−1</sup>), OMe (1620 cm<sup>−1</sup>)] because of the contribution of the resonance form [Ph<sub>3</sub>P<sup>(+)</sup>CH=C(R)–O<sup>(−)</sup>]. When such ylides are C-protonated,<sup>14</sup> to give phosphonium salts, or are C-coordinated to a metal, the bond order of the CO group increases because the only possible resonance form is M<sup>(−)</sup>–CH(P<sup>(+)</sup>Ph<sub>3</sub>){C(R)=O}. Correspondingly, upon C-coordination, the band assigned to the ν(C=O) stretching mode for a given M, ν<sub>M</sub>(C=O), must appear at higher frequencies than in the free ylide. We have shown that for a given R the higher frequency corresponds to the phosphonium salt ν<sub>H<sup>+</sup></sub>(C=O) and that in a series of gold(I) and gold(III) complexes the value of Δν<sub>[Au]</sub>(C=O) = ν<sub>H<sup>+</sup></sub>(C=O) – ν<sub>[Au]</sub>(C=O) decreases when the electron-withdrawing character of the group [Au] is increased. For example, when R = OMe, OEt, Δν<sub>AuCl<sub>3</sub></sub>(C=O) = 0–5 cm<sup>−1</sup> and Δν<sub>Au(ylide)</sub><sup>−</sup>

**Table 1. Crystallographic Data for *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}](DMF)**

empirical formula	C <sub>24</sub> H <sub>29</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>3</sub> PPt
fw	761.35
temp, K	120(2)
λ, Å	0.71073
space group	P $\bar{1}$ (No. 2)
a, Å	10.0137(1)
b, Å	10.7147(1)
c, Å	27.8702(4)
α, deg	79.3810(6)
β, deg	80.5840(5)
γ, deg	73.0038(5)
V, Å <sup>3</sup>	2791.50(6)
Z	4
ρ <sub>calcd</sub> , g/cm <sup>3</sup>	1.812
μ(Mo Kα), mm <sup>−1</sup>	5.496
R <sub>1</sub> <sup>a</sup> (I ≥ 2σ)	0.0351
wR <sub>2</sub> <sup>b</sup> (I ≥ 2σ)	0.0739

$$^a R_1 = \sum |F_o| - |F_c| / \sum |F_o|, \quad ^b wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Table 2. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}](DMF) (**4**)**

	A	B
Pt(1)–Cl(1)	2.3673(16)	2.3799(15)
Pt(1)–Cl(2)	2.3259(15)	2.3309(16)
Pt(1)–Cl(3)	2.3157(15)	2.3062(15)
Pt(1)–Cl(4)	2.3323(16)	2.3221(16)
Pt(1)–N(1)	2.043(5)	2.057(5)
Pt(1)–C(1)	2.121(6)	2.131(6)
C(1)–P(1)	1.827(6)	1.833(6)
C(1)–C(2)	1.526(8)	1.504(8)
C(2)–O(3)	1.335(7)	1.339(7)
C(2)–O(4)	1.202(7)	1.217(7)
O(3)–C(3)	1.456(8)	1.459(8)
Pt(1)–C(1)–P(1)	120.0(3)	119.7(3)
Cl(1)–Pt(1)–C(1)	178.22(15)	179.04(17)
Cl(4)–Pt(1)–N(1)	177.17(15)	177.28(15)
Cl(2)–Pt(1)–Cl(3)	176.70(6)	176.75(6)
C(1)–C(2)–O(4)	124.9(5)	125.0(5)
C(1)–C(2)–O(3)	110.1(5)	110.8(5)
C(2)–O(3)–C(3)	115.2(5)	115.7(5)

**Table 3. Cyclic Voltammetric Data<sup>a</sup> for the Complexes *cis*-[PtCl<sub>4</sub>(amine)(ylide)]**

complex	E <sub>p</sub> <sup>red</sup>	E <sub>p/2</sub> <sup>red</sup>
<b>4</b>	−0.60	−0.49
<b>5</b>	−0.67	−0.55
<b>6</b>	−0.62	−0.45
<b>7</b>	−0.62	−0.48

<sup>a</sup> Values in V ± 0.02 vs SCE, measured by CV at 200 mV s<sup>−1</sup> scan rate, at a platinum-disk electrode, in 0.2 mol dm<sup>−3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> in the presence of ferrocene as the internal standard.

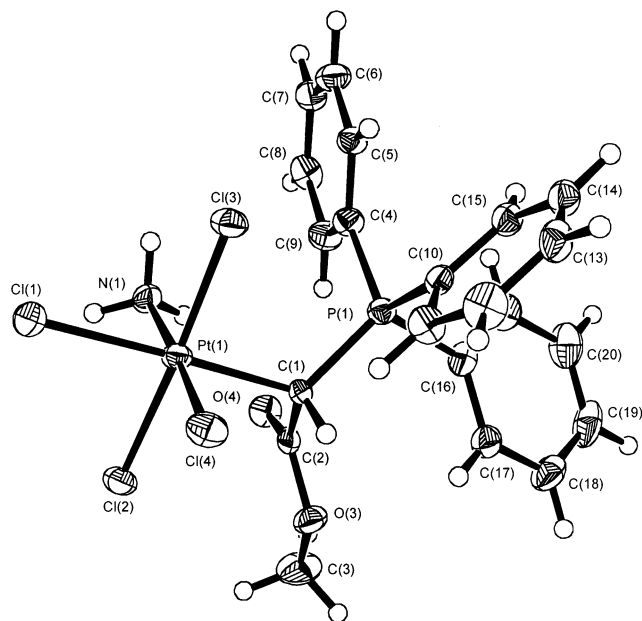
(C=O) = 35–40 cm<sup>−1</sup>.<sup>15</sup> In the isolated complexes **4–6**, the values of ν(C=O) are in the range 1686–1691 cm<sup>−1</sup> and Δν<sub>PtCl<sub>4</sub>(amine)</sub>(C=O) are in the range 27–34 cm<sup>−1</sup>. These values of Δν are similar to those of the groups [Au(PPh<sub>3</sub>)]<sup>+</sup> (**30**),<sup>15</sup> [PtCl(dppe)]<sup>+</sup> (dppe = 1,2-bis-dipheylphosphinoethane, Δν = 32),<sup>3d</sup> [PtCl(cyclometalated phosphine)] (**32**),<sup>3e</sup> or [Pt(Me)(dppe)]<sup>+</sup> (**20**).<sup>3f</sup>

**Electrochemical Characterization.** The electrochemical behavior of the complexes was investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in 0.2 mol dm<sup>−3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub>. They exhibit an irreversible reduction wave at a potential (Table 3) that is somewhat sensitive to a change of the amine or ylide ligand (E<sub>p</sub><sup>red</sup> in the range from −0.60

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**Figure 1.** ORTEP view of *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}] (**4**) with atomic numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

to  $-0.67$  V vs SCE). By exhaustive cathodic CPE at the potential of this wave, two electrons per molecule are transferred and a new irreversible anodic wave is then detected by CV at  $E_p^{ox}$  of 1.30 (**4**), 1.32 (**5**), 1.27 (**6**), or 1.32 (**7**) V vs SCE, conceivably due to the oxidation of the cathodically generated Pt(II) product. In accord with the proposed reduction of the starting Pt(IV) complexes at the metal center, no reduction wave was detected for any of the free ligands.

**X-ray Crystal Structure of Complex 4.** The coordination geometry at platinum is essentially octahedral (Figure 1). The bond distances between Pt and Cl *trans* to the ylide ligand [Pt–Cl(1): 2.3673(16), 2.3799(15) Å] are much longer than the other three [2.3062(15)–2.3323(16) Å] because of the greater *trans* influence of carbon donors than chloro or amine ligands. Surprisingly, the bond distances between Pt and mutually *trans* Cl ligands are significantly different in molecule B, the distances Pt–Cl(2) [2.3309(16) Å] being longer than Pt–Cl(3) [2.3062(15) Å]. Probably, this difference is due to packing effects because the environment of Cl(2) is more crowded than that of Cl(3) in molecule B. The Pt–C bond distances [2.121(6), 2.131(6) Å] are shorter than that reported for the Pt(II) complex *cis*-[Pt(Me){CH(PPh<sub>3</sub>)CO<sub>2</sub>Et}(dppe)] [2.162(7) Å].<sup>3f</sup> The C=O bond distance in this complex [1.203(9) Å] is similar to those found in complex **4** [1.202(7), 1.217(7) Å].

### Concluding Remarks

An easy method has been found for the synthesis of the first family of Pt(IV) complexes with phosphorus ylide ligands, showing the possibility of generating this type of high-valent metal complexes despite the known reducing power of the ylides on Pt(IV) centers. Hence, this study opens up the possibility of extending to Pt(IV) a promising ylide-based organometallic chemistry. Once it has been proved that such complexes can exist, other synthetic ways can be attempted, for example, oxidation of platinum(II) ylide complexes

### Experimental Section

The yields, elemental analyses, and FAB, IR, and NMR data for the complexes are in the Supporting Information (see below).

**Materials and Instrumentation.** Solvents were obtained from commercial sources and used as received. Ph<sub>3</sub>P=CHCO<sub>2</sub>Me and [(Ph<sub>3</sub>P)<sub>2</sub>N]Cl were purchased from Lancaster and Aldrich, respectively, while other ylides<sup>16</sup> and the platinum(IV) complexes [PtCl<sub>4</sub>(amine)(Me<sub>2</sub>SO)]<sup>17</sup> 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. 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.  $1.28 \times 10^{15}$  J) Xe atoms. Mass calibration for data system acquisition was achieved using CsI. Negative-ion FAB mass spectra were obtained on a Fisons VG-Autospec spectrometer by bombarding NBA matrixes of the samples. Infra-red spectra (4000–400 cm<sup>-1</sup>) were recorded on a BIO-RAD FTS 3000MX instrument in KBr pellets.

**NMR Studies.** All NMR spectra were recorded at ambient temperature on a Varian UNITY 300 [299.95, 121.42, 75.42, and 64.48 MHz for <sup>1</sup>H, <sup>31</sup>P, <sup>13</sup>C, and <sup>195</sup>Pt, respectively] and/or Bruker DPX 300 [300.13, 121.49, and 75.47 MHz for <sup>1</sup>H, <sup>31</sup>P, and <sup>13</sup>C, respectively]. <sup>1</sup>H and <sup>13</sup>C chemical shifts are given relative to dmsd ( $\delta = 2.50$  and 39.5, respectively). <sup>31</sup>P chemical shifts were measured relative to 80% H<sub>3</sub>PO<sub>4</sub> as standard ( $\delta = 0$  ppm). <sup>195</sup>Pt chemical shifts are given relative to Na<sub>2</sub>[PtCl<sub>6</sub>] (by using K<sub>2</sub>[PtCl<sub>4</sub>],  $\delta = -1630$  ppm, as a standard), and the half-height line width is given in parentheses. The inverse detection HMQC method with the BIRD sequence during the preparation period<sup>18</sup> was used to determine the heteronuclear spin–spin coupling constants  $J_{Pt-^{13}C}$ . HMQC spectra resulted from  $128 \times 1024$  data matrix size with 256 scans per  $t_1$  value (the delay for creation of antiphase magnetization was 3.5 ms and the relaxation delay was 1.0 s), and broadband <sup>13</sup>C decoupling with GARP-1<sup>19</sup> was applied during the acquisition (<sup>13</sup>C 90° pulse of 60 ms). The data were zero-filled in  $t_1$  dimension and a sine-bell filter was applied in both dimensions before the Fourier transformation. The coupling constants  $J_{H-^{13}C}$  were defined from the INEPT spectrum.

**X-ray Structure Determination of *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}] (**4**).** The yellow crystal plates for the X-ray analysis were obtained by slow diffusion of Et<sub>2</sub>O in a DFM solution of the complex. X-ray diffraction data were collected with a Nonius KappaCCD diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Denzo and Scalepack<sup>20</sup> programs were used for cell refinements and data reduction. The structure was solved by direct methods using the SHELXS-97<sup>21</sup> program with the WinGX<sup>22</sup> graphical user interface. The structure refinement was carried out with SHELXL-97.<sup>23</sup> A multiscan absorption correction, based on equivalent reflections (XPERP in SHELXTL v5.1),<sup>24</sup> was applied to the data ( $T_{max}/T_{min}$  0.29588/0.22433). All hydrogen atoms were placed on idealized

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positions and constrained to ride on their parent atom. The asymmetric unit consists of two independent *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}] molecules and two DMF solvent molecules. Crystallographic data are summarized in Table 1 and selected bond lengths and angles in Table 2.

**Electrochemical Study.** The electrochemical experiments were performed on an EG&G PARC 273A potentiostat/galvanostat connected to a PC computer through a GPIB interface (National Instruments PC-2A). Cyclic voltammetry (CV) experiments were undertaken in a two-compartment three-electrode cell, at a platinum-disk working electrode probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum auxiliary electrode was employed. Controlled potential electrolyses (CPE) were carried out in a two-compartment three-electrode cell with platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The electrochemical experiments were performed in a N<sub>2</sub> atmosphere at room temperature. The potentials were measured by CV at 200 mV s<sup>-1</sup> scan rate, in 0.2 mol dm<sup>-3</sup> [NBu<sub>4</sub>][BF<sub>4</sub>]/CH<sub>2</sub>Cl<sub>2</sub> in the presence of ferrocene as the internal standard, and the values are quoted relative to the saturated calomel electrode (SCE) by using the [Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> redox couple (*E*<sup>o</sup> = 0.53 vs SCE, in CH<sub>2</sub>Cl<sub>2</sub>). The use, as reference electrode, of the SCE or other electrode in aqueous medium was avoided due to the sensitivity of the systems to water. The CPE experiments were monitored regularly by CV to ensure that no significant potential drift occurred along the electrolyses.

**Preparation of the Starting Materials.** A suspension of [PtCl<sub>4</sub>(amine)(Me<sub>2</sub>SO)] (0.25 mmol) and [PPN]Cl (0.25 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was heated at 45 °C until homogenization of the reaction mixture occurred (ca. 12 h). The resulting orange solution was evaporated in a vacuum at 20–25 °C to give an orange oily residue that was stirred with Et<sub>2</sub>O to give an orange solid that was collected on a filter and dried in air at room temperature.

**Synthesis of (Ylide)Pt(IV) Complexes.** The ylide (0.030 mmol) was added to a solution of [PPN][PtCl<sub>5</sub>(NH<sub>2</sub>R)] (R = H, Me) (25 mg, 0.027 mmol) in CHCl<sub>3</sub> (0.7 mL). The reaction mixture was left to stand at room temperature for 12 h, and the resulting pale yellow crystals released (**4**, **5**) were filtered off, washed with CHCl<sub>3</sub> (two 1 mL portions), and dried in air at room temperature. When complexes were not released from the reaction mixture (**6**, **7**), they were isolated by removal of the solvent in a vacuum followed by column chromatography on silica gel upon elution with CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. The isolation of complexes **8** and **9** was unsuccessfully attempted because they rapidly decomposed either on SiO<sub>2</sub> or upon washing with Et<sub>2</sub>O after removal of the solvent in a vacuum. However, they were characterized by FAB-MS and NMR spectroscopy from their CDCl<sub>3</sub> solutions.

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**Supporting Information Available:** X-ray crystallographic files for the complex *cis*-[PtCl<sub>4</sub>(NH<sub>3</sub>){CH(PPh<sub>3</sub>)CO<sub>2</sub>Me}](DMF). The yields, elemental analyses, and FAB, IR, and NMR data for complexes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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