Reactions of Acetylenes with Noble-Metal Carbonyl Halides. 12.[1] Synthesis, Reactivity, and Solution Structures by Multinuclear NMR Studies of σ-Alkenylplatinum(II) Complexes. X-ray Structure Analysis of $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(CO)Cl]$ and $[Pt\{C(C_6H_5)=C(H)C(=NC_6H_5)Me\}(PPh_3)_2Cl]$

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The cluster compound $[Pt(CO)_2]_{3n}{}^{2-}$, in chloroform solution at room temperature, reacts with $H[Pt(CO)Cl_3]$ and $C_6H_5C{\equiv}CC(O)Me$ to give $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(CO)Cl]$, **1**. With PPh_3, compound **1** yields $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(PPh_3)_2Cl]$, **3**, and with aromatic amines $[Pt\{C(C_6H_5)=C(H)C(=NR)Me\}(CO)Cl]$ (**4**, R = p-MeC_6H_4; **5**, R = C_6H_5). Derivative **5** reacts with 1 and 2 mol equiv of triphenylphosphine to give complexes $[Pt\{C(C_6H_5)=C(H)C(=NC_6H_5)Me\}(PPh_3)Cl]$, **6**, or $[Pt\{C(C_6H_5)=C(H)C(=NC_6H_5)Me\}(PPh_3)_2Cl]$, **7**, respectively. The solution structures of compounds **1**–**7** was determined by a multinuclear NMR study (^1H, ^{13}C, ^{15}N, ^{31}P, and ^{195}Pt), and the crystal structures of **1** and **7** were determined by X-ray diffraction. Crystals of **1** are monoclinic, space group $C2/c$, $a = 18.516$ (4) Å, $b = 8.501$ (1) Å, $c = 14.108$ (3) Å, $\beta = 91.16$ (2)°, $Z = 8$. The final disagreement factor was $R = 0.0282$ for 1199 observed reflections. The Pt atom adopts a square-planar coordination with distortions imposed by the coplanar five-membered metallacycle. An extensive π delocalization, not involving the Pt atom, spans the organic fragment. Relevant distances are Pt–C(1) = 2.017 (11) Å, Pt–O [trans to (CO)] = 2.048 (7) Å, and Pt–Cl [trans to $C(sp^2)$] = 2.360 (3) Å. The molecules are arranged in the crystal in infinite stacks running parallel to the c axis with alternating Pt···Pt separations of 3.4467 (9) and 3.6675 (10) Å. Crystals of **7** are triclinic, space group $P\bar{1}$, $a = 9.0807$ (14) Å, $b = 13.0394$ (8) Å, $c = 19.4935$ (24) Å, $\alpha = 80.239$ (7)°, $\beta = 78.065$ (12)°, $\gamma = 72.667$ (8)°, $Z = 2$. The final disagreement factor is $R = 0.0229$ for 6240 observed reflections. The Pt atom has a distorted square-planar coordination with the phosphine ligands in the trans position; relevant distances are Pt–C(1) = 2.014 (4) Å, Pt–P(1) = 2.3045 (9) Å, Pt–P(2) = 2.3097 (10) Å, Pt–Cl = 2.4067 (11) Å. The organic moiety is perpendicular to the metal coordination plane due to the presence of the bulky triphenylphosphine ligands and is oriented so that the nitrogen approaches the platinum atom at the short Pt···N separation of 3.109 (3) Å.

Introduction

Metal carbonyls react with alkynes[2] and olefins[3] to afford addition products containing a five-membered ring. These reactions frequently proceed via carbonyl insertion or the β-addition of a halide group on the alkyne triple bond. For example, the reaction of *cis*-$Pt(CO)_2Cl_2$ with the dicarboalkoxyacetylenes ($RCO_2C{\equiv}CCO_2R$, R = Me, Et)[4] affords the cyclometalated product $[Pt\{C(CO_2R)=C(Cl)COOR\}(CO)Cl]$, whereas with the dialkyl- and diarylacetylenes, it produces a mixture containing two neutral metalloorganic compounds, $[Pt\{\eta^4\text{-}C(=O)C(R)=C(R)C(R)=C(R)\}Cl_2]$ and $[Pt\{C(=O)C(R)=C(R)C(R)=C(R)Cl\}Cl]_2$ (R = Me, Et, Pr),[5] and the cationic tetrasubstituted cyclobutadiene complex $[Pt_2(C_4R_2R'_2)_2Cl_3][Pt(CO)Cl_3]$ (R = R′ = Me,[6,7] Et,[6,7] Pr^n;[7] R = Me, R′ = Ph[8]).

The hydrometalation of acetylenic derivatives, as unsaturated compounds, with metal hydrides directly affords

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a five-membered ring complex containing an olefinic ligand.[9] By treatment of *cis*-$Pt(CO)_2Cl_2$ with water it is possible to obtain a mixture of the metal carbonyls $[Pt(CO)_2]_{3n}^{2-}$ (n = ~10) and $H[Pt(CO)Cl_3]$ which reacted with $MeC{\equiv}CCO_2Me$ yields compounds $[Pt\{C(Me){=}C(H)COOMe\}(CO)Cl]$[1] and $[Cl(CO)Pt\{C(Me){=}C(COOMe)C({=}O)\}PtCl(CO)]$,[10] both derivatives containing a metallacyclic ring. The structural formulation was based on the reactivity and on NMR and IR spectroscopic results for these compounds. In this paper, we describe the hydrometalation reaction of $C_6H_5C{\equiv}CC(O)Me$ with a mixture of $[Pt(CO)_2]_{3n}^{2-}$ and $H[Pt(CO)Cl_3]$. The neutral cyclometalated species $[Pt\{C(C_6H_5){=}C(H)C({=}O)Me\}(CO)Cl]$, 1 where the oxygen of the ketonic group is coordinated to the platinum atom, was the result of this reaction. Further reaction of 1 with aromatic amines leads to a metalloorganic ketimine $[Pt\{C(C_6H_5){=}C(H)C({=}NR)Me\}(CO)Cl]$ (R = *p*-MeC_6H_4 (4), C_6H_5 (5)). Multinuclear NMR studies of 1–7 and the X-ray crystal structures of complex 1 and of the disubstituted derivative of the ketimine with triphenylphosphine $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl]$, 7, are reported.

Results and Discussion

Synthesis and Chemical Characterization of $[Pt\{C(C_6H_5){=}C(H)C({=}O)Me\}(CO)Cl]$, 1.

At room temperature and under carbon monoxide atmosphere *cis*-$Pt(CO)_2Cl_2$, in $CHCl_3$ solution, reacts with water and is partially reduced by nucleophilic attack of an OH^- group to the platinum oligomer $[Pt(CO)_2]_{3n}^{2-}$ (n = ~10), with concomitant formation of $H[Pt(CO)Cl_3]$ (eq 1). In reaction 1 carbon monoxide is not required as a reagent, but it prevents the formation of the platinum metal during the reduction of $Pt(CO)_2Cl_2$.

$$(9n)Pt(CO)_2Cl_2 + (3n+1)H_2O \rightarrow [Pt(CO)_2]_{3n}^{2-} + (3n+1)CO_2 + 2H^+ + (6n)H[Pt(CO)Cl_3] + (3n-1)CO \quad (1)$$

The reaction of $Pt(CO)_2Cl_2$ with water has already been described both by Chini et al.[11] and by us. It was pointed out, in previous papers dealing with the chemistry of alkynes and platinum carbonyls, that the reduction of *cis*-$Pt(CO)_2Cl_2$ gives a mixture of $[H_3O]_2[Pt(CO)_2]_{3n}$ (n = ~10) and $H[Pt(CO)Cl_3]$.[1,10] We also proposed that the mixture of $[H_3O]_2[Pt(CO)_2]_{3n}$ and $H[Pt(CO)Cl_3]$ acts as a source of "$[Pt(CO)_2]$" units.[1] In the present case the mixture of $[Pt(CO)_2]_{3n}^{2-}$ and $H[Pt(CO)Cl_3]$ acts as a source of the never isolated species "$[HPt(CO)_2Cl]$", which would be the most suitable metal carbonyl to synthesize compound 1.

By addition of $C_6H_5C{\equiv}CC(O)Me$ (4-phenyl-3-butyn-2-one) to the products of eq 1 an orange solution was obtained containing the keto vinyl complex $[Pt\{C(C_6H_5){=}C(H)C({=}O)Me\}(CO)Cl]$, 1, stabilized by an interaction involving the oxygen atom of the ketonic group, together with an uncharacterized metalloorganic byproduct, tentatively formulated as $[Pt(CO)Cl_2(alkyne)_n]$ (see Experimental Section), which is currently under investigation. The infrared spectrum of the mother liquor revealed the disappearance of the platinum carbonyl and the presence of an excess of unreacted $H[Pt(CO)Cl_3]$, in agreement with the stoichiometry of eq 2. Compound 1 was always isolated in almost quantitative yield according to eq 2 [up to 30% based on the starting $Pt(CO)_2Cl_2$].

$$3[Pt(CO)_2Cl_2] + H_2O \xrightarrow{\text{alkyne}} H[Pt(CO)Cl_3] + 2CO + CO_2 + [Pt\{C(C_6H_5){=}C(H)C({=}O)Me\}(CO)Cl] + [Pt(CO)Cl_2(alkyne)_n] \quad (2)$$

Derivative 1 was pure because it is insoluble in acetone whereas $H[Pt(CO)Cl_3]$ and the uncharacterized byproduct are soluble. The same products, with comparable yields, were obtained by carrying out the reaction in acetone (Experimental Section and ref 1).

Complex 1 is stable in the air and in solution for prolonged periods of time, slightly soluble in CH_2Cl_2 and $CHCl_3$, and insoluble in acetone and aliphatic and aromatic hydrocarbons. The analytical data (elemental analysis, IR, ^1H and ^{195}Pt NMR, and mass spectra) are in agreement with the proposed formulation. The molecular formula of 1 immediately became evident from its mass spectrum, which shows the parent ion and the fragments derived by the loss of the carbon monoxide group. The observed intensity pattern of the molecular ion fitted the computer-simulated pattern. The IR spectrum of complex 1 shows a band at 2100 (vs) cm^{-1}, due to the stretching of a carbonyl group terminally bonded to platinum, and no absorption band at 1700 cm^{-1}, where the stretching of the uncoordinated ketonic group occurs; the band at 1540 (m) cm^{-1} was attributed to the stretching of the ketonic group bonded to platinum through the oxygen atom, in agreement with literature data[12] and with what was previously found for $[Cl(CO)Pt\{CMe{=}C(COOMe)C({=}O)\}PtCl(CO)]$.[10] The formation of the five-membered ring was easily detected in compound 1 and in the related complexes by large shifts in the IR carbonyl stretching vibration of 150–200 cm^{-1} with respect to that of the uncoordinated ketonic group.[12] The 200-MHz ^1H NMR spectrum of compound 1 shows three sets of signals, in the range δ 0–10; the first is due to the aromatic hydrogens, the second to the vinyl hydrogen, and the third to the methyl hydrogens; the integration is correct for the proposed formulation. The vinyl hydrogen signal is coupled with platinum and therefore appears as a pseudotriplet due to the presence of ^{195}Pt NMR active nuclei. The $^{195}Pt\{^1H\}$ NMR spectrum (Figure 1a) exhibits only one resonance, indicating only one compound in solution. It is evident from the NMR data that the reaction between $[Pt(CO)_2]_{3n}^{2-}$, $H[Pt(CO)Cl_3]$, and $C_6H_5C{\equiv}CC(O)Me$ gives only one isomer, with the platinum atom in the trans position with respect to the hydrogen on the alkene double bond. The formation of this isomer is in agreement with the mechanism proposed for $[Pt\{C(Me){=}C(H)COOMe\}(CO)Cl]$.[1] The results of the NMR studies on alkenyl stereochemistry in compound 1 were confirmed by an X-ray structure analysis.

Molecular Structure of $[Pt\{C(C_6H_5){=}C(H)C({=}O)$-

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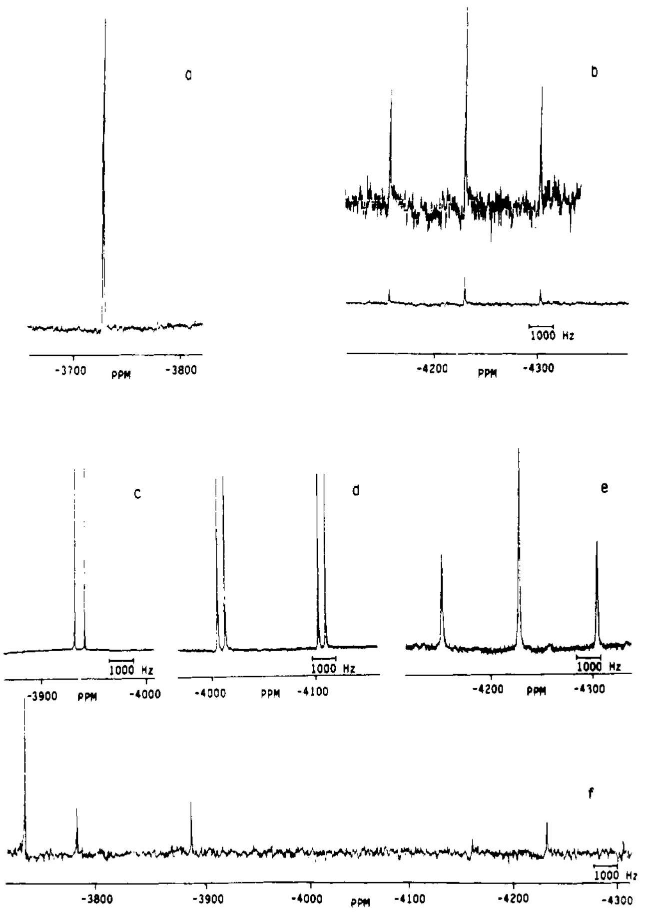

Figure 1. $^{195}Pt\{^1H\}$ NMR spectra ($CDCl_3$ solution, room temperature) of selected compounds: (a) compound 1; (b) compound 3; (c) compound **5b**; (d) compound **6b**; (e) compound **7b** at -50 °C; (f) compound 2, δ -3829, in mixture with compounds 1, δ -3728, and 3, δ -4230.

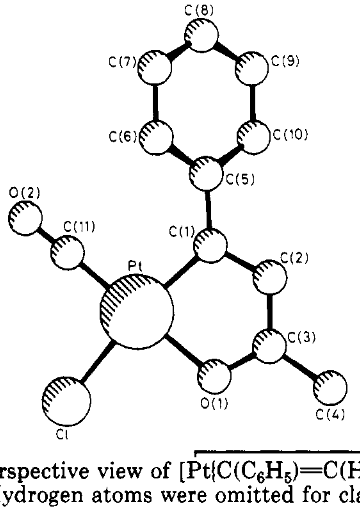

Figure 2. Perspective view of $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(CO)Cl]$, 1. Hydrogen atoms were omitted for clarity.

Me}(CO)Cl], 1. A perspective view of compound 1 is shown in Figure 2, relevant bond lengths and angles are reported in Table I, and some torsion angles are given in Table II.

The Pt(II) atom adopts a distorted square-planar coordination defined by atoms Cl, C(1), O(1), and C(11), the large deviations from ideality being due to the presence of the five-membered metallacycle. These deviations are similar to those reported by us[10] for the complex $[Cl(CO)Pt\{C(Me)=C(OOMe)C(=O)\}PtCl(PPh_3)]$ and hereafter referred to as compound A.[10] In particular, the angles Cl–Pt–C(1) and O(1)–Pt–C(1) [169.5 (3)° and 81.1 (4)°, respectively] compare well with the corresponding angles in the similar metallacycle of compound A [170.6 (3)° and 81.6 (3)°].[10] Also, C(1) deviates by 0.11 (1) Å from the best-fit coordination plane of the metal atom, whereas the five-membered ring is strictly planar, the largest deviations from the least-squares plane through atoms Pt, C(1), C(2), C(3), O(1) being within ±0.007 (11) Å; the two planes form a dihedral angle of 3.4 (2)°. The bond distances involving the Pt atom are, in general, consistent with those already reported. The CO ligand has the expected low trans influence,[13] so that the Pt–O(1) distance of 2.048 (7) Å, though somewaht larger than the corresponding separation found in compound A,[10] is shorter than in the presence of a trans phosphine ligand,[10,14,15] (distances in the range 2.110–2.130 Å). The Pt–C(1) length, 2.017 (11) Å, is in good agreement with the proposed value of 2.02 Å for a Pt–C(sp^2) single bond[16] and is equal to the separation found in related compounds.[1,17,18] On the other hand, the bond lengths in the organic fragment show an extensive π delocalization involving atoms C(1), C(2), C(3), and O(1), the C=C and C=O bonds being greatly lengthened and the C(sp^2)–C(sp^2) bond shortened

Table I. Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (Esd's) on the Last Significant Digit in Parentheses for $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(CO)Cl]$, 1

	Interatomic Distances		
Pt–Cl	2.360 (3)	C(2)–H(2)	1.05 (11)
Pt–O(1)	2.048 (7)	C(3)–C(4)	1.495 (17)
Pt–C(1)	2.017 (11)	C(5)–C(6)	1.413 (15)
Pt–C(11)	1.851 (12)	C(5)–C(10)	1.424 (17)
O(1)–C(3)	1.278 (15)	C(6)–C(7)	1.407 (15)
O(2)–C(11)	1.111 (15)	C(7)–C(8)	1.383 (19)
C(1)–C(2)	1.368 (15)	C(8)–C(9)	1.377 (18)
C(1)–C(5)	1.451 (15)	C(9)–C(10)	1.404 (17)
C(2)–C(3)	1.388 (16)		
	Bond Angles		
C(1)–Pt–C(11)	98.1 (5)	C(3)–C(2)–H(2)	125 (5)
O(1)–Pt–C(11)	178.0 (4)	O(1)–C(3)–C(2)	119 (1)
O(1)–Pt–C(1)	81.1 (4)	C(2)–C(3)–C(4)	123 (1)
Cl–Pt–C(1)	169.5 (3)	O(1)–C(3)–C(4)	117 (1)
Cl–Pt–C(11)	91.9 (4)	C(1)–C(5)–C(6)	123 (1)
Cl–Pt–O(1)	89.0 (2)	C(1)–C(5)–C(10)	119 (1)
Pt–O(1)–C(3)	111.8 (7)	C(6)–C(5)–C(10)	118 (1)
Pt–C(1)–C(5)	128.2 (8)	C(5)–C(6)–C(7)	120 (1)
Pt–C(1)–C(2)	110.5 (8)	C(6)–C(7)–C(8)	121 (1)
Pt–C(11)–O(2)	177 (1)	C(7)–C(8)–C(9)	121 (1)
C(2)–C(1)–C(5)	121 (1)	C(8)–C(9)–C(10)	119 (1)
C(1)–C(2)–H(2)	118 (5)	C(5)–C(10)–C(9)	122 (1)
C(1)–C(2)–C(3)	117 (1)		

Table II. Selected Torsion Angles (deg) with Esd's in Parentheses for Compound 1

Cl–Pt–O(1)–C(3)	177.0 (8)	Pt–C(1)–C(5)–C(6)	41 (2)
C(1)–Pt–O(1)–C(3)	0.7 (8)	Pt–C(1)–C(5)–C(10)	-141 (1)
O(1)–Pt–C(1)–C(2)	-0.7 (8)	C(2)–C(1)–C(5)–C(6)	-140 (1)
C(11)–Pt–C(1)–C(2)	177.5 (8)	C(2)–C(1)–C(5)–C(10)	38 (2)
Pt–O(1)–C(3)–C(4)	178.8 (8)	C(1)–C(2)–C(3–)O(1)	0 (2)
Pt–O(1)–C(3)–C(2)	-1 (1)	C(1)–C(2)–C(3)–C(4)	-179 (1)
Pt–C(1)–C(2)–C(3)	1 (1)	H(2)–C(2)–C(3)–O(1)	-178 (7)
Pt–C(1)–C(2)–H(2)	179 (6)		

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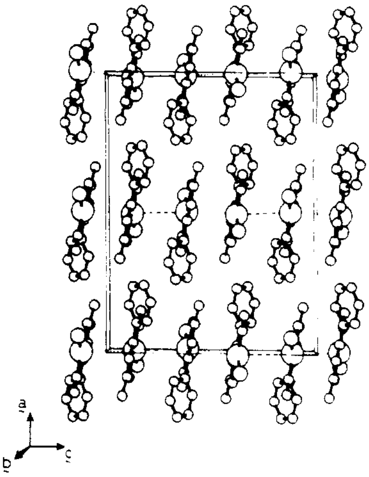
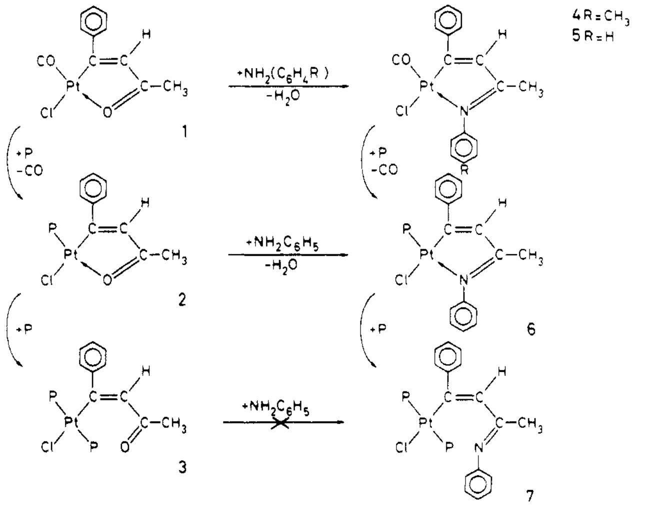


Figure 3. Packing diagram of compound $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(CO)Cl]$, 1. Dashed lines indicate a Pt···Pt separation of 3.6675 (10) Å, dotted lines of 3.4467 (9) Å.

Scheme I



(see Table I); the phenyl ring does not take part in this conjugation as it is rotated by 39.2 (3)° with respect to the plane of the five-membered metallacycle (see also the relevant torsion angles in Table II).

The molecules are arranged in the crystal in infinite stacks running parallel to the *c* axis as shown in Figure 3. The Pt···Pt distances are 3.4467 (9) and 3.6675 (10) Å; a van der Waals radius of 1.7–1.8 Å for Pt as proposed by Bondi[19] alternately rules out any significant bonding. It is interesting to note the similarity with $K_2[Pt(CN)_4]\cdot 3H_2O$, where the separation of 3.48 Å between the metal atoms, arranged in a similar fashion, prevents any appreciable electrical conductivity.[20]

Reactivity of Complex 1. The reactivity of complex 1 is shown in Scheme I together with the numbering scheme adopted to identify the different derivatives; a and b labels are used to indicate the ^{15}N natural abundance and enriched derivatives, respectively. At room temperature complex 1 reacts rapidly, in $CHCl_3$ solution, with 2 equiv of PPh_3 to give carbon monoxide and the pale yellow microcrystalline compound 3, analyzing as $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(PPh_3)_2Cl]$. Compound 3 is stable in air, soluble in CH_2Cl_2 and $CHCl_3$, and insoluble in alcohols and aliphatic hydrocarbons. The analytical and spectroscopic data (Experimental Section) are consistent with the proposed stoichiometry. The IR spectrum shows only one band at 1700 (s) cm^{-1}, attributed to the uncoordinated ketonic group, implying that the five-membered ring was opened by the phosphine ligands, as observed in previous work.[4] The ^1H NMR spectrum of compound 3 contains three sets of signals in the range δ 0–10 in the correct integrated ratio; the overlapping sets of signals from δ 7.2 to 7.8 are assigned to the aromatic hydrogens of the phosphine ligands and of the organic fragment, a signal centered at δ 6.3, assigned to the vinyl hydrogen, is coupled with ^{195}Pt and therefore appears a pseudotriplet, and a singlet at δ 1.55, in the region typical of alkyl groups, is assigned to the hydrogens of the methyl group of the organic fragment. The structural assignment for compound 3, in solution, with the two triphenylphosphine in a trans position to each other, is based on $^{31}P\{^1H\}$ and $^{195}Pt\{^1H\}$ NMR methods in that both spectra show $^1J(^{195}Pt,^{31}P)$ coupling constants. The $^{31}P\{^1H\}$ NMR spectrum exhibits a single resonance from the equivalent triphenylphosphines flanked by ^{195}Pt satellites. The $^{195}Pt\{^1H\}$ NMR spectrum (Figure 1b) reflects the $^{31}P\{^1H\}$ observations and shows a triplet due to the one-bond platinum–phosphorus coupling constant.

The reactions of compound 1 with 1 mol of PPh_3, at room temperature and in $CHCl_3$ solution, leads to the immediate formation of a clear solution; upon treatment of this solution with hexane, an orange precipitate is formed. The $^{195}Pt\{^1H\}$ NMR spectrum (Figure 1f) of this material shows, besides the resonances due to compounds 1 and 3, a new signal, a doublet at δ −3829 ($^1J(P-^{195}Pt)$ = 4700 Hz), attributable to the derivative $[Pt\{C(C_6H_5)=C(H)C(=O)Me\}(PPh_3)Cl]$, 2. The $^{31}P\{^1H\}$ NMR spectrum is in agreement with the presence in solution of an equimolar mixture of compounds containing 1 and 2 mol of PPh_3, respectively. In compound 2, in keeping with the observed reactivity (see later), the triphenylphosphine ligand simply replaces the carbon monoxide group instead of removing the chelation of the oxygen of the ketonic group. The reaction of complex 1 with 1 equiv of primary amines gives, in quantitative yield, the species $[Pt\{C(C_6H_5)=C(H)C(=NR)Me\}(CO)Cl]$ (4, R = *p*-MeC_6H_4; **5a**, R = C_6H_5); no further reaction is observed when compounds 1, 4, or **5a** reacts with an excess of nitrogen donor ligands. The reaction of a ketone with aromatic amines to give an imine derivative usually proceeds only with an acidic catalyst; in the present case, this role is played by the metal atom coordinated to the oxygen. Compounds 4 and **5a** are stable in the air for a long time. The formula of both compounds was inferred from elemental analysis and mass spectra, which contained the parent ions; fragmentation occurs by the loss of CO so that the $[Pt\{C(C_6H_5)=C(H)C(=NR)Me\}Cl]^+$ ions were observed for both compounds. The presence of the Pt–N bond, which gives rise to the formation of a five-membered ring, was inferred from spectroscopic data. The IR spectra of compounds 4 and **5a** are very similar, the main feature being a stretching band at 2100 (vs) cm^{-1} due to the presence of a terminal carbonyl group bonded to platinum. The ^1H NMR spectra of both compounds show all the expected signals with the correct intensity ratios (Experimental Section).

The $^{195}Pt\{^1H\}$ NMR spectra for compounds 4 and **5a** shows only one sharp signal in the region expected for Pt(II) organometallic compounds, in agreement with the

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(19) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(20) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*; Wiley: New York, 1986.

presence in solution of a single compound. The $^{13}C\{^1H\}$ NMR spectrum of compound 4, recorded in the region 0–200 ppm, shows all the signals, with the correct coupling constants, expected for the proposed structure (Experimental Section). All the resonances of the different carbon atoms in compound 4 could be assigned by the analysis of the ^{13}C–^{15}N coupled NMR spectrum of compound **5b** (Experimental Section).

We had some difficulty in recording the ^{15}N NMR spectrum of compound 4 owing to the low natural abundance of this nucleus. For this reason we prepared the enriched derivative containing $^{15}NH_2C_6H_5$ with 99% of ^{15}N. The product $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}^{15}N}C_6H_5)Me\}(CO)Cl]$, **5b**, was isolated as an analytically pure, orange, microcrystalline derivative in up to 87% yield. The ^1H NMR spectrum of compound **5b** shows all the resonances of compound **5a** (Experimental Section). The additional ^{15}N–^{13}C coupling constants in the $^{13}C\{^1H\}$ NMR spectrum allow us to unambiguously assign the resonances of the nitrogen-coupled carbon atoms [C(2), C(3), C(4), C(12)]. The $^{15}N\{^1H\}$ NMR spectrum displays only one resonance, at δ -190, and the platinum satellites are clearly observable with the expected value for the one-bond coupling constant platinum nitrogen. In the $^{195}Pt\{^1H\}$ NMR spectrum (see Figure 1c) there is only one signal, centered at δ −3972; this signal shows the coupling constant with nitrogen.

Reactivity of Compound 5b. The reaction of **5b** with a stoichiometric amount of PPh_3 proceeds smoothly at room temperature with gas evolution, giving the mono or bis complexes $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}N}C_6H_5)Me\}(PPh_3)Cl]$, **6b**, and $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl]$, **7b**, respectively. In the mono adduct **6b** the first ligand replaces the carbonyl group terminally bonded to platinum, while in compound **7b** the second ligand breaks the bond between platinum and nitrogen.

Compounds **6b** and **7b** are air stable, easily soluble in CH_2Cl_2, $CHCl_3$, and aromatic hydrocarbons, and insoluble in alcohols and aliphatic hydrocarbons.

The IR spectra of compounds **6b** and **7b** show that the carbon monoxide group is not present on platinum (absence of the 2100-cm^{-1} band); the absorption due to the uncoordinated C=N group is not easily detected because around 1650 cm^{-1} there is also the stretching of the carbon–carbon double bond.[21]

The 200-MHz ^1H NMR spectra of compounds **6b** and **7b** fully confirm the proposed structures. The ^1H NMR spectrum of compound **6b** shows the coupling between ^{15}N and the vinyl and methyl hydrogens; the latter coupling is not present in compound **7b**. The $^{31}P\{^1H\}$ NMR spectrum of compound **6b** shows a pseudotriplet of doublets, $^1J(^{195}Pt\text{–}P) = 4145$ Hz, in agreement with the one-bond coupling constant of platinum–phosphorus; the further coupling between phosphorus and nitrogen confirms that the metallacycle is present in compound **6b**. The structure proposed for **6b** is confirmed by ^{15}N and ^{195}Pt NMR spectra (see Figure 1d). The presence in all the NMR spectra of the splittings arising from different nuclei confirmed the linkage P–Pt–N in derivative **6b**.

At room temperature the ^{15}N NMR spectrum of compound **7b** does not show any signal, whereas the ^{31}P and ^{195}Pt NMR spectra show only nonresolved signals with broad resonances. At a low temperature, −50 °C, well-resolved spectra are observable: the low-temperature ^{15}N NMR spectrum has only one sharp signal; this is consistent with the proposed structure as the spectrum does not show the coupling between platinum and nitrogen. The ^{31}P NMR spectrum shows only one signal, a pseudotriplet centered at δ 20.94, with a one-bond Pt–P coupling constant value; the multiplicity of the signal is in agreement with the two phosphorus donor ligands in a trans position to each other. The interpretation of the ^{195}Pt NMR spectrum (Figure 1e) is straightforward considering the information obtained from the ^{15}N and ^{31}P NMR spectra.

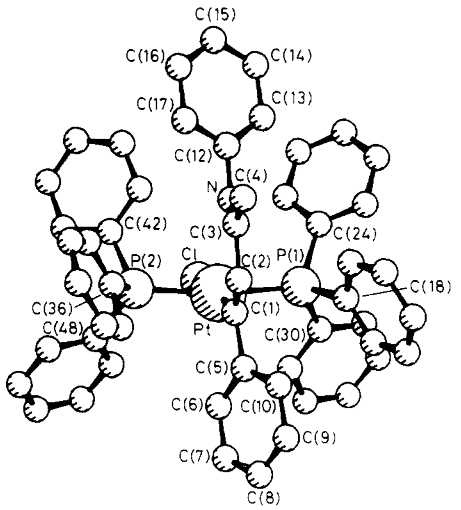

Figure 4. Perspective view of $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl]$, **7b**. Hydrogen atoms were omitted for clarity.

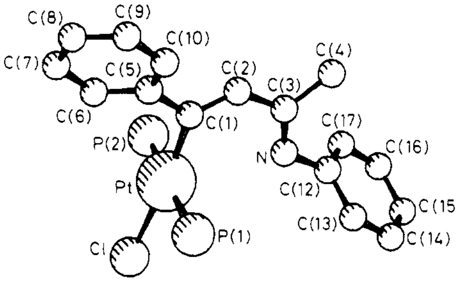

Figure 5. Inner coordination sphere of the Pt atom and the organic ligand in compound $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl]$, **7b**. The phenyl rings of the two phosphines were omitted for clarity.

All these arguments and the data reported in the Experimental Section support the formulation and the coordination mode of the ligands in compounds **6b** and **7b**. The molecular geometry of compound **7b** was confirmed by single-crystal X-ray analysis, thus allowing us to establish a unique relationship between this compound and complexes 5 and 6.

Molecular Structure of $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl]$, 7b. An overall view of the compound is given in Figure 4; the metal coordination sphere and the organic ligand are shown in Figure 5 from a different view. Relevant bond lengths and angles are reported in Table III and some torsion angles are given in Table IV.

The Pt(II) atom has a square-planar coordination defined by atoms Cl, P(1), P(2), and C(1). Severe distortions from ideality are present, as indicated by the bond angles in Table III, in particular P(1)–Pt–P(2) [172.29 (4)°] and Cl–Pt–C(1) [173.73 (10)°], and by the large deviations from the best-fit coordination plane: C(1) is 0.244 (3) Å above it and the two P atoms are 0.114 (1) Å below it, thus giving a tetrahedral deformation. A similar pattern was also reported for the related Pt–isoprenyl compound[22]

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[21] Nakanishi, K. In *Practical Absorption Spectroscopy*; Holden-Day: San Francisco, 1966.

[22] Furlani, A.; Russo, M. V.; Chiesi Villa, A.; Gaetani Manfredotti, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1977**, 2154.

Table III. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for $[Pt\{C(C_6H_5)=C(H)C(=NC_6H_5)Me\}(PPh_3)_2Cl]$, 7b

Interatomic Distances			
Pt-P(1)	2.3045 (9)	C(2)-C(3)	1.461 (6)
Pt-P(2)	2.3097 (10)	C(2)-H(2)	0.92 (5)
Pt-Cl	2.4067 (11)	C(3)-C(4)	1.490 (6)
Pt-C(1)	2.014 (4)	P-C[a]	1.828 ± 0.011
N-C(3)	1.260 (5)	C-C[a,b]	1.384 ± 0.013
N-C(12)	1.429 (5)	C-C[a,c]	1.381 ± 0.014
C(1)-C(2)	1.341 (5)	Pt···N	3.109 (3)
C(1)-C(5)	1.498 (5)		

Bond Angles			
P(1)-Pt-Cl	90.23 (4)	N-C(3)-C(2)	121.0 (4)
P(1)-Pt-P(2)	172.29 (4)	N-C(3)-C(4)	123.5 (4)
P(1)-Pt-C(1)	90.29 (11)	C(2)-C(3)-C(4)	115.4 (4)
P(2)-Pt-Cl	86.63 (5)	C(1)-C(5)-C(6)	121.9 (4)
P(2)-Pt-C(1)	93.61 (11)	C(1)-C(5)-C(10)	121.0 (3)
Cl-Pt-C(1)	173.73 (10)	N-C(12)-C(13)	119.9 (4)
C(3)-N-C(12)	122.5 (4)	N-C(12)-C(17)	121.4 (4)
Pt-C(1)-C(2)	126.7 (3)	Pt-P-C[a]	114.8 ± 3.3
Pt-C(1)-C(5)	116.0 (3)	C-P-C[a]	103.6 ± 1.1
C(2)-C(1)-C(5)	117.3 (4)	P-C-C[a]	120.6 ± 1.8
C(1)-C(2)-C(3)	128.7 (4)	C-C-C[a,b]	120.0 ± 1.4
C(1)-C(2)-H(2)	120 (3)	C-C-C[a,c]	120.0 ± 0.8
C(3)-C(2)-H(2)	111 (3)		

[a] Average value; the ± refers to the root-mean-square deviation from the mean according to $s = [\sum(x_i - \bar{x})^2/(N - 1)]^{1/2}$, where $\bar{x}$ is the average value and N is the number of observations. [b] Performed over the phenyl rings of the organic ligand. [c] Performed over the phenyl rings of the triphenylphoshine ligands.

Table IV. Selected Torsion Angles (deg) with Esd's in Parentheses for Compound 7b

P(1)-Pt-C(1)-C(2)	92.7 (3)	Pt-C(1)-C(5)-C(6)	-33.0 (5)
P(1)-Pt-C(1)-C(5)	-86.7 (3)	Pt-C(1)-C(5)-C(10)	147.5 (3)
P(2)-Pt-C(1)-C(2)	-80.7 (3)	C(5)-C(1)-C(2)-H(2)	-5 (3)
P(2)-Pt-C(1)-C(5)	100.0 (3)	C(5)-C(1)-C(2)-C(3)	174.4 (4)
C(3)-N-C(12)-C(13)	119.1 (5)	C(2)-C(1)-C(5)-C(6)	147.6 (4)
C(3)-N-C(12)-C(17)	-68.1 (6)	C(2)-C(1)-C(5)-C(10)	-32.0 (5)
C(12)-N-C(3)-C(2)	178.3 (4)	C(1)-C(2)-C(3)-N	-2.7 (7)
C(12)-N-C(3)-C(4)	-5.6 (7)	C(1)-C(2)-C(3)-C(4)	-179.1 (5)
Pt-C(1)-C(2)-C(3)	-4.9 (6)	H(2)-C(2)-C(3)-N	177 (3)
Pt-C(1)-C(2)-H(2)	175 (3)	H(2)-C(2)-C(3)-C(4)	1 (3)

trans-$[Pt\{C(=CH_2)C(Me)=CH_2\}(PPh_3)_2Cl]$ and Pt-styryl compound *trans*-$[Pt\{$*trans*-$CH=CHPh\}(PPh_3)_2Br]$.[17] The organic ligand is planar to within ±0.040 (4) Å [least-squares plane through atoms Pt, C(1), C(2), C(3), C(5)] and is almost perpendicular to the metal coordination plane, forming a dihedral angle of 84.87 (8)°. This geometry is imposed by the steric requirements of the two bulky triphenylphosphine ligands (Figure 4). On the other hand, large deviations from ideality are present in the bond angles of the carbon atoms, e.g., Pt-C(1)-C(2) 126.7 (3)° and C(1)-C(2)-C(3), 128.7 (4)°. These values may be compared with those found in the Pt-isoprenyl [Pt—C=C 126.4 (1.2)°][22] and Pt-styryl [Pt—C=C 123.8 (6)° and C=C—C 125.7 (9)°][17] complexes. Values larger than 120° for these angles therefore appear as a common feature in σ-alkenyl compounds (e.g., refs 15 and 16); some enhancement in the present case is needed to optimize the position of nitrogen, bringing it to 3.109 (3) Å from the metal atom. This Pt···N distance rules out any actual bonding but is indicative of a favorable interaction, analogous to that found in the anion $[Pt\{C(Me)=C(H)CO_2Me\}(CO)Cl_2]^-$ with a Pt···O distance of 3.163 (7) Å in a similar geometry.[1]

Other bond lengths are as expected, with a long Pt-Cl distance [2.4067 (11) Å] trans to the σ-alkenyl ligand and with the usual Pt-P separation [average 2.3071 (10) Å].[16,17,22] The Pt-C(sp²) distance, 2.014 (4) Å, is equal to that found in compound 1, thus again suggesting the presence of a single bond,[16] consistent with the rotation of the organic moiety discussed above. A π delocalization involves atoms C(1), C(2), C(3), and N, in analogy to what is observed in compound 1, though not to the same extent (Tables I and III).

No relevant intermolecular contacts are present, and the molecules are held together by van der Waals interactions only.

Concluding Remarks

The multinuclear NMR technique used in this study is a useful tool to determine the solution structures of organometallic compounds containing several NMR active nuclei.[23] In previous work we observed the selective transesterification of the β-carboalkoxy group in $[Pt\{C(CO_2R)=C(Cl)COOR\}(CO)Cl]$ (R = Me, Et)[4] and in related anions.[4] We attributed this behavior to the interaction of the carboxylate carbonyl group with platinum and proposed that some interaction also occurs in the anions where the coordination of the oxygen of the carboxylate carbonyl group is removed, as revealed by X-ray analysis.[4] In the present work we observed by reacting **1** the easy formation of the imine derivative. To prove the role played by the coordinated ketonic group, we reacted the uncoordinated compound **3** with $^{15}NH_2C_6H_5$: the ^{31}P and ^{195}Pt NMR spectra showed only the presence of the starting material. Moreover, upon reacting $^{15}NH_2C_6H_5$ with compounds **1** and **2**, where the ketonic oxygen is coordinated to platinum, mixed with complex **3**, the ^{15}N, ^{31}P, and ^{195}Pt NMR spectra showed that compounds **1** and **2** are transformed into compounds **4b** and **6b** whereas complex **3** does not react. The facile reaction of the amine with complexes **1** and **2** is again favored by the polarization of the ketonic carbon atom due to the coordination of the oxygen to platinum.

Experimental Section

General Comments. Microanalyses were determined by Laboratorio Analisi Universita' di Milano and by Pascher Mikroanalytisches Laboratorium, Remagen, FRG.

The numbering scheme adopted for labeling the carbon atoms in the NMR spectra is the same as that used in the crystallographic study; for the sake of consistency, the label C(11) is not employed in the X-ray structure of compound **7b**. ^1H and $^{13}C\{^1H\}$ nuclear magnetic resonance spectra were recorded on a Bruker WP 80 spectrometer (80 MHz for proton and 20.14 MHz for carbon) or on a Varian XL-200 spectrometer (200 MHz for proton and 50.3 MHz for carbon) and are reported as parts per million (ppm) downfield from the internal standard Me_4Si. $^{15}N\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer (operating at 20.28 MHz) with the INEPT and DEPT techniques and are reported downfield from the external standard CH_3NO_2. $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WP 80 (operating at 32.4 MHz) and on AC 200 (operating at 81.05 MHz) spectrometers and are reported downfield from the external standard (85% H_3PO_4 in D_2O). $^{195}Pt\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 42.8 MHz (Na_2PtCl_6 external standard, pulse angle 50–60°, delay 1.5 s). For the ^{31}P and ^{195}Pt NMR spectra the acquisition time was about 0.15 s. Coupling constants (hertz) for N, P, and Pt are correct to within ±1.2, ±2.4, and ±12.2 Hz, respectively. Infrared (IR) spectra were recorded on a Perkin-Elmer 781 grating spectrophotometer calibrated with polystyrene film or on a Nicolet MX-1 FT-IR Fourier transform interferometer using Nujol mull and NaCl plates (abbreviations: v, very; s, strong; w, weak; m, medium; sh, shoulder). Electron-impact mass spectra were registered by using a VG 7070 mass spectrometer, calibrated against known masses of perfluorokerosene, with a source voltage of 70 eV and probe temperature in the 100–200 °C range. Fast atom bombardment (FAB) mass

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[23] Bonfa', M.; Garlaschelli, L.; Malatesta, M. C. *Gazz. Chim. Ital.* 1986, *116*, 317 and references therein.

spectra were registered by using a V.G. 7070 EQ mass spectrometer equipped with a high-field (HF) magnet and standard FAB source with gas xenon at 8 keV (sulfolane and glycerine mull).

Although the products were rarely air-sensitive, all the reactions were conducted with anhydrous solvents and under a nitrogen or carbon monoxide atmosphere using the Schlenk tube technique. Solvents were purified and dried by standard methods.

cis-$Pt(CO)_2Cl_2$ was prepared as previously described.[5]

Synthesis of $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}O}Me\}(CO)Cl]$, 1. (a) *cis*-$Pt(CO)_2Cl_2$ (2.44 g, 7.6 mmol) was dissolved in $CHCl_3$ (30 mL) in a carbon monoxide stream, H_2O (0.2 mL, 11.1 mmol) was added under magnetic stirring in 1 h: a black suspension of $[H_3O]_2[Pt(CO)_2]_{3n}$ was obtained. When the IR spectrum of the solution did not reveal the bands of $Pt(CO)_2Cl_2$ [2180 (vs) and 2140 (vs) cm^{-1}], $C_6H_5C{\equiv}CC(O)Me$ (1.15 mL, 8.0 mmol) was added and the suspension stirred for 4 h; the color of the solution turned from black to orange and at the end was almost clear. The $CHCl_3$ solution was extracted with an aqueous solution of HCl (2 M, 100 mL); the water solution was treated with $[N(PPh_3)_2]Cl$ (2.2 g, 3.7 mmol), and the ivory solid that formed was filtered off and stirred with 2-propanol (30 mL), filtered, and dried. $[N(PPh_3)_2][Pt(CO)Cl_3]$ was isolated and characterized by comparison with a known sample ($[N(PPh_3)_2][Pt(CO)Cl_3]$ [0.553 g, 0.63 mmol, 8.3% based on starting platinum]). The $CHCl_3$ solution was filtered and left over $MgSO_4$ for 24 h. The $MgSO_4$ was filtered off, and the $CHCl_3$ solution evaporated in vacuo to dryness. The residual orange oil was pumped at 30 °C for 4 h, and the viscous semisolid material was treated with acetone ($\simeq$10 mL) to give complex **1**. The bright orange precipitate was filtered off, washed with acetone (2 × 5 mL) and hexane (3 × 10 mL), and dried; yield 1.0 g (32% based on starting Pt).

The acetone solution was pumped to dryness and treated with hexane. The solid material displays, in the IR spectrum, a band due to the stretching of a carbonyl group bonded to platinum ($\sim$2100 cm^{-1}). Elemental analysis, nonreproducible, suggests more than one alkyne for platinum. Compound **1**: IR (cm^{-1}, Nujol mull) 2100 (vs) (ν(Pt-CO)), 1540 (s) (ν(C=O—Pt)). Anal. Calcd for $C_{11}H_9ClO_2Pt$: C, 32.72; H, 2.25; Cl, 8.78; O, 7.93; Pt, 48.32. Found: C, 32.38; H, 2.23; Cl, 9.51; O, 7.9; Pt, 47.9. MS, *m/e* 403 [M$^+$, ^{35}Cl, ^{195}Pt], 375 [M$^+$ – CO]; ^{1}H NMR ($CDCl_3$ solution) δ 2.5, 6.7 [^3J(^{195}Pt–H) = 59 Hz, =C*H*], 7.4–7.8 (C_6H_5, multiplet]; ^{195}Pt NMR ($CDCl_3$ solution) δ –3728 (singlet).

(b) The preparation of compound **1** was also performed in acetone starting from $Pt(CO)_2Cl_2$ (4.97 g, 15.4 mmol), H_2O (0.5 mL, 27.7 mmol), acetone (130 mL), and $C_6H_5C{\equiv}CC(O)Me$ (1.5 mL, 15.4 mmol). Compound **1** was isolated in comparable yield as in preparation (a). Compound **1** yield 1.77 g, (4.38 mmol) 28.5%; $[N(PPh_3)_2[Pt(CO)Cl_3]$ yield 2.87 g, (3.30 mmol), 21%.

Synthesis of $[Pt\{C(C_6H_5){=}C(H)C({=}O)Me\}(PPh_3)_2Cl]$, 3. PPh_3 (0.60 g, 2.29 mmol) dissolved in $CHCl_3$ (20 mL) was added, under magnetic stirring, to a suspension of **1** (0.388 g, 0.94 mmol) in $CHCl_3$ (20 mL). After a few minutes a clear yellow solution was obtained. The $CHCl_3$ solution was filtered (leaving some black material) and concentrated to a small volume ($\sim$10 mL), and after hexane addition, the pale yellow compound **3** was obtained; the microcrystalline material was filtered off, washed with hexane (3 × 10 mL), and crystallized from CH_2Cl_2 and heptane, yield 0.7 g (83%). Anal. Calcd for $C_{46}H_{39}ClOP_2Pt$: C, 61.37; H, 4.37. Found: C, 60.55; H, 4.19. MS, *m/e* 899 [M$^+$, ^{35}Cl, ^{195}Pt]; IR (cm^{-1}, Nujol mull) 1700 (s) (ν(C=O)); ^{1}H NMR ($CDCl_3$ solution) δ 1.55 (C*H*$_3$), 6.3 [*H*C=, ^3J(^{195}Pt–H) = 113 Hz], 7.2–7.8 (C_6H_5, multiplet); ^{31}P NMR ($CDCl_3$ solution) δ 22.28 [pseudotriplet, ^1J(^{195}Pt–P) = 3156 Hz]; ^{195}Pt NMR ($CDCl_3$ solution) δ –4230 [triplet, ^1J(P–^{195}Pt) = 3156 Hz].

Synthesis of $[Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_4Me\text{-}p)Me\}(CO)Cl]$, 4. To a suspension of **1** (1.38 g, 3.41 mmol) in CH_2Cl_2 (30 mL) *p*-toluidine (0.382 g, 3.57 mmol) dissolved in 10 mL of CH_2Cl_2 was added. Instantaneously a clear, orange solution was obtained; the solution was stirred at room temperature for 15 m and filtered, and after the addition of hexane (20 mL) and concentration in vacuo to eliminate the major part of CH_2Cl_2, a yellow–orange powder was obtained. This was filtered, washed with hexane (3 × 10 mL), and dried; compound **4** yield 1.6 g (93%). Anal. Calcd for $C_{18}H_{16}NClOPt$: C, 43.86; H, 3.27; N, 2.84. Found: C, 43.68; H, 3.44; N, 2.88. IR (Nujol mull, cm^{-1}) 2100 (vs) (ν(Pt–CO)); ^{1}H NMR ($CDCl_3$ solution) δ 7.3–7.5 (multiplet, C_6H_5), 6.49 [=C*H*; ^3J(^{195}Pt–H) = 85 Hz, ^4J(H–H) = 2 Hz], 2.4 ($CH_3C_6H_5$), 2.09 [C*H*$_3$, ^4J(^{195}Pt–H) = 5.4 Hz, ^4J(H–H) = 2 Hz]; ^{13}C NMR ($CDCl_3$ solution) δ 193.26 {^2J[^{195}Pt–^{13}C(3)] = 110 Hz}, 177.7 {^1J[^{195}Pt–^{13}C(1)] = 950 Hz}, 163.7 {^1J[^{195}Pt–^{13}C(11)] = 1830 Hz}, 146.17 {^2J[^{195}Pt–^{13}C(5)] = 84 Hz}, 141.8 {^2J[^{195}Pt–^{13}C(12)], 28 Hz}, 137.0 (C(15)), 135.6 {^2J[^{195}Pt–^{13}C(2)] = 49 Hz}, 129.4 (C(14,16)), 129.2 (C(8)), 128.56 (C(7,9)), 126.13 {^3J[^{195}Pt–^{13}C(6,10)] = 35 Hz}, 124.3 (C(13,17)), 21.34 (*C*$H_3C_6H_4N$=), 19.35 {^3J[^{195}Pt–^{13}C(4)] = 37 Hz}; ^{15}N NMR ($CDCl_3$ solution) δ –169; ^{195}Pt NMR ($CDCl_3$ solution) δ –3970 (singlet); MS, *m/e* 492 (M$^+$, ^{35}Cl, ^{195}Pt), 464, [M$^+$ – CO].

Synthesis of $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}N}C_6H_5)Me\}(CO)Cl]$, 5a. Compound **5a** was prepared via a reaction similar to that for compound **4** by reacting **1** (0.38 g, 0.94 mmol) with $C_6H_5NH_2$ (0.10 mL, 1.07 mmol) in CH_2Cl_2 (10 mL); yield 0.39 g (86.5%). Anal. Calcd for $C_{17}H_{14}NClOPt$: C, 42.64; H, 2.95; N, 2.93. Found: C, 43.23; H, 3.12; N, 3.11. MS, *m/e* 478 [M$^+$, ^{35}Cl, ^{195}Pt], 450, [M$^+$ – CO]; IR (cm^{-1} Nujol mull) 2100 (vs) (ν(Pt-CO)); ^{1}H NMR ($CDCl_3$ solution) δ 7–8 (multiplet, C_6H_5), 6.5 [=C*H*, ^3J(^{195}Pt–H) = 85 Hz], 2.09 [C*H*$_3$, ^4J(^{195}Pt–H) = 5.2 Hz]; ^{13}C NMR ($CDCl_3$ solution) δ 193.2 {^2J[^{195}Pt–^{13}C(3)] = 109 Hz}, 178.0 {^1J[^{195}Pt–^{13}C(1)] = 945 Hz}, 163.6 {^1J[^{195}Pt–^{13}C(11)] = 1840 Hz}, 146.1 {^2J[^{195}Pt–^{13}C(5)] = 84 Hz], 144.2 {^2J[^{195}Pt–^{13}C(12)] = 28 Hz}, 135.6 {^2J[^{195}Pt–^{13}C(2)] = 48 Hz}, δ 129.2 (C(8)), 128.8 (C(14,16)), 128.6 (C(7,9)), 127.5 (C(15)), 126.3 {^3J[^{195}Pt–^{13}C(6,10)] = 34 Hz}, 124.3 (C(13,17)), 19.4 {^3J[^{195}Pt–^{13}C(4)] = 37 Hz}; ^{15}N NMR ($CDCl_3$ solution) δ –190 ppm [pseudotriplet, ^1J(^{195}Pt–^{15}N) = 400 Hz]; ^{195}Pt NMR ($CDCl_3$ solution) δ –3972 (singlet).

Synthesis of $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}^{15}N}C_6H_5)Me\}(CO)Cl]$, 5b. Compound **5b** was prepared as for compound **5a** by reacting **1** (0.427 g, 1.06 mmol) with aniline (99% enriched in ^{15}N; 0.11 mL, 1.17 mmol), yield 0.42 g (87%). Anal. Calcd for $C_{17}H_{14}NClOPt$: C, 42.64; H, 2.95; N, 2.93. Found: C, 43.12; H, 3.07; N, 3.01. ^{1}H NMR ($CDCl_3$ solution) δ 7–8 (multiplet, C_6H_5), 6.5 [=CH, ^3J(^{195}Pt–H) = 85 Hz, ^3J(^{15}N–H) = 7 Hz], 2.09 [C*H*$_3$, ^4J(^{195}Pt–H) = 5.2 Hz, ^3J(^{15}N–H) = 2.5 Hz]; ^{13}C NMR ($CDCl_3$) δ 193.2 {^2J[^{195}Pt–^{13}C(3)] = 109 Hz, ^1J[^{15}N–^{13}C(3)] = 12 Hz}, 178.0 {^1J[^{195}Pt–^{13}C(1)] = 945 Hz}, 163.6 {^1J[^{195}Pt–^{13}C(11)] = 1840 Hz, ^2J[^{15}N–^{13}C(11)] = 20 Hz}, 146.1 {^2J[^{195}Pt–^{13}C(5)] = 84 Hz}, 144.2 {^2J[^{195}Pt–^{13}C(12)] = 28 Hz, ^1J[^{15}N–^{13}C(12)] = 9 Hz}, 135.6 {^2J[^{195}Pt–^{13}C(2)] = 48 Hz, ^2J[^{15}N–^{13}C(2)] = 4 Hz}, 129.2 (C(8)), 128.8 [C(14,16), nonresolved ^{15}N–^{13}C coupling], 128.6 (C(7,9)), 127.5 [C(15), nonresolved ^{15}N–^{13}C coupling], 126.3 {^3J[^{195}Pt–^{13}C(6,10)] = 34 Hz}, 124.3 [nonresolved ^{15}N–^{13}C coupling, C(13,17)], 19.4 {^3J[^{195}Pt–^{13}C(4)] = 37 Hz}; ^{15}N NMR ($CDCl_3$ solution) δ –190 ppm [pseudotriplet, ^1J(^{195}Pt–^{15}N) = 400 Hz]; ^{195}Pt NMR ($CDCl_3$ solution) δ –3972 [doublet, ^1J(^{15}N–^{195}Pt) = 400 Hz].

Synthesis of $[\overline{Pt\{C(C_6H_5){=}C(H)C({=}^{15}N}C_6H_5)Me\}(PPh_3)Cl]$, 6b. To a solution of compound **5b** (0.418 g, 0.87 mmol) in CH_2Cl_2 (10 mL) PPh_3 (0.230 g, 0.870 mmol) dissolved in CH_2Cl_2 (10 mL) was added. After stirring for 10 m at room temperature, the solution was filtered and the solvent removed in vacuo. Hexane (20 mL) was added to the pale orange solid, and the suspension stirred for 30 m; the orange microcrystalline compound was collected by filtration, washed with hexane (3 × 10 mL), and dried. Compound **6b** yield 0.495 g (79%). Anal. Calcd for $C_{34}H_{29}NClPPt$: C, 57.26; H, 4.1; N, 1.96. Found: C, 56.75; H, 3.98; N, 1.76. ^{1}H NMR ($CDCl_3$ solution) δ 7–8 (multiplet, C_6H_5), 6.2 [=C*H*, ^3J(^{195}Pt–H) = 84 Hz, ^3J(^{15}N–H) = 6.8 Hz], 2.0 [C*H*$_3$, ^3J(^{15}N–H) = 2.3 Hz]; ^{13}C NMR ($CDCl_3$ solution) δ 185.5 {^2J[^{195}Pt–^{13}C(3)] = 78 Hz, ^1J[^{15}N–^{13}C(3)] = 12 Hz, ^3J[P–^{13}C(3)] = 3 Hz}, 179.7 {^1J[^{195}Pt–^{13}C(1)] = 1060 Hz, ^2J[P–^{13}C(1)] = 6 Hz}, δ 148.7 {^2J[^{195}Pt–^{13}C(5)] = 96 Hz}, 147.2 {^1J[^{15}N–^{13}C(12)] = 8 Hz}, 138 (C(2)), 135–120 (phenyl carbon atoms), 18.82 {^3J[P–^{13}C(4)] = 5 Hz}; ^{15}N NMR ($CDCl_3$ solution) δ –178 Hz [pseudotriplet of doublets, ^1J(^{195}Pt–^{15}N) = 301 Hz, ^2J(P–^{15}N) = 53 Hz]; ^{31}P NMR ($CDCl_3$ solution) δ 15.9 [pseudotriplet of doublets, ^1J(^{195}Pt–P) = 4145 Hz, ^2J(^{15}N–P) = 53 Hz]; ^{195}Pt NMR ($CDCl_3$ solution) δ –4041 (^1J(P–^{195}Pt) = 4145 Hz, doublet of doublets, ^1J(^{15}N–^{195}Pt) = 301 Hz).

Synthesis of $[Pt\{C(C_6H_5){=}C(H)C({=}^{15}NC_6H_5)Me\}(PPh_3)_2Cl]$, 7b. A solution of PPh_3 (0.231 g, 0.88 mmol) in $CHCl_3$ (20 mL) was added dropwise to a solution of complex **6b** (0.621 g, 0.870 mmol) in $CHCl_3$ (20 mL). The solution was stirred for

Table V. Crystal Data and Intensity Collection Parameters for Compounds 1 and 7b

	1	7b
formula:	$C_{11}H_9ClO_2Pt$	$C_{52}H_{44}ClNP_2Pt$
FW	403.73	975.42
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
a, Å	18.516 (4)	9.0807 (14)
b, Å	8.501 (1)	13.0394 (8)
c, Å	14.108 (3)	19.4935 (24)
α, deg		80.239 (7)
β, deg	91.16 (2)	78.065 (12)
γ, deg		72.667 (8)
V, Å^3	2220 (1)	2141.3 (5)
Z	8	2
$F(000)$	1488	976
calcd density, g cm^{-3}	2.416	1.513
radiation (Mo K$\bar{\alpha}$)	graphite monochromated, λ = 0.71069 Å	
μ, cm^{-1}	129.9	34.8
θ range, deg	$2.2 \leqslant \theta \leqslant 25.0$	$2.1 \leqslant \theta \leqslant 25.0$
octant explored	$\pm h,+k,+l$	$\pm h,\pm k,+l$
scan type	$\theta/2\theta$	$\theta/2\theta$
max scan speed, deg min^{-1}	10	10
scan width, deg	$1.1 + 0.35 \tan \theta$	$1.1 + 0.35 \tan \theta$
max counting time, s	55	60
prescan reject limit	0.5 (2σ)	
prescan accept limit	0.03 (33σ)	
total background time, s	0.5xscan time	
receiving aperture (hor, mm)	$1.9 + \tan \theta$	$2 + \tan \theta$
receiving aperture (vert, mm)	2	2
no. of indep data coll	1932	7518
no. of obsd data ($I \geqslant 3\sigma(I)$)	1199	6240
no. of params refined	141	520
R^a	0.0282	0.0229
$R_w{}^b$	0.0271	0.0238
S^c	1.16	1.62

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \sum w^{1/2}||Fo| - |F_c||/\sum w^{1/2}|F_o|$. [c] Goodness of fit $S = [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$, where m = number of data used and n = number of parameters refined.

Table VI. Positional Parameters and Their Esd's for [Pt{C(C_6H_5)=C(H)C(=O)Me}(CO)Cl], 1

atom	x/a	y/b	z/c
Pt	0.49565 (2)	0.53535 (6)	0.12003 (3)
Cl	0.4370 (2)	0.2894 (4)	0.1285 (2)
O(1)	0.3976 (4)	0.6388 (9)	0.0922 (6)
O(2)	0.6389 (5)	0.3870 (11)	0.1504 (7)
C(1)	0.5277 (6)	0.7621 (12)	0.1171 (8)
C(2)	0.4701 (6)	0.8587 (14)	0.0980 (8)
C(3)	0.4030 (6)	0.7882 (15)	0.0854 (9)
C(4)	0.3354 (6)	0.8783 (16)	0.0632 (9)
C(5)	0.5996 (6)	0.8251 (13)	0.1338 (8)
C(6)	0.6623 (6)	0.7532 (13)	0.0982 (8)
C(7)	0.7305 (5)	0.8196 (15)	0.1187 (9)
C(8)	0.7368 (6)	0.9553 (18)	0.1723 (9)
C(9)	0.6767 (7)	1.0330 (17)	0.2041 (9)
C(10)	0.6082 (6)	0.9677 (16)	0.1857 (8)
C(11)	0.5853 (7)	0.4441 (14)	0.1411 (8)
H(2)	0.479 (5)	0.981 (12)	0.095 (7)

Table VII. Positional Parameters and Their Esd's for [Pt{C(C_6H_5)=C(H)C(=NC_6H_5)Me}(PPh_3)$_2$Cl], 7b

atom	x/a	y/b	z/c
Pt	0.26374 (1)	0.25450 (1)	0.22442 (1)
P(1)	0.30947 (10)	0.07112 (7)	0.22347 (5)
P(2)	0.22533 (11)	0.43259 (7)	0.24064 (5)
Cl	0.53407 (11)	0.22869 (8)	0.23158 (6)
N	0.0226 (4)	0.2376 (3)	0.3616 (2)
C(1)	0.0441 (4)	0.2795 (3)	0.2069 (2)
C(2)	−0.0847 (4)	0.2847 (3)	0.2559 (2)
C(3)	−0.0975 (4)	0.2661 (3)	0.3327 (2)
C(4)	−0.2591 (6)	0.2768 (7)	0.3727 (3)
C(5)	0.0247 (4)	0.2923 (3)	0.1312 (2)
C(6)	0.1190 (5)	0.3409 (3)	0.0770 (2)
C(7)	0.0925 (5)	0.3582 (4)	0.0078 (2)
C(8)	−0.0233 (6)	0.3234 (4)	−0.0099 (2)
C(9)	−0.1125 (5)	0.2725 (4)	0.0421 (2)
C(10)	−0.0891 (5)	0.2570 (4)	0.1117 (2)
C(12)	0.0143 (5)	0.2216 (4)	0.4365 (2)
C(13)	0.0835 (6)	0.1204 (4)	0.4696 (2)
C(14)	0.0918 (7)	0.1058 (5)	0.5406 (3)
C(15)	0.0341 (7)	0.1923 (6)	0.5800 (3)
C(16)	−0.0343 (7)	0.2910 (5)	0.5482 (3)
C(17)	−0.0461 (6)	0.3072 (4)	0.4766 (3)
C(18)	0.1481 (4)	0.0236 (3)	0.2104 (2)
C(19)	0.1462 (5)	−0.0093 (4)	0.1474 (2)
C(20)	0.0193 (6)	−0.0408 (5)	0.1375 (3)
C(21)	−0.1054 (6)	−0.0380 (5)	0.1904 (3)
C(22)	−0.1075 (6)	−0.0035 (5)	0.2535 (3)
C(23)	0.0192 (5)	0.0278 (4)	0.2639 (2)
C(24)	0.3629 (5)	−0.0097 (3)	0.3064 (2)
C(25)	0.3228 (6)	−0.1055 (4)	0.3310 (3)
C(26)	0.3639 (7)	−0.1631 (5)	0.3946 (3)
C(27)	0.4501 (7)	−0.1298 (6)	0.4303 (3)
C(28)	0.4923 (7)	−0.0349 (6)	0.4071 (3)
C(29)	0.4466 (6)	0.0266 (5)	0.3448 (3)
C(30)	0.4680 (4)	0.0160 (3)	0.1539 (2)
C(31)	0.5332 (5)	−0.0946 (3)	0.1537 (2)
C(32)	0.6494 (6)	−0.1350 (4)	0.0986 (3)
C(33)	0.7013 (5)	−0.0651 (4)	0.0447 (2)
C(34)	0.6374 (6)	0.0437 (4)	0.0444 (2)
C(35)	0.5217 (5)	0.0857 (3)	0.0988 (2)
C(36)	0.0239 (5)	0.5164 (3)	0.2572 (2)
C(37)	−0.0684 (5)	0.5388 (4)	0.2037 (2)
C(38)	−0.2202 (6)	0.6008 (4)	0.2143 (3)
C(39)	−0.2834 (6)	0.6445 (5)	0.2768 (3)
C(40)	−0.1967 (7)	0.6230 (5)	0.3291 (3)
C(41)	−0.0436 (6)	0.5581 (4)	0.3203 (3)
C(42)	0.3010 (5)	0.4377 (3)	0.3187 (2)
C(43)	0.2814 (5)	0.3612 (4)	0.3763 (2)
C(44)	0.3207 (6)	0.3662 (5)	0.4404 (3)
C(45)	0.3826 (7)	0.4458 (5)	0.4475 (3)
C(46)	0.4087 (8)	0.5198 (5)	0.3908 (3)
C(47)	0.3676 (6)	0.5185 (4)	0.3256 (3)
C(48)	0.3200 (5)	0.5168 (3)	0.1710 (2)
C(49)	0.4530 (6)	0.4696 (4)	0.1257 (3)
C(50)	0.5317 (6)	0.5329 (4)	0.0761 (3)
C(51)	0.4760 (6)	0.6431 (4)	0.0701 (3)
C(52)	0.3436 (6)	0.6910 (4)	0.1134 (3)
C(53)	0.2640 (5)	0.6289 (3)	0.1639 (3)
H(2)	−0.182 (5)	0.302 (3)	0.243 (2)

1 h at room temperature, the solvent removed in vacuo, and hexane (30 mL) added to the solid. The pale yellow microcrystalline solid was filtered off, washed with hexane (2 × 10 mL) and dried. Compound **7b** yielded 0.704 g (82%). Anal. Calcd for $C_{52}H_{44}NClP_2Pt$: C, 64.03; H, 4.55; N, 1.44. Found: C, 63.2; H, 4.15; N, 1.28. ^1H NMR ($CDCl_3$ solution, room temperature) δ 6.6–8.0 (multiplet, C_6H_5), 6.25 [=CH, $^3J(^{195}Pt-H)$ = 99 Hz, $^3J(^{15}N-H)$ = 4.7 Hz], 1.6 (CH_3). ^{15}N NMR ($CDCl_3$ solution, −50 °C) δ −100 (singlet); ^{31}P NMR ($CDCl_3$ solution, −50 °C) δ 20.94 [pseudotriplet, $^1J(^{195}Pt-P)$ = 3250 Hz]; ^{195}Pt ($CDCl_3$ solution, −50 °C) δ −4262 ppm [triplet, $^1J(P-^{195}Pt)$ = 3250 Hz].

Reaction of 1 with PPh_3 in the Molar Ratio 1:1. Compound 1 (0.29 g, 0.72 mmol) was suspended in $CDCl_3$ (3 mL), and PPh_3 (0.19 g, 0.725 mmol) was added. A pale yellow solution was obtained in a few minutes; this was concentrated in vacuo to dryness, and the orange solid dissolved in $CDCl_3$. ^{31}P and ^{195}Pt NMR spectra revealed a mixture of unreacted compounds **1** and **3** and compound **2**, [Pt{C(C_6H_5)═C(H)C(═O)Me}(PPh_3)Cl], characterized on the basis of NMR spectra; ^{31}P NMR ($CDCl_3$ solution) δ 11.34 ($^1J(^{195}Pt-P)$ = 4636 Hz); ^{195}Pt NMR ($CDCl_3$ solution) δ −3829 ($^1J(P-^{195}Pt)$ = 4636 Hz).

Reaction of 2 with $^{15}NH_2C_6H_5$. In the NMR tube a mixture of compounds **1**, **2**, and **3** was treated, in $CDCl_3$ solution, with a stoichiometric amount of aniline (99% labeled ^{15}N). The ^{15}N, ^{31}P, and ^{195}Pt NMR spectra revealed the presence of compound **6b** mixed with complexes **3** and **5b**.

Reaction of 3 with $^{15}NH_2C_6H_5$. In the NMR tube compound **3** was treated with a stoichiometric amount of aniline (99% ^{15}N). The ^{15}N, ^{31}P, and ^{195}Pt NMR spectra revealed the presence of unreacted compound **3** with no trace of compound **7b**.

Crystallography. Single crystals of compounds **1** and **7b** having a prismatic habit were mounted on a CAD4 diffractometer.

Cell constants (room temperature) and data collection conditions are reported in Table V. Intensities were corrected for Lp factors and for absorption and were considered as observed if $I_{net} \geq 3\sigma(I)$. The structures were solved by Patterson and Fourier methods and refined by least-squares analysis using anisotropic thermal factors for all the non-hydrogen atoms. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights chosen as $w = k/[\sigma^2(F_o) + g|F_o|^2]$. The solution and refinement of the structures were carried out by using the program SHELX 76;[24] atomic scattering factors, with correction for the real and imaginary part of atomic dispersion, were taken from ref 25. Geometrical calculations were done using the program PARST.[26]

Structural Study of $[\overline{\mathrm{Pt\{C(C_6H_5){=}C(H)C({=}O}}\mathrm{)Me\}(CO)Cl}]$, 1. Prismatic colorless crystals of compound 1 were obtained by the slow evaporation of a dichloromethane/heptane solution of the complex. An individual of approximate dimensions 0.1 × 0.1 × 0.05 mm was used for all the analysis. Cell constants were obtained by a least-squares fit of the 2θ values of 25 reflections having $16° \leq 2\theta \leq 28°$. The intensities of three standard reflections (134, $\bar{1}\bar{3}\bar{4}$, $\bar{6}\bar{2}\bar{0}$) measured every hour did not show any significant variation in the experimental setup. The orientation of the crystal was checked by measuring three reflections (134, $\bar{1}3\bar{4}$, $\bar{1}3\bar{4}$) every 300 reflections. An empirical absorption correction was applied using the azimuthal ψ scans of reflections $\bar{5}14$,$\bar{7}17$, and $\bar{9}18$; transmission factors were in the range 68.18–99.97%.

The structure was refined by full matrix least-squares analysis; the vinyl hydrogen atom was refined isotropically, whereas the other hydrogens were held fixed during the last cycles of refinement in the position found in a Fourier difference map with an optimized thermal factor $B = 5$ (1) Å^2. Upon convergence (largest $\Delta/\sigma = 0.1$), the largest residual electron density (0.24 e Å^{-3}) was found around the Pt atom, being otherwise featureless. The refined k and g values in the weighting scheme were $k = 1.0864$ and $g = 2.30 \times 10^{-4}$. The final coordinates are reported in Table VI.

Structural Study of Compound $[\mathrm{Pt\{C(C_6H_5){=}C(H)C({=}NC_6H_5)Me\}(PPh_3)_2Cl}]$, 7b. Prismatic, pale orange crystals of 7b were obtained by a slow diffusion of hexane into a dichloromethane solution of the complex. A single crystal of approximate dimensions 0.4 × 0.3 × 0.2 mm was mounted on a CAD4 diffractometer. Cell constants were determined by a least-squares refinement of the 2θ values of 23 high-angle reflections ($20° \leq 2\theta \leq 34°$). The stability of the crystal and of the experimental setup was monitored by measuring the intensities of three standard reflections (308, $\bar{3}0\bar{8}$, and 060) every hour and the orientation of three reflections ($\bar{3}0\bar{8}$, 192, and 1,5,13) every 300 reflections; no significant variation was detected. The absorption correction was applied as before using the azimuthal ψ scans of reflections $31\bar{5}$ and $52\bar{8}$; transmission factors were in the range 80.58–99.88%. The structure was refined by blocked full-matrix least-squares; the vinyl hydrogen was refined isotropically while the other H atoms were held fixed during the final stage of refinement in the positions found in a difference Fourier map with an optimized thermal factor $B = 6.6$ (2) Å^2. The methyl hydrogens could not be located satisfactorily due to the large thermal motion and were therefore placed in the calculated positions with a collective thermal factor $B = 16$ (2) Å^2. Upon convergence (largest $\Delta/\sigma = 0.3$), the final Fourier difference map did not show any significant feature, the largest residual electron density (0.38 e Å^{-3}) being around the Pt atom. The refined k and g values in the weighting scheme were $k = 1.7102$ and $g = 2.91 \times 10^{-4}$. The final coordinates are given in Table VII.

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Registry No. **1**, 126136-26-3; **2**, 126136-27-4; **3**, 126136-28-5; **4**, 126136-29-6; **5a**, 126136-30-9; **5b**, 126136-33-2; **6**, 126136-31-0; **7**, 126136-32-1; *cis*-$\mathrm{Pt(CO)_2(Cl_2)}$, 15020-32-3; $\mathrm{C_6H_5C{\equiv}CC(O)Me}$, 1817-57-8; $\mathrm{[N(PPh_3)_2]Cl}$, 21050-13-5; $\mathrm{[N(PPh_3)_2][Pt(CO)Cl_3]}$, 116746-89-5; $\mathrm{^{15}NH_2C_6H_5}$, 7022-92-6; *p*-toluidine, 106-49-0.

Supplementary Material Available: Listings of thermal factors (Tables S3 and S4), H atom coordinates (Tables S5 and S6), and least-squares planes (Tables S7 and S8) for compounds 1 and **7b** and full lists of bond lengths (Table S9) and angles (Table S10) for compound **7b** (9 pages); tables of observed and calculated structure factors (Tables S1 and S2) (44 pages). Ordering information is given on any current masthead page.

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