

# Chemistry and Molecular Structure of a Product Formed through Enamine–Ketimine Tautomerism in a Pd–C(CH<sub>3</sub>)=NR Fragment

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**Abstract:** The carbon-bonded imine, *trans*-Pd[C(CH<sub>3</sub>)=N(*p*-tolyl)]Cl(Et<sub>3</sub>P)<sub>2</sub>, reacts with the disubstituted acetylene CH<sub>3</sub>OOC≡CCOCH<sub>3</sub> to form two new compounds, each containing a substituted pyrrole derivative as a ligand. A single-crystal x-ray diffraction study of one product shows that the crystals are triclinic, space group *P* $\bar{1}$  with *Z* = 2 in a unit cell of dimensions *a* = 10.960 (2), *b* = 17.825 (3), *c* = 8.235 (2) Å,  $\alpha$  = 99.90 (1),  $\beta$  = 98.13 (1), and  $\gamma$  = 77.05 (1)°. The structure was refined by full-matrix least-squares methods on *F* to an agreement factor of *R* = 0.046 employing 5043 observations. The coordination geometry about the Pd atom is essentially square planar with the two phosphine ligands *trans* to each other. The chlorine atom and the 1-*p*-tolyl-3-oxo-2-(*E*)-carbomethoxymethylidene-2,3-dihydropyrrole ligand occupy the remaining sites. The mechanism of the reaction has been elucidated through infrared and NMR spectroscopy, as well as deuterium exchange studies of the starting material, the intermediate, and the products. The starting imine exists as two tautomers, the enamine form and the ketimine form. The N–H fragment of the enamine form adds across the triple bond of the acetylene to give an intermediate which then undergoes ring closure with elimination of methanol.

## Introduction

In previous studies of the reactivity of the platinum–hydrogen bond, we have demonstrated<sup>2</sup> the formation of platinum(II)–formimidoyl complexes through isocyanide insertion reactions. Some aspects of the chemistry of the formimidoyl ligand were described,<sup>3</sup> including its facile and reversible conversion to a metal-bound secondary carbene. Since palladium(II) hydrides are fewer in number and less stable than those of platinum(II), we have extended this work to the preparation and study of comparable palladium-bound imine ligands prepared by the insertion of isocyanide ligands into the Pd–CH<sub>3</sub> bond. In this paper we describe an interesting reaction of such an imine which demonstrates the occurrence of enamine–ketimine tautomerism.

Such tautomerism is well known in organic chemistry, and is frequently invoked in mechanistic proposals. However, for transition metal carbon-bonded imine species, which possess  $\alpha$ -hydrogen atoms, <sup>1</sup>H NMR and infrared studies show only the presence of the ketimine form.<sup>4</sup> In contrast, the reaction described here is best explained by a reaction mechanism which proceeds through the enamine form.

## Experimental Section

Melting points were uncorrected and infrared spectra were obtained from solutions in dichloromethane using a Perkin-Elmer 621 grating spectrophotometer. <sup>1</sup>H and <sup>19</sup>F NMR spectra were recorded in CDCl<sub>3</sub> solution on a Varian HA-100 spectrometer using Me<sub>4</sub>Si and CFCl<sub>3</sub> as internal standards, respectively. <sup>13</sup>C spectra were recorded in CDCl<sub>3</sub> on an XL-100 spectrometer using CDCl<sub>3</sub> as an internal standard.

**Preparation of the Compounds.** *trans*-PdCl(CH<sub>3</sub>)[P(Et)<sub>3</sub>]<sub>2</sub> was prepared by a method analogous to that employed to make *trans*-Pd(Cl)(CH<sub>3</sub>)[(CH<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>5</sub>].<sup>5</sup>

**Preparation of *trans*-Pd(Cl)[C(CH<sub>3</sub>)N(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)](PEt<sub>3</sub>)<sub>2</sub> (1).** To a dichloromethane solution (20 mL) of *trans*-PdCl(CH<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub> (300 mg) was added 1 equiv of *p*-tolyl isocyanide. After 12 h, the solvent was removed and the product recrystallized from *n*-pentane to give white crystals in 85% yield.

Anal. Calcd for C<sub>21</sub>H<sub>40</sub>ClNP<sub>2</sub>Pd: C, 49.42; H, 7.90; N, 2.74. Found: C, 49.53; H, 7.74; N, 2.65.

**Reaction of *trans*-Pd(Cl)[C(CH<sub>3</sub>)N(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)](PEt<sub>3</sub>)<sub>2</sub> with Dimethyl Acetylenedicarboxylate (DMA).** To 0.500 g of the imine **1** in CDCl<sub>3</sub> was added 1 equiv of DMA and the reaction was monitored by <sup>1</sup>H NMR. An immediate reaction occurred with the disappearance of the methyl resonance of the imine and of the methoxy resonance of the acetylene to give two distinct sets of new signals. The less intense set had signals at 2.34, 3.19, 3.30, 5.53, and 5.85 ppm in the relative

ratios of 3:3:3:1:1, as well as peaks in the region of 1–3 and 7 ppm characteristic of triethylphosphine ligands and the aromatic protons of the *p*-tolyl group. The more intense set had signals at 2.35, 3.43, 3.60, 4.03, 4.25, and 7.73 ppm in the ratios of 3:3:3:1:1:1, along with peaks at 1–3 and 7 ppm due to *trans* triethylphosphine ligands and the aromatic protons of the *p*-tolyl group. Over a period of 24 h the intensities and positions of the weaker set of signals remained constant, while those of the other set slowly vanished with the formation of a third set of resonances at 2.34, 3.82, 5.43, and 5.65 ppm in the ratio of 3:3:1:1, as well as the peaks of an aromatic AB quartet at 7.21 ppm and peaks between 1 and 3 ppm indicative of *trans* phosphine ligands. A peak of intensity 3 also appeared at exactly the same chemical shift (3.30 ppm) as that of one of the peaks of the less intense set. Upon removal of the solvent and redissolution in CDCl<sub>3</sub>, the <sup>1</sup>H NMR spectrum was exactly the same except that the signal at 3.30 ppm was absent for both species. Addition of methanol regenerated this peak, and thus it was attributed to methanol which had been formed in the reaction. The solvent was removed and the dark red-orange product chromatographed on silica gel using diethyl ether as the eluent. Two bands were observed in the ratio of 1:4. The first band, which contained the minor product, gave dark, red-orange crystals. Their <sup>1</sup>H NMR spectrum (Table VIII) was identical with that of the less intense set, except that the peak at 3.30 ppm ascribed to methanol was absent, mp 165 °C.

Anal. Calcd for C<sub>26</sub>H<sub>42</sub>ClNO<sub>3</sub>P<sub>2</sub>Pd: C, 50.33; H, 6.82; N, 2.26. Found: C, 50.22; H, 6.68; N, 2.36.

The second band, which contained the major product, gave yellow-orange crystals. Their <sup>1</sup>H NMR spectrum was identical with that of the third set (Table VIII) except that the peak at 3.30 ppm ascribed to methanol was missing, mp 176 °C.

Anal. Calcd for C<sub>26</sub>H<sub>42</sub>ClNO<sub>3</sub>P<sub>2</sub>Pd: C, 50.33; H, 6.82; N, 2.26. Found: C, 50.06; H, 6.76; N, 2.31.

**Reaction of the Intermediate **2** with D<sub>2</sub>O.** A mixture of the intermediate **2** and **3** in CDCl<sub>3</sub> solution was prepared as above. D<sub>2</sub>O was added and the <sup>1</sup>H NMR spectrum monitored. After 2 h the signals at 4.03 and 4.23 ppm belonging to the intermediate **2** had disappeared and a signal at 4.62 ppm due to DOH was observed. Further reaction occurred to produce **2a** with deuterium incorporated only for the signal at 5.53 ppm.

**Reaction of Pd(Cl)[C(CH<sub>3</sub>)N(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)](PEt<sub>3</sub>)<sub>2</sub> with D<sub>2</sub>O.** A solution of the imine in CDCl<sub>3</sub> together with a large excess of D<sub>2</sub>O was shaken in an NMR tube and the <sup>1</sup>H NMR spectrum monitored. After 2 h the methyl peak of the imine had vanished and a signal at 4.61 ppm due to DOH was observed.

**Reaction of Pd(Cl)[C(CH<sub>3</sub>)N(C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>)](PEt<sub>3</sub>)<sub>2</sub> with Hexafluoro-2-butyne.** Hexafluoro-2-butyne was bubbled through a chloroform solution of **1** for several minutes. The solution was stirred for an additional 10 min and then stripped to dryness. The rather unstable product was characterized by its <sup>1</sup>H and <sup>19</sup>F NMR spectra.

**Collection and Reduction of X-Ray Data.** Well-developed orange crystals of PdCl(P(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>)<sub>2</sub>(C<sub>14</sub>H<sub>12</sub>NO<sub>3</sub>) with acicular habit were recrystallized from a mixture of toluene and hexane. A preliminary photographic examination employing Weissenberg and precession techniques indicated that the crystals were triclinic. Cell constants derived from the films were subjected to a cell reduction.<sup>6</sup> The density of the crystals was measured by flotation in an aqueous solution of zinc chloride. *P* $\bar{1}$  was chosen as the space group, and later confirmed by a successful analysis. No symmetry constraints are imposed upon the molecule. Crystal data are summarized in Table I.

A crystal of approximate dimensions 0.45 × 0.13 × 0.12 mm was chosen from which to record intensity data. It was mounted with the long dimension [001] offset from coincidence with the diffractometer  $\phi$  axis by some 7°. Nine faces were identified by optical goniometry as (110), ( $\bar{1}\bar{1}0$ ), (001), (11 $\bar{2}$ ), ( $\bar{1}\bar{1}\bar{2}$ ), and the forms {100} and {010}. After data collection the crystal dimensions were accurately measured on a microscope fitted with a filar eyepiece.

Intensity data were recorded on a Picker FACS-1 automatic diffractometer. Cell constants and an orientation matrix were refined<sup>8</sup> using 27 carefully centered reflections with 32 < 2 $\theta$  < 65° covering the regions of reciprocal space from which data were to be collected.  $\omega$  scans of several intense, low-angle reflections, recorded with a takeoff angle of 0.7° and a wide-open counter, had an average width at half-height of 0.11°. Full details of the experimental conditions are presented in Table I. During the collection of data, the standard reflections were examined regularly. Two showed only random fluctuations, while the remaining three increased in intensity, by an average of 10%, an effect attributed to an increase in crystal mosaicity resulting from the x-ray exposure.  $\omega$  scans were recorded both prior to, and at the conclusion of, the data collection run for these standards, but an average increase in width at half-height of only 0.01° was observed. No correction was made to the data for this effect. Coincidence losses in counting for strong reflections were minimized by the use of copper foil attenuators.

A total of 5761 reflections was measured. The recorded intensities were corrected for Lorentz and polarization effects. A standard deviation  $\sigma(I)$  was assigned to each intensity ( $I$ ), where  $(\sigma(I))^2 = C + \frac{1}{4}(tc/tb)^2(bl + bh) + (pI)^2$  where  $I = C - \frac{1}{2}(bl + bh)tc/tb$ ,  $C$  = total count measured in time  $tc$ , and  $bl$  and  $bh$  are background counts each measured in time  $tb$ .  $p$  was chosen as 0.03.<sup>10</sup> Of the 5629 reflections processed (excluding the standard reflections), 5043 with  $I > 3\sigma(I)$  were used in the solution and refinement of the structure.

**Solution and Refinement of the Structure.** The structure was solved by the heavy atom method, and refined by full-matrix least-squares techniques on  $F$ . Scattering factors for neutral nonhydrogen atoms were taken from Cromer and Waber,<sup>11</sup> while those for H were from Stewart, Davidson, and Simpson.<sup>12</sup> The real and imaginary anomalous dispersion corrections of Cromer and Liberman<sup>13</sup> were included for the Pd, Cl, and P atoms.

Two cycles of refinement varying positional and isotropic thermal parameters for all 34 nonhydrogen atoms gave agreement factors  $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$  and  $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.15$ . The function minimized was  $\Sigma w(|F_o| - |F_c|)^2$ , and the weight  $w$  was calculated as  $4F_o^2/\sigma^2(F_o^2)$ . The data were then corrected for absorption effects. The analytical method was used.<sup>8</sup> Transmission coefficients varied from 0.187 to 0.342.

In further refinement cycles the phenyl ring was included as a rigid group ( $D_{6h}$ , C-C 1.392 Å).<sup>14</sup> All other atoms were assigned anisotropic thermal parameters. Two cycles of refinement (5043 observations, 265 variables) converged the model at  $R_1 = 0.049$  and  $R_2 = 0.074$ . An inspection of the molecular geometry at this stage revealed only one unsatisfactory feature. One ethyl group of a triethylphosphine ligand contained a short C-C bond of 1.361 (13) Å, compared to the others, which averaged 1.537 (8) Å.

Accordingly atoms C(22) and C(23) of this group were omitted, structure factors were computed after one cycle of refinement, and a difference Fourier synthesis was examined. Atoms C(22) and C(23) were present as a poorly resolved region of electron density. Also apparent on the synthesis were 41 of the 42 hydrogen atoms. With this evidence to support the choice of space group, and the essential validity of the model, it was decided to include the C atoms of the ethyl group in ideal positions (C-C 1.54 Å, P-C-C 109.8°). Idealized coordinates were also calculated for the 42 H atoms (C-H 1.00 Å). Thereafter the contributions from the ethyl group atoms and the H atoms were included in calculation of  $F_c$ , but no attempt was made to refine these atoms further.

**Table I.** Summary of Crystal Data and Experimental Conditions

Compd	C <sub>24</sub> H <sub>42</sub> ClNO <sub>3</sub> P <sub>2</sub> Pd	mol wt 620.43
Unit cell dimensions	$a = 10.960$ (2) Å $b = 17.825$ (3) Å $c = 8.235$ (2) Å	$\alpha = 99.90$ (1)° $\beta = 98.13$ (1)° $\gamma = 77.06$ (1)°
Cell volume	1535.7 Å <sup>3</sup>	
Z	2	
Density observed	1.35 (1) g cm <sup>-3</sup>	
calculated	1.343 g cm <sup>-3</sup>	
Space group	<i>P</i> $\bar{1}$ ( $C_i$ <sup>1</sup> no. 2) <sup>6</sup>	
Absorption coefficient	$\mu = 66.22$ cm <sup>-1</sup> (Cu K $\alpha$ )	
Crystal volume	0.0272 mm <sup>3</sup>	
Transmission coefficients	0.187 to 0.342	
Radiation	Cu $\lambda(K\alpha_1) = 1.54056$ Å prefiltered with 0.018 mm Ni foil	
Temperature	20 °C	
Receiving aperture	5.0 by 5.0 mm, 33 cm from crystal	
Takeoff angle	2.0°, 90% of available Bragg intensity	
Scan	$\theta - 2\theta$ at 2° min <sup>-1</sup>	
Background	Stationary crystal, stationary counter background counts of 10 s at the scan limits	
Scan range	1.4°, corrected for dispersion	
2 $\theta$ limits	2 ≤ 2 $\theta$ ≤ 130°	
Data collected	$\pm h, \pm k, l$	
Standard reflections	Five, recorded every 200 observations: 020, 100, 020, 001, and $\bar{1}00$ .	

After three cycles of refinement the fixed atom parameters were recalculated. Two final cycles (5043 observations with  $F^2 > 3\sigma(F_o^2)$  and 247 variables) converged at agreement values  $R_1 = 0.046$  and  $R_2 = 0.067$ . In the final cycle the greatest shift, 1.95 esd, was associated with the  $x$  coordinate of C(15), one of the ethyl group C atoms. Of the data for which  $0 < F^2 < 3\sigma(F_o^2)$  no structure factor was in error by greater than 6 $\sigma$ .

A statistical analysis of  $R_2$  over various ranges of  $|F_o|$ ,  $\lambda^{-1} \sin \theta$ , and diffractometer setting angles  $\chi$  and  $\phi$  showed no abnormal trends. A comparison of  $F_o$  and  $F_c$  suggested that extinction effects were minimal, and could be ignored. The error in an observation of unit weight is 2.98 electrons. A total difference Fourier synthesis computed from structure factors based upon the final model showed no features of chemical significance. The highest peak, of electron density 1.031 e Å<sup>-3</sup> at fractional coordinates (-0.4518, 0.2056, 0.3389), is of no chemical significance, and lies close to one of the phenyl ring C atoms.

Final positional and thermal parameters for the nongroup atoms are given in Table II. Parameters associated with the rigid group are presented in Table III. Hydrogen atom parameters are given in Table IV, and structure amplitudes, listed in Table V as  $10|F_o|$  and  $10|F_c|$  in electrons, have been deposited.

**Description of the Structure.** The crystal structure consists of discrete molecules, for the closest intermolecular distance of approach is 2.38 Å between hydrogen atom H1C(36) and the same atom in the equivalent position  $1 - x, 1 - y, 1 - z$ . The shortest Pd-Pd distance of approach is 8.026 (1) Å.

A perspective drawing of the molecule showing the atom numbering scheme is presented in Figure 1, while details of the cyclic ligand formed by reaction of the coordinated imine with the disubstituted acetylene are given in Figure 2. Selected bond distances and bond angles are presented in Table VI, and some weighted least-squares planes are presented in Table VII.

The coordination geometry around the Pd atom is approximately square planar. A weighted least-squares plane through the Pd, the two P, the Cl, and the C(30) atoms shows that the largest deviation from the plane is that of P(2) by 0.225 (2) Å. The Pd-P distances differ by 6 $\sigma$ , though the phosphorus ligands occupy similar environments in the molecule. This probably reflects an underestimation of the standard deviations of these lengths rather than any intrinsic difference. Values of 2.308 (4) Å were obtained for *trans*-Pd(H)Cl(Et<sub>3</sub>P)<sub>2</sub>, and 2.306 (5) Å for *trans*-Pd(C<sub>6</sub>H<sub>4</sub>NNC<sub>6</sub>H<sub>5</sub>)Cl(Et<sub>3</sub>P)<sub>2</sub>.<sup>16</sup> The Pd-C(30) distance of 1.942 (4) Å is comparable to other Pd-C distances found so far.<sup>17</sup> If the Pd-Cl distance of 2.408 (1) Å is averaged over thermal motion, using a model in which the Cl atom is assumed to ride on the

Table II. Positional and Thermal Parameters for Nongroup Atoms

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (1,1) <sup>b</sup>	<i>U</i> (2,2)	<i>U</i> (3,3)	<i>U</i> (1,2)	<i>U</i> (1,3)	<i>U</i> (2,3)
Pd	657.8 (3) <sup>a</sup>	2160.4 (2)	551.7 (4)	519 (2)	489 (2)	570 (2)	-128 (1)	52 (1)	145 (1)
Cl	-437.1 (14)	1388.2 (7)	1728 (2)	966 (9)	557 (7)	1028 (11)	-275 (6)	382 (8)	206 (7)
P(1)	-699.4 (11)	3257.1 (7)	1726 (2)	484 (6)	589 (7)	565 (7)	-116 (5)	54 (5)	124 (5)
P(2)	1711.2 (14)	1040.2 (7)	-951 (2)	775 (8)	520 (7)	782 (9)	-73 (6)	98 (7)	95 (6)
C(10)	-614 (5)	4238 (3)	1453 (7)	710 (31)	609 (28)	793 (36)	-65 (24)	142 (28)	195 (26)
C(12)	-708 (5)	3291 (3)	3940 (7)	746 (33)	898 (38)	636 (33)	-151 (28)	105 (27)	200 (29)
C(14)	-2298 (5)	3185 (4)	829 (8)	513 (27)	934 (40)	938 (43)	-154 (27)	52 (28)	79 (34)
C(11)	551 (6)	4526 (3)	2321 (9)	901 (39)	669 (32)	1020 (47)	-211 (29)	209 (36)	89 (32)
C(13)	-1773 (7)	3908 (5)	4710 (9)	916 (45)	1557 (66)	702 (42)	-31 (45)	262 (36)	33 (43)
C(15)	-2442 (6)	3122 (6)	-1028 (10)	670 (38)	2345 (103)	839 (48)	-91 (52)	-206 (36)	-207 (58)
C(20)	2874 (7)	1137 (4)	-2215 (10)	1012 (47)	822 (40)	1260 (60)	-235 (35)	485 (45)	-169 (40)
C(21)	3342 (8)	434 (5)	-3469 (12)	1369 (68)	1061 (56)	1460 (77)	-100 (50)	639 (62)	-154 (54)
C(22)	2381	238	218	1393					
C(23)	3287	502	1702	1773					
C(24)	550 (8)	588 (4)	-2369 (11)	1368 (66)	859 (44)	1323 (67)	-529 (45)	393 (56)	-337 (46)
C(25)	-160 (9)	1105 (7)	-3627 (14)	1354 (76)	1995 (105)	1573 (92)	62 (75)	-516 (71)	-664 (82)
C(30)	1487 (4)	2791 (2)	-455 (6)	441 (21)	524 (23)	621 (28)	-83 (18)	76 (20)	119 (21)
C(31)	1048 (4)	3133 (3)	-1871 (6)	495 (23)	610 (26)	575 (27)	-140 (20)	-29 (20)	180 (22)
C(32)	1936 (4)	3538 (2)	-2241 (6)	549 (24)	511 (24)	609 (28)	-76 (19)	88 (21)	166 (21)
C(33)	2983 (4)	3437 (3)	-862 (7)	458 (22)	528 (24)	783 (33)	-84 (19)	130 (22)	149 (23)
C(34)	3957 (5)	3796 (3)	-591 (8)	525 (25)	636 (29)	1093 (46)	-159 (22)	12 (28)	228 (30)
C(35)	4183 (5)	4262 (3)	-1860 (10)	502 (28)	750 (37)	1520 (66)	-175 (26)	5 (35)	518 (41)
C(36)	4783 (8)	4155 (5)	-4492 (14)	1341 (68)	1539 (75)	2091 (103)	-12 (57)	790 (70)	1123 (75)
C(7)	6003 (7)	1676 (4)	5456 (10)	1183 (54)	977 (48)	1032 (52)	-25 (41)	-471 (45)	127 (40)
O(32)	1899 (3)	3924 (2)	-3358 (5)	687 (20)	728 (21)	785 (24)	-126 (17)	121 (18)	296 (19)
O(35)	3996 (4)	4956 (2)	-1689 (8)	947 (31)	681 (26)	1932 (56)	-243 (23)	-64 (34)	448 (31)
O(36)	4633 (4)	3776 (3)	-3175 (7)	779 (25)	844 (27)	1426 (41)	-27 (21)	436 (27)	536 (28)
N	2672 (3)	2971 (2)	145 (5)	423 (17)	643 (22)	597 (23)	-141 (16)	-17 (17)	175 (18)

<sup>a</sup> Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. All parameters have been multiplied by 10<sup>4</sup>. <sup>b</sup>  $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*) A^2$ . The thermal ellipsoid is given by  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ .

Table III

Rigid Group Parameters					
<i>x<sub>g</sub></i> <sup>a</sup>	<i>y<sub>g</sub></i>	<i>z<sub>g</sub></i>	$\delta$	$\epsilon$	$\eta$
0.4301 (2)	0.23217 (12)	0.2742 (3)	1.575 (3)	-2.404 (2)	-1.158 (3)
Derived Group Atom Parameters					
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å <sup>2</sup>	
C(1)	3492 (3) <sup>b</sup>	2643 (2)	1465 (4)	4.56 (9)	
C(2)	4737 (3)	2299 (2)	1222 (3)	5.28 (10)	
C(3)	5547 (2)	1978 (2)	2500 (4)	5.87 (11)	
C(4)	5111 (3)	2001 (2)	4020 (4)	6.41 (12)	
C(5)	3866 (3)	2345 (2)	4262 (3)	6.41 (12)	
C(6)	3056 (2)	2666 (2)	2984 (4)	5.48 (10)	

<sup>a</sup> *x<sub>g</sub>*, *y<sub>g</sub>*, and *z<sub>g</sub>* are the fractional coordinates of the group origin;  $\delta$ ,  $\epsilon$ , and  $\eta$  (radians) are the group orientation angles. See ref 14.  
<sup>b</sup> Derived group atom positional parameters have been multiplied by 10<sup>4</sup>.

Pd atom, a value of 2.427 (1) Å is obtained. Both of these distances are significantly longer than the sum of the covalent radii, which is 2.30 Å.<sup>18</sup> The normal length of a terminal Pd-Cl bond is between 2.30 and 2.33 Å.<sup>19</sup> This lengthening of the bond can be attributed to the

strong trans influence of the sp<sup>2</sup>-hybridized atom C(30). A similar lengthening of the Pd-Cl bond trans to a sp<sup>2</sup> carbon atom has been observed by Weaver.<sup>16</sup>

The five ethyl groups refined without constraints gave a mean P-C distance of 1.821 (4) Å. Comparable means of 1.84 (2) Å in Pd(H)-Cl(Et<sub>3</sub>P)<sub>2</sub><sup>15</sup> and 1.82 (1) Å in (C<sub>6</sub>H<sub>4</sub>NNC<sub>6</sub>H<sub>5</sub>)PdCl(Et<sub>3</sub>P)<sub>2</sub><sup>16</sup> have been obtained. The mean Pd-P-C angle, excluding that formed by the fixed carbon atom C(22), is 113.7 (28)°, and the mean C-P-C angle is 104.8 (7)°. A similar distortion from tetrahedral geometry is observed for triethylphosphine ligands in other complexes.<sup>15,16</sup>

The organic group trans to the Cl atom is best formulated as a pyrrole derivative. The short distances between C(33) and C(34) of 1.336 (6) Å, between C(32) and O(33) of 1.231 (5) Å, and between O(35) and C(35) of 1.195 (7) Å imply multiple bond character. Both the C(30)-C(31) bond length of 1.384 (6) Å and the value of C(31)-C(32) of 1.427 (6) Å are short. From chemical and spectroscopic considerations, the C(30)-C(31) bond may be assigned as a double bond with an H atom bonded to C(31), and the shortness of the C(31)-C(32) bond can be attributed to resonance structures of the type shown in eq 1.

A least-squares plane through O(32) and the five atoms of the ring shows the greatest deviation from planarity to be that of C(32) by 0.015 (5) Å. The geometry about the N atom is essentially trigonal planar. The two groups are cis about the exocyclic double bond imposing the *E* configuration. These considerations lead to the organic group being formulated as 1-*p*-tolyl-3-oxo-2-(*E*)-carbomethoxy-methylidene-2,3-dihydropyrrole.

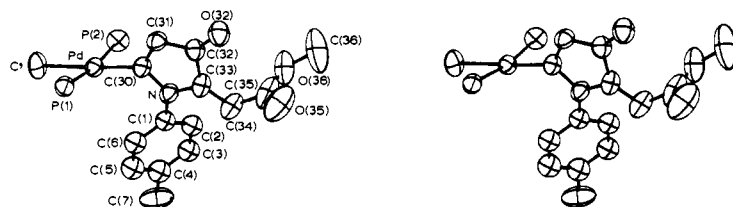
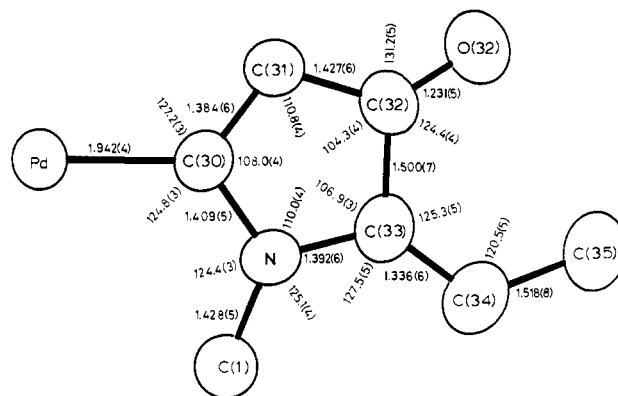


Figure 1. A stereoview of the molecule, showing the atom labeling scheme; 50% probability thermal ellipsoids are shown.

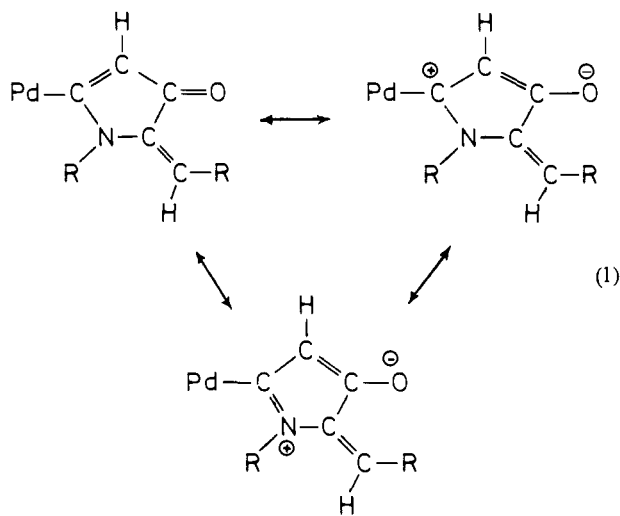
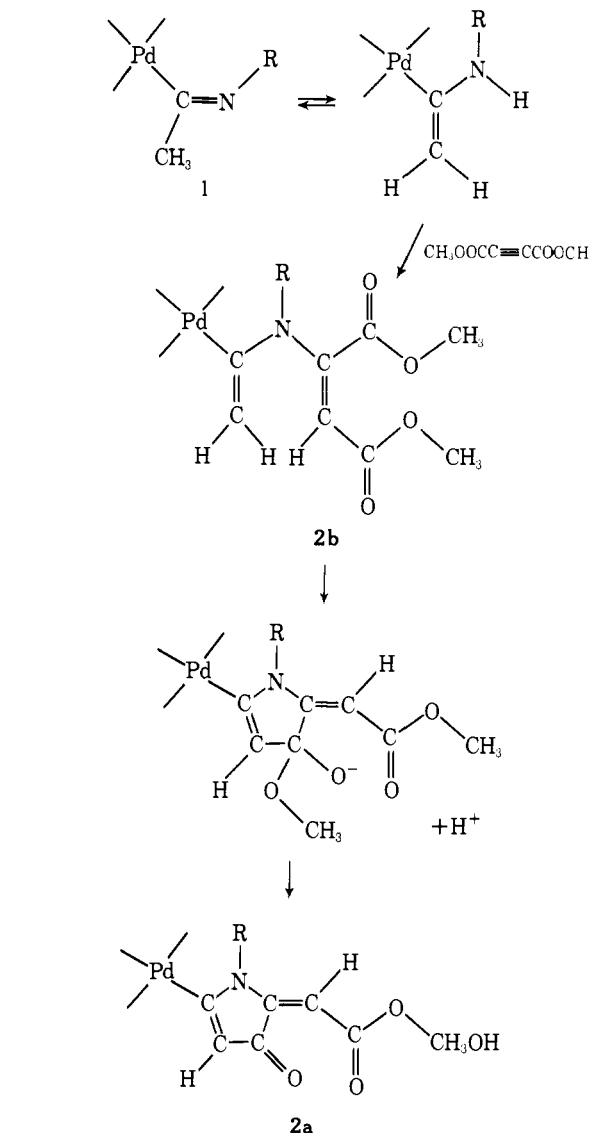
**Table VI.** Selected Intramolecular Bond Distances (Å) and Angles (deg)

Distances			
Pd-C(30)	1.942 (4)	N-C(1)	1.428 (5)
Pd-Cl	2.408 (1)	C(31)-C(32)	1.427 (6)
Pd-P(1)	2.329 (1)	C(32)-O(32)	1.231 (5)
Pd-P(2)	2.318 (1)	C(32)-C(33)	1.500 (7)
P(1)-C(10)	1.825 (5)	C(33)-N	1.392 (6)
P(1)-C(12)	1.816 (6)	C(33)-C(34)	1.336 (6)
P(1)-C(14)	1.826 (5)	C(34)-C(35)	1.518 (8)
P(2)-C(20)	1.809 (7)	C(35)-O(35)	1.195 (7)
P(2)-C(24)	1.830 (8)	C(35)-O(36)	1.343 (8)
C(30)-C(31)	1.384 (6)	O(36)-C(36)	1.418 (8)
C(30)-N	1.409 (5)		
Angles			
P(1)-Pd-P(2)	170.1 (1)	Pd-C(30)-C(31)	127.2 (3)
C(30)-Pd-Cl	177.9 (1)	C(30)-C(31)-C(32)	110.8 (4)
C(30)-Pd-P(1)	91.7 (1)	C(31)-C(32)-C(33)	104.3 (4)
C(30)-Pd-P(2)	90.5 (1)	C(31)-C(32)-O(32)	131.2 (5)
Cl-Pd-P(1)	87.6 (1)	C(33)-C(32)-O(32)	124.4 (4)
Cl-Pd-P(2)	89.8 (1)	C(32)-C(33)-N	106.9 (3)
Pd-P(1)-C(10)	121.9 (2)	C(32)-C(33)-C(34)	125.3 (5)
Pd-P(1)-C(12)	112.7 (2)	N-C(33)-C(34)	127.5 (5)
Pd-P(1)-C(14)	107.4 (2)	C(33)-N-C(30)	110.0 (4)
Pd-P(2)-C(20)	117.9 (2)	C(33)-N-C(1)	125.1 (4)
Pd-P(2)-C(24)	108.5 (2)	C(30)-N-C(1)	124.4 (3)
C(10)-P(1)-C(12)	105.4 (3)	C(33)-C(34)-C(35)	120.5 (5)
C(10)-P(1)-C(14)	102.9 (3)	C(34)-C(35)-O(35)	124.5 (8)
C(12)-P(1)-C(14)	105.1 (3)	C(34)-C(35)-O(36)	109.7 (5)
C(20)-P(2)-C(24)	105.9 (4)	O(35)-C(35)-O(36)	125.8 (7)
C(31)-C(30)-N	108.0 (4)	C(35)-O(36)-C(36)	114.1 (6)
Pd-C(30)-N	124.8 (3)		

**Figure 2.** Interatomic dimensions in the cyclic pyrrole ligand.

a chloride ligand and a pyrrole derivative, bonded to the metal via a carbon atom (Figure 1).

The knowledge of this structure permits the assignment of the resonances of the <sup>13</sup>C spectrum. Signals at 7.8 and 14.5 ppm could be assigned to the phosphine carbons, at 20.7, 124, 130, 136, and 141 ppm to the *p*-tolyl carbons, at 52 ppm to a methoxy carbon, at 100 and 110 ppm to two olefinic carbons each of which are bonded to one hydrogen, at 142 ppm to one olefinic carbon, and at 166 ppm to an ester carbonyl carbon.<sup>20</sup> The resonance at 182 ppm can be assigned to the carbon atom



## Results and Discussion

The carbon-bonded metal imine complex *trans*-Pd(Cl)-[C(CH<sub>3</sub>)=N(R)](PEt<sub>3</sub>)<sub>2</sub> (**1**) reacts readily with dimethyl acetylenedicarboxylate in chloroform to eliminate methanol and form two new crystalline products **2a** and **3**. The formation of **2a** proceeds through an intermediate **2** which is detectable by <sup>1</sup>H NMR spectroscopy and which has not lost methanol. The spectroscopic data given in Tables VIII and IX for **2a** and **3** were not sufficient to identify their structures. However, these data, which were very similar for the two compounds, suggested the presence of a heterocyclic ring attached to the metal via a carbon atom.

Accordingly an x-ray crystallographic analysis of **2a** was undertaken. This study showed that the structure of **2a** consists of a square planar arrangement about the Pd atom with *trans* triethylphosphine ligands. Occupying the other two sites are

Table VIII

Complex	Infrared frequencies	<sup>1</sup> H NMR signals, ppm	<sup>19</sup> F NMR signals, ppm
3	$\nu(\text{C}=\text{O})$ 1716 (s)	Me (tolyl) 2.34	
	$\nu(\text{C}=\text{O})$ 1664 (vs)	OMe 3.19	
	$\nu(\text{C}=\text{C})$ 1621 (vs)	$\text{C}=\text{C}-\text{H}$ 5.53	
2a	$\nu(\text{C}=\text{O})$ 1728 (s)	$\text{C}=\text{C}-\text{H}$ 5.85	
	$\nu(\text{C}=\text{O})$ 1667 (vs)	Me (tolyl) 2.34	
	$\nu(\text{C}=\text{C})$ 1631 (vs)	OMe 3.82	
2	$\nu(\text{C}=\text{O})$ 1731 (s)	$\text{C}=\text{C}-\text{H}$ 5.43	
	$\nu(\text{C}=\text{O})$ 1682 (s)	$\text{C}=\text{C}-\text{H}$ 5.65	
		Me (tolyl) 2.35	
		OMe 3.43	
		OMe 3.60	
		$\text{C}=\text{C}-\text{H}$ 4.03, 4.25	
4		$\text{C}=\text{C}-\text{H}$ 7.73	
		Me (tolyl) 2.25	$\text{CF}_3^2$ 57.61, 57.68
		$\text{C}=\text{C}-\text{H}$ 4.15, 4.42	$\text{CF}_3^1$ 58.35, 58.45
5a		$\text{C}=\text{C}-\text{H}$ 6.32 $J_{\text{F}^1\text{H}} = 8.75$ Hz	
		Me (tolyl) 2.38	
		OMe 3.76	
		OMe 3.84	
		PdC (Me) 3.03 $J_{\text{PH}} = 2.0$ Hz	
5b		$\text{C}=\text{C}-\text{H}$ 7.16	
		Me (tolyl) 2.30	
		OMe 3.69	
		OMe 3.78	
		PdC (Me) 2.79 $J_{\text{PH}} = 2.0$ Hz	
	$\text{C}=\text{C}-\text{H}$ 7.16		

bonded to the palladium atom and the resonance at 205 ppm to the oxo carbon atom. These latter two resonances are very similar in magnitude to the values for the  $\beta$  carbon (179 ppm) and the carbonyl carbon atom (208 ppm) of 1-methylcyclopenten-2-one.<sup>21</sup>

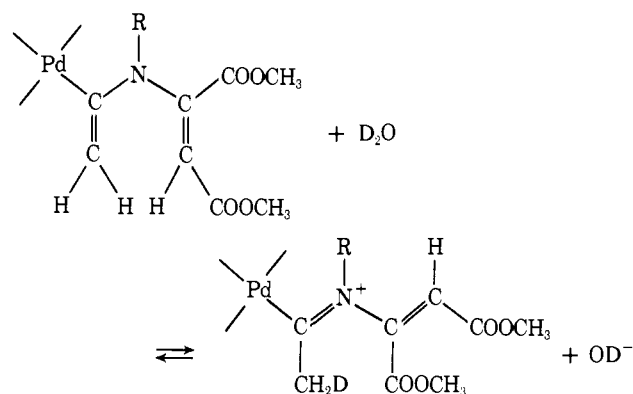
The simplest mechanism to account for this product is one which involves the enamine form of the carbon bonded metal imine as shown in Scheme I. The N-H fragment of the enamine can add across the triple bond of the acetylene to give an intermediate **2b**.<sup>22</sup> The original double bond of the enamine can now act as a nucleophile and attack one of the carbonyl carbon atoms to eliminate methanol to form **2a**.

Support for this mechanism is found in four experimental observations.

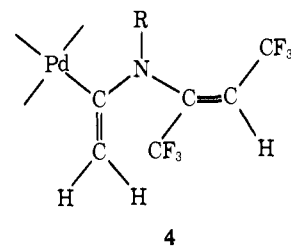
Firstly, the protons of the methyl group on the imine exchange with D<sub>2</sub>O to give the deuterated species. This strongly implies the existence of the ketimine-enamine tautomerism. Secondly, the <sup>1</sup>H NMR and infrared data of the observed intermediate **2** (Table VIII) are consistent with the proposed intermediate **2b**. Furthermore, the proposed intermediate possesses two protons which should be readily exchangeable with the deuterium of D<sub>2</sub>O through a mechanism involving a quaternary nitrogen atom (Scheme II). The observed intermediate **2** also has two exchangeable hydrogens.

Thirdly, the starting imine reacts with hexafluoro-2-butyne to give a rather unstable product **4** which can be characterized by its <sup>1</sup>H and <sup>19</sup>F NMR spectra (Table VIII). The <sup>1</sup>H NMR spectrum has peaks at 1–3 ppm due to mutually trans phosphine ligands, at 2.3 and 7.0 ppm due to a *p*-tolyl group, as well as three olefinic protons at 4.15, 4.42, and 6.32 ppm, the latter being a quartet due to coupling to only one CF<sub>3</sub> group. The two high-field protons exchange with D<sub>2</sub>O. The <sup>19</sup>F NMR spectrum consists of two sets of resonances in the ratio of 1:4. The more intense set is comprised of two equally intense signals,

Scheme II



a singlet of 57.51 ppm and a doublet at 58.35 ppm. The weaker set is also comprised of two equally intense signals, a singlet at 57.68 ppm and a doublet at 58.45 ppm. Each of these sets of signals is consistent with a structure similar to that of the proposed intermediate **2b** except that the addition of enamine has been trans across the triple bond to form **4**.



The presence of two sets of signals in the <sup>19</sup>F NMR spectrum can be explained if there is restricted rotation about either the

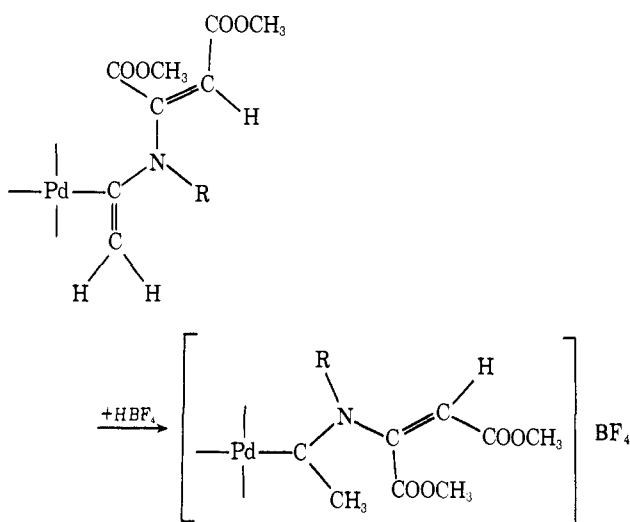
Table IX. <sup>13</sup>C NMR Data for Compounds **3** and **2a**

Carbon	δ ppm <b>3</b>		δ ppm <b>2a</b>
PCCH <sub>3</sub>	7.8		7.6
PCH <sub>2</sub>	14.6	←J <sub>PC</sub> = 13.5 Hz→	14.4
CH <sub>3</sub> ( <i>p</i> -tolyl)	20.8		20.6
O-CH <sub>3</sub>	51.3		52.0
C=C-H	98.5		101.7
C=C-H	110.5		109.6
Tolyl (ortho)	123.7		124.2
(meta)	129.5		129.7
(para)	135.9		136.5
C <sub>1</sub>	141.4		138.2
C=C	141.8		141.7
O=C-O	165.6		166.8
Pd-C=C	184.4		181.4
O=C	205.1	J <sub>NC</sub> = 6.3 Hz	202.2

vinyl carbon-nitrogen bond or about the nitrogen-carbon bond of the carbon bonded to the palladium atom.<sup>23</sup> Either of these situations would produce two geometrical isomers. The <sup>1</sup>H chemical shifts of the vinylic protons are not sensitive enough to determine such a difference, although it appears that the <sup>19</sup>F chemical shifts are.

Fourthly, if a solution of the intermediate **2** in CDCl<sub>3</sub> is treated with HBF<sub>4</sub>, the <sup>1</sup>H NMR spectrum changes. The original resonances of **2** are replaced by two new sets of signals **5a** and **5b** in the ratio of 4:1. The basic pattern is the same for each of these new sets as for the original set belonging to **2**, except that the signals for the two high-field olefinic protons are absent (Table VIII). Instead, for each set a peak corresponding to 3 protons at around 2.8 ppm is observed which is a 1:2:1 triplet due to coupling to the mutually trans phosphine atoms. This result is consistent with the proposed structure of the intermediate **2**. A proton of the acid adds to the geminal carbon of the olefin to form a carbene, Scheme III.

Scheme III



Two isomers are possible due to restricted rotation about the C-N bond of the carbene ligand.<sup>23</sup> It is also interesting to note that the similar platinum carbon bonded imine, *trans*-Pt(Cl)[C(CH<sub>3</sub>):N(R)](PMe<sub>2</sub>Ph)<sub>2</sub>, reacts with DMA to give analogous products. The methyl protons of this platinum-imine also exchange in D<sub>2</sub>O. However, the imine *trans*-Pt(Cl)-[C(CH<sub>3</sub>):NR](PPh<sub>3</sub>)<sub>2</sub> does not react with DMA and the

methyl protons do not exchange in D<sub>2</sub>O. This implies that a necessary criterion for the reaction of metal carbon-bonded imines with activated acetylenes to form heterocycles is the presence of exchangeable α protons which allow the presence of a ketimine-enamine tautomerism to form the reactive enamine tautomer.

The identity of the minor species **3** is not certain, but in view of its very similar spectroscopic properties to those of **2a** and the observation that if a solution of pure **3** or **2a** in CDCl<sub>3</sub> is left to stand for a few days, small amounts of the other product are formed, it seems that it has the structure analogous to **2a** but the *Z* configuration about the exocyclic double bond. The same mechanism for the formation of **3** as for **2a** is possible, except that the addition of the enamine across the triple bond has occurred in a *trans* fashion as was observed for the case of hexafluoro-2-butyne.

**Acknowledgments.** We wish to thank the National Research Council of Canada for financial support of this work and C.R.C.M. is grateful for the award of an O.G.S. Scholarship. We also thank Dr. J. B. Stothers for obtaining the <sup>13</sup>C NMR spectra and Dr. E. W. Warnhoff for helpful discussions.

**Supplementary Material Available:** Table IV, calculated hydrogen atom parameters, Table V, observed and calculated structure amplitudes, and Table VII, weighted least-squares planes (36 pages). Ordering information is given on any current masthead page.

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