Unexpected Rearrangement of Palladacycles Derived from 2-Oxopropionaldehyde Phenylhydrazones. Synthesis of Palladium Complexes Containing a Bianionic Tridentate C, N, O Ligand

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The synthesis of bidentate monoanionic C−N derivatives of 2-oxopropionaldehyde phenylhydrazones, compounds **3**, [Pd(2-{NH−N=CH−C(O)Me}-3-RC$_6$H$_3$)Cl(PPh$_3$)] is described. The structure of **3b** (R = Me) was determined by X-ray diffraction. The bond distances and angles are similar to those reported for related metallacycles. The distance N(2)···O(1) (2.583(7) Å) shows the existence of a strong intramolecular hydrogen bond between the NH and COCH$_3$ groups. The C(9)−O(1) (1.224(9) Å), C(8)−C(9) (1.46(1) Å), C(8)−N(1) (1.307(8) Å), and N1−N2 (1.325(7) Å) bond lengths indicate that **3b** exists mainly in the keto−hydrazo form. The action of NaMeO on **3** in MeOH afforded deep violet compounds which did not contain chlorine atoms. The analytical data, the infrared spectra, and the NMR studies, including ^{1}H−^{1}H COSY and NOESY experiments, showed that deprotonation of the N−H bond took place to give **4**, [Pd(2-{N=N−CH=C(O)Me}-3-RC$_6$H$_3$)(PPh$_3$)] by means of an unexpected hydrazo−azo tautomerization. The structure of **4c** (R = Et) was determined by X-ray diffraction. The C(10)−O(1) (1.32(1) Å), C(10)−C(9) (1.37(1) Å), C(9)−N(2) (1.33(1) Å), and N(1)−N(2) (1.25(1) Å) bond lengths indicate that **4c** exists mainly in the azo−enol form. The action of HCl (0.5 N) on the tridentate metallacycles **4** regenerated the bidentate derivatives **3**, showing the reversibility of this process.

Introduction

In recent years, many multidentate ligands have been developed in order to obtain new organometallic complexes. Among these, the palladium complexes with polydentate ligands are especially interesting because of their reactivity and catalytic activity. It has recently been shown that palladacycles with anionic P−C or N−C ligands are efficient catalysts for a range of processes including the Heck olefination of chloro and bromoarenes,[1] aryl coupling reactions,[2] telomerization of butadiene with alcohols,[3] and asymmetric cyclopropanation.[4]

Organopalladium compounds containing tridentate ligands have been extensively studied,[5] but only a few of these species are reported to contain a bianionic tridentate ligand.[6] In this paper, we describe the synthesis of palladacycles containing the bianionic tridentate C−N−O ligand from cyclopalladated hydrazones by deprotonation of the N−H bond and tautomerization of the metalated ligand.

The equilibrium between the hydrazo−keto and azo−enol forms of organic molecules, containing the HN−N=C−C=O fragment, is well-known,[7] and it has been shown that the presence of a specific organic fragment may shift the equilibrium in favor of one of the two tautomeric forms.[8] In contrast, to the best of our knowledgement, this tautomerization process has not been studied in organometallic derivatives in which the

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[1] Hermann, W. A.; Brossmer, C.; Öfele, K.; Reisinger, C.; Priermeier, T.; Beller, M.; Fischer, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1844.

[2] (a) Beller, M.; Fischer, H.; Hermann, W. A.; Öfele, K.; Brossmer, C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1848. (b) Hermann, W. A.; Reisinger, C.; Öfele, K.; Brossmer, C.; Beller, M.; Fischer, H. *J. Mol. Catal.* **1996**, *108*, 51.

[3] Camargo, M.; Dani, P.; Dupont, J.; de Souza, R. F.; Pfeffer, M.; Tkatchenko, I. *J. Mol. Catal.* **1996**, *109*, 127

[4] Navarro, R.; Urriolabeitia, E. P.; Cativiela, C.; Diaz de Villegas, M. D.; López, M. P.; Alonso, E. *J. Mol. Catal.* **1996**, *105*, 111.

[5] For a review on tridentate N-donor ligands, see: van Kotten G. *Pure Appl. Chem.* **1989**, *61*, 1681. For specific and recent palladium examples, see: (a) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831. (b) Garcia-Herbosa, G.; Muñoz, A.; Miguel, D.; Garcia-Granda, S. *Organometallics* **1994**, *13***,** 1775 (c) Cross, R. J.; Kennedy, A. R.; Muir, K. W. *J. Organomet. Chem.* **1995**, *487*, 227. (d) Kraatz, H.; Milstein, D. *J. Organomet. Chem.* **1995**, *488*, 223. (e) Chan, C.; Mingos, D. M. P.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Chem. Commun.* **1996**, 81. (f) Perera, S. D.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1995**, 641.

[6] For some examples of bianionic tridentate ligands, see: (a) Hedden, D.; Roundhill, D. M.; Fultz, W. C.; Reingold, A. L. *Organometallics* **1986**, *5*, 336. (b) Mahapatra, A. K.; Bandyopadhyay, D.; Bandyopadhyay, P.; Chakravorty, D. *Inorg. Chem.* **1986**, *25*, 2214. (c) Yang, H.; Khan, M. A.; Nicholas, K. M. *J. Chem. Soc. Chem. Commun.* **1992**, 210. (d) Yoneda, A.; Newkome, G. R.; Theriot, K. J. *J. Organomet. Chem.* **1991**, *401*, 217. (e) Yoneda, A.; Hakushi, T.; Newkome, G. R.; Fronczek, F. R. *Organometallics* **1994**, *13*, 4912. (f) Albert, J.; Granell, J.; Sales, J.; Font-Bardia, M.; Solans, X. *Organometallics* **1995**, *14*, 1393.

[7] Cox, R. C.; Buncel, E. In *The Chemistry of the Hydrazo, Azo and Azoxy Groups*; Patai, S., Ed; Wiley: Chichester, U.K. 1970; pp 838−851 and references therein.

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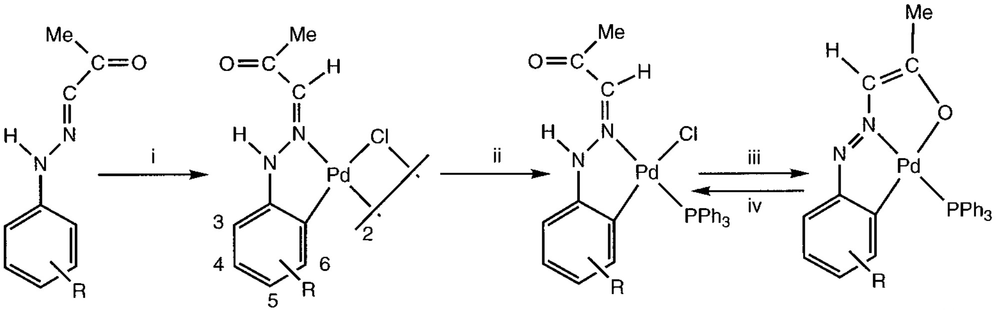
Scheme 1[a]



1a, R = H
1b, R = 2-Me
1c, R = 2-Et

2a, R = H
2b, R = 3-Me
2c, R = 3-Et

3a, R = H
3b, R = 3-Me
3c, R = 3-Et

4a, R = H
4b, R = 3-Me
4c, R = 3-Et

[a] (i) $PdCl_2$, EtOH, 3 days, room temperature. (ii) PPh_3, acetone, 30 min, room temperature. (iii) NaMeO, MeOH, 2 h, room temperature. (iv) 0.5 N HCl, room temperature, 5 min.

presence of a transition metal atom, strongly bonded to the organic ligand and with available coordination positions, can influence the equilibrium position.

Results and Discussion

The action of $PdCl_2$ on hydrazones **1**, derived from 2-oxopropionaldehyde, leads to the cyclopalladated complexes **2** in high yield (80–90%). The dinuclear compounds obtained react with PPh_3 affording the cyclometalated complexes [PdCl(C–N)PPh_3] **3** (see Scheme 1). The new compounds obtained were characterized by elemental analysis, IR spectra, and ^1H and ^{31}P NMR spectra.[9] In several cases, COSY experiments were carried out to complete the NMR studies. The aromatic protons of the palladated ring in **3** appear high-field-shifted in the ^1H NMR spectra, indicating a *cis* arrangement of the phosphine and the metalated carbon atom.[6f] The signal assigned to the methinic proton in the cyclometalated compounds is low-field-shifted in relation to the free ligand. This shift can be explained by the paramagnetic anisotropy of the palladium atom and indicates that the metalated phenyl ring and the $COCH_3$ group adopt a *cis* disposition around the C=N bond, thus an *E*–*Z* isomerization occurs during the cyclometalation process,[10] as reported for similar cyclopalladated derivatives from imines.[11] The signal assigned to the NH proton in the ^1H NMR spectra appears strongly shifted to low fields (δ = 13.9–14.5 ppm), indicating a strong hydrogen bond between the CH_3CO and the NH groups.[8,12] The crystal structure of **3b** has been determined (Figure 1). Crystallographic data and selected bond lengths and angles are listed in Tables 1, 2, and 3. The crystal structure consists of discrete molecules separated by van der Waals distances. The bond distances and angles are similar to those reported for related metallacycles.[6f,11] The palladium atom is in a slightly distorted square-planar environment coordinated to phosphorus, carbon, chloride, and the iminic nitrogen atom (the largest deviation from the mean plane determined by the five atoms is 0.14 Å for N(1)). The iminic nitrogen and the phosphine molecule adopt a *trans* arrangement. The metalated phenyl ring and the $COCH_3$ groups adopt a *cis* disposition around the C=N bond. The distance N(2)···O(1) (2.583(7) Å) confirms a strong intramolecular hydrogen bond between the NH and $COCH_3$ groups, similar to those found for related free hydrazones. The C(9)–O(1) (1.224(9) Å), C(8)–C(9) (1.46(1) Å), C(8)–N(1) (1.307(8) Å), and N1–N2 (1.325(7) Å) bond lengths indicate that **3b** exists mainly in the keto–hydrazo form.[8,12]

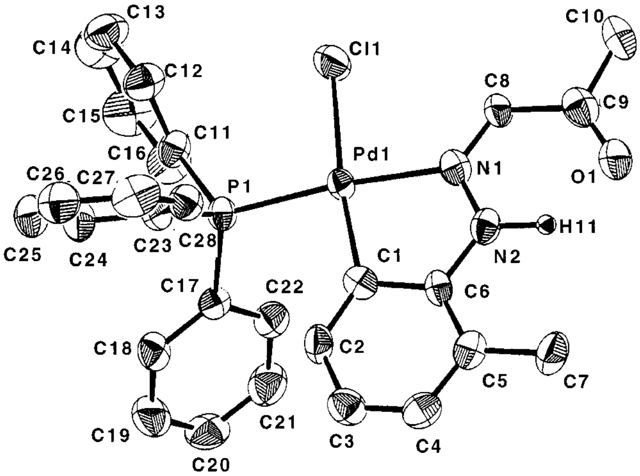


Figure 1. Molecular structure of **3b**.

The action of NaMeO on **3** in MeOH affords deep violet compounds which do not contain chlorine atoms. The analytical data, the infrared spectra (absence of the strong bands of the C=O and C=N bonds and the existence of a weak band assigned to the N=N group), and the NMR studies, including ^1H–^1H COSY and NOESY experiments, show that deprotonation of the N–H bond takes place to give **4** by means of an unexpected hydrazo–azo tautomerization.

The crystal structure of **4c** has been determined (Figure 2). Crystallographic data and selected bond

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(8) (a) Connor, J. A.; Kennedy, R. J.; Dawes, H. M.; Hursthouse, M. B.; Walker, N. P. C. *J. Chem. Soc., Perkin Trans.* **1990**, 203. (b) Olivieri, A. C.; Wilson, R. B.; Paul, I. C.; Curtin, D. Y. *J. Am. Chem. Soc.* **1989**, *111*, 5525.

(9) Due to the insolubility of **2**, their NMR spectra were recorded in the presence of pyridine-d_5, which affords the mononuclear complexes [PdCl(C–N)(py-d_5)].

(10) The coordination of palladium to methinic nitrogen changes the order of precedence order, and strictly speaking, the ligand is in the *E*-form in **2** and **3**.

(11) Albert, J.; Gómez, M.; Granell, J.; Sales, J.; Solans, X. *Organometallics* **1990**, *9*, 1405.

(12) The model RAHB (resonance-assisted hydrogen bonding) has been used to interpret the intramolecular hydrogen bond in the O=C–C=N–NH fragments, see: (a) Bertolasi, V.; Ferreti, V; Gilli, G.; Issa, Y. M.; Sherif, O. E. *J. Chem. Soc., Perkin Trans.* **1993**, 2223. (b) Bertolasi, V.; Nanni, L.; Gilli, P.; Ferreti, V.; Gilli, G.; Issa, Y. M.; Sherif, O. E. *New J. Chem.* **1994**, *18*, 251 and references therein.

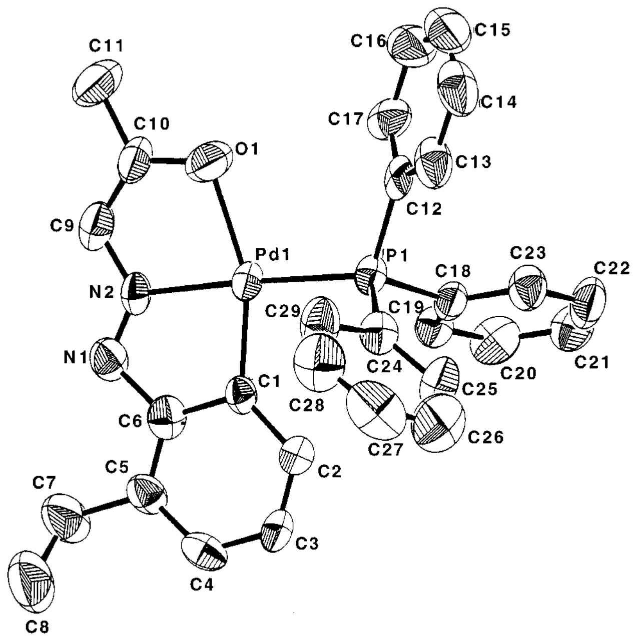

Figure 2. Molecular structure of **4c**.

Table 1. Summary of Crystal Data Collection and Structure Analysis

compound	**4c**	**3b**
formula	$C_{29}H_{27}N_2OPPd$	$C_{28}H_{26}ClN_2OPPd$
fw	556.92	579.35
cryst size (mm)	0.14 × 0.07 × 0.40	0.34 × 0.14 × 0.17
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
cell param	$a = 15.633(4)$ Å $b = 8.602(3)$ Å $c = 18.809(3)$ Å $\beta = 96.66(2)°$	$a = 18.082(5)$ Å $b = 9.184(2)$ Å $c = 18.752(6)$ Å $\beta = 114.66(2)°$
volume	2512(1) Å^3	2830(1) Å^3
Z	4	4
ρcalcd	1.472 g cm^{-3}	1.360 g cm^{-3}
λ(Mo Kα)	0.710 69 Å	0.710 69 Å
μ(Mo Kα)	8.14 cm^{-1}	8.18 cm^{-1}
F(000)	1136	1176
transmission factors	0.89−1.00	no correction
decay	−1.66%	−7.80%
temperature	290(1) K	290(1) K
scan speed (ω)	8° min^{-1}	4° min^{-1}
2θ interval	$5° < 2\theta < 50°$	$5° < 2\theta < 50°$
no. of measd reflns	4066	4582
no. of unique reflns	3936 ($R_{int} = 0.090$)	4447 ($R_{int} = 0.089$)
no. of obsd reflns ($I > 3\sigma_I$)	2172	3161
no. of params	307	335
refln/param ratio	7.07	9.44
R^a	0.048	0.047
R_w ($w = \sigma_F^{-2}$)^b	0.055	0.057
max Δ/σ in final cycle	1.06	1.37
gof	1.48	1.75

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

Table 2. Selected Bond Lengths (Å) for 3b

Pd(1)−Cl(1)	2.360(2)	N(1)−N(2)	1.325(7)
Pd(1)−P(1)	2.257(2)	N(1)−C(8)	1.307(8)
Pd(1)−N(1)	2.098(6)	N(2)−C(6)	1.402(8)
Pd(1)−C(1)	2.004(7)	C(8)−C(9)	1.46(1)
O(1)−C(9)	1.224(9)	C(9)−C(10)	1.49(1)

Table 3. Selected Bond Angles (deg) for 3b

Cl(1)−Pd(1)−P(1)	93.32(7)	N(1)−N(2)−C(6)	117.5(5)
Cl−Pd(1)−N(1)	91.1(2)	N(1)−C(8)−C(9)	124.5
P(1)−Pd(1)−C(1)	93.8(2)	O(1)−C(9)−C(8)	122.1(7)
N(1)−Pd(1)−C(1)	81.9(3)	O(1)−C(9)−C(10)	121.7(7)
N(2)−C(6)−C(5)	118.3(6)	C(8)−C(9)−C(10)	116.2(7)
N(1)−N(2)−C(8)	119.3(6)		

Table 4. Selected Bond Lengths (Å) for 4c

Pd(1)−P(1)	2.262(2)	N(1)−N(2)	1.25(1)
Pd(1)−O(1)	2.166(7)	N(1)−C(6)	1.41(1)
Pd(1)−N(2)	2.011(7)	N(2)−C(9)	1.33(1)
Pd(1)−C(1)	1.975(9)	C(9)−C(10)	1.37(1)
O(1)−C(10)	1.32(1)	C(10)−C(11)	1.47(1)

Table 5. Selected Bond Angles (deg) for 4c

Pd(1)-Pd(1)-O(1)	103.3(2)	N(1)-C(6)-C(5)	118.8(8)
O(1)-Pd(1)-N(2)	79.9(3)	N(2)-C(9)-C(10)	118.4(9)
P(1)-Pd(1)-C(1)	97.9(2)	O(1)-C(10)-C(9)	121.4(9)
N(2)-Pd(1)-C(1)	78.8(3)	O(1)-C(10)-C(11)	116.1(1)
N(2)-N(1)-C(6)	110.9(7)	C(9)-C(10)-C(11)	123.1(1)
N(1)-N(2)-C(9)	126.2(8)		

lengths and angles are listed in Tables 1, 4, and 5. The crystal structure consists of discrete molecules separated by van der Waals distances. The palladium atom is in a square-planar environment coordinated to phosphorus, carbon, oxygen, and the iminic nitrogen atom, (the largest deviation from the mean plane determined by the five atoms is 0.076 Å for N(2)). The C(10)−O(1) (1.32(1) Å), C(10)−C(9) (1.37(1) Å), C(9)−N(2) (1.33(1) Å), and N(1)−N(2) (1.25(1) Å) bond lengths indicate that **4c** exists mainly in the azo−enol form.[8,12]

When the deprotonation reaction was performed with benzylamine in toluene, a white compound precipitated, which was identified as benzylamine hydrochloride, and compounds **4** and a small quantity of the starting materials **3** were obtained from the solution. The action of HCl (0.5 N) on the tridentate metallacycles **4** regenerates the bidentate derivatives **3**, showing the reversibility of this process.

The results here described contrasts with those previously reported by Espinet *et al.*[13] which have shown that the deprotonation of cyclopalladated hydrazone derivatives affords binuclear amido complexes. The main difference between both types of hydrazones relies in the presence, in our case, of the $COCH_3$ group which permits the hydrazone to act as a tridentate ligand by the tautomerization reaction here described.

The deprotonation of the N−H bond, leading to a highly conjugated anion which can adopt the "azobenzene-like" resonance structure, has recently been proposed to explain the metalation of aromatic hydrazones.[5b] Here, for the first time, we show the existence of this metalated azobenzene derivative and the reversibility of the rearrangement between the hydrazo and azo tautomers in palladium metallacyles, which produces a reversible change in the coordination mode of the ligand from monoanionic bidentate C,N to bianionic tridentate C,N,O.

Experimental Section

^{1}H NMR spectra at 200 MHz and 500 MHz and ^{31}P{^{1}H} NMR spectra at 101.26 MHz were recorded, respectively, on Varian Gemini 200, Varian VXR 500, and Bruker DRX 250 spectrometers. Chemical shifts (in ppm) were measured relative to $SiMe_4$ for the ^{1}H NMR and to 85% H_3PO_4 for the ^{31}P NMR studies. The solvents used were $CDCl_3$ in the ^{1}H NMR and $CHCl_3$ in the ^{31}P NMR studies. Microanalyses were performed at the Institut de Química Bio-Orgànica de Barcelona and the Serveis Científico-Tècnics de la Universitat de Barcelona.

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(13) Espinet, P.; Garcia, G.; Herrero, F. J.; Jeannin, Y.; Philoche-Levisalles, M. *Inorg. Chem.* **1989**, *28*, 4207.

Crystallographic Studies. A crystal was selected and mounted on a Rigaku AFC6S diffractometer. Unit cell parameters were determined from automatic centering of 25 reflections ($12.5 \le \theta \le 15°$) and refined by the least-squares method. Intensities were collected with graphite-monochromated Mo Kα radiation, using the ω-scan technique. Reflections having $I \ge 3\sigma(I)$ were used for structure resolution. All calculations for data reduction, structure solution, and refinement were carried out using the TEXSAN software system.[14] The structures were solved by Patterson synthesis and refined by the full-matrix least-squares method. Hydrogen atoms were included in idealized positions. Crystal parameters, data collection details, and results of the refinements are summarized in Table 1.

Materials and Syntheses. All chemicals and solvents were commercial grade and used as received, except ethanol, chloroform, methanol, and acetone which were dried over $CaCl_2$ and distilled before use. Hydrazones were obtained according to procedures described elsewhere.[15] X-ray quality crystals were obtained by slow evaporation (at room temperature *ca.* 20 °C) of a saturated $CHCl_3$ solution layered with MeOH.

Compounds 2. A stirred suspension of $PdCl_2$ (1.69 mmol, 0.3 g) in ethanol (30 cm^3) was treated with the corresponding hydrazone (1.69 mmol) for 3 days at room temperature. The solid obtained was filtered, washed with ethanol (2 × 15 cm^3), and dried in vacuo to afford **2** as orange or brown solids. Characterization data: **2a** yield 445 mg (87%). Anal. Calcd (found) for $C_{18}H_{18}N_4O_2Cl_2Pd_2$: C, 35.67 (35.8); H, 2.99 (3.0); N, 9.24 (9.2). ^{1}H NMR **(2a** + py-d_5): δ 13.96 (s, 1H, *NH*), 8.02 (s, 1H, *H*C=N), 7.00 (td J_{HH} = 7.5, 1.0 Hz, 1H, H_4), 6.70 (dd, J_{HH} = 8.0, 1.0 Hz, 1H, H_3), 6.12 (d, J_{HH} = 8.0 Hz, 1H, H_6), 2.36 (s, 3H, CH_3CO). **2b:** yield 487 mg (91%). Anal. Calcd (found) for $C_{20}H_{22}N_4O_2Cl_2Pd_2$: C, 37.88 (38.2); H, 3.50 (3.4); N, 8.84 (8.8). ^{1}H NMR (**2b** + py-d_5): δ 14.14 (s, 1H, *NH*), 8.02 (s, 1H, *H*C=N), 6.70 (d, J_{HH} = 7.5 Hz, 1H, H_4) , 6.46 (t, J_{HH} = 7.5 Hz, 1H, H_5), 5.84 (d, J_{HH} = 8.0 Hz, 1H, H_6), 2.24 (s, 3H, CH_3CO), 2.15 (s, 3H, CH_3). **2c**: yield 466 mg (83%). Anal. Calcd (found) for $C_{22}H_{26}N_4O_2Cl_2Pd_2$: C, 40.00 (39.9); H, 3.97 (3.8); N, 8.46 (8.4). ^{1}H NMR (**2c** + py-d_5): δ 14.33 (s, 1H, *NH*), 8.14 (s, 1H, *H*C=N), 6.85 (dd, J_{HH} = 7.5, 0.5 Hz, 1H, H_4), 6.59 (t, J_{HH} = 7.5 Hz, 1H, H_5), 5.92 (dd, J_{HH} = 7.5, 1.0 Hz, 1H, H_6), 2.55 (q, J_{HH} = 7.5 Hz, 2H, CH_2CH$_3$), 2.31 (s, 3H, CH_3CO), 1.20 (t, J_{HH} = 7.5 Hz, 3H, CH_3CH$_2$).

Compounds 3. A stirred suspension of **2** (0.3 mmol) was treated with PPh_3 (0.6 mmol, 0.157 g) in acetone (30 cm^3) for 30 min at room temperature and then filtered. The filtrate was concentrated in vacuo, and the deep orange solid obtained after addition of ether was recrystallized from chloroform−ether to obtain **3**. Characterization data: **3a** yield 361 mg (97%). Anal. Calcd (found) for $C_{27}H_{24}N_2OClPPd$: C, 57.36 (57.3); H, 4.28 (4.4); N, 4.95 (4.9).^{1}H NMR: δ 14.20 (d, J_{HP} = 3.0 Hz, 1H, *NH*), 8.16 (d, J_{HP} = 3.5 Hz, 1H, *H*C=N), 7.76−7.34 (br m, 15H, PPh_3), 6.85 (td, J_{HH} = 7.0, 1.0 Hz, 1H, H_4), 6.72 (dd, J_{HH} = 7.5, 1.0 Hz, 1H, H_3), 6.30 (td, J_{HH} = 7.0, 1.0 Hz, 1H, H_5), 6.22 (td, J_{HH} = 7.5 Hz, J_{HP} = 1.0 Hz, 1H, H_6), 2.37 (s, 3H, CH_3CO). ^{31}P NMR: δ 43.83 ppm. **3b**: yield 365 mg (78%). Anal. Calcd (found) for $C_{28}H_{26}N_2OClPPd$: C, 58.05 (57.8); H, 4.53 (4.5); N, 4.84 (4.8).^{1}H NMR: δ 14.39 (d, J_{HP} = 3.5 Hz, 1H, *NH*), 8.19 (d, J_{HP} = 3.5 Hz, 1H, *H*C=N), 7.59−7.34 (br m, 15H, PPh_3), 6.68 (t, J_{HH} = 7.5 Hz, 1H, H_5), 6.16 (m, 2H, H_4, H_6), 2.37 (s, 3H, CH_3CO), 2.28 (s, 3H, CH_3). ^{31}P NMR: δ 44.28 ppm. **3c**: yield 322 mg (93%). Anal. Calcd (found) for $C_{29}H_{28}N_2OClPPd$: C, 57.70 (57.9); H, 4.76 (4.7); N, 4.73 (4.6). ^{1}H NMR: δ 14.54 (d, J_{HP} = 2.0 Hz, 1H, *NH*), 8.19 (d, J_{HP} = 3.5 Hz, 1H, *H*C=N), 7.76−7.24 (br m, 15H, PPh_3), 6.70 (dd, J_{HH} = 8.5, 1.5 Hz, 1H, H_4), 6.20−6.18 (m, 2H, H_5, H_6), 2.60 (q, 2H, CH_2CH$_3$), 2.37 (s, 3H, CH_3CO), 1.27 (t, 3H, CH_3CH$_2$). ^{31}P NMR: δ 43.14 ppm.

Compounds 4. NaMeO (0.34 mmol, 0.0184 g) was added to a solution of **3** (0.34 mmol) in methanol, and the mixture was stirred under nitrogen for 2 h at room temperature. The solvent was removed in vacuo, and the residue was washed with ether (2 × 10 cm^3) and then dried in vacuo to give a violet solid **4**. Characterization data: **4a** yield 135 mg (72%). Anal. Calcd (found) for $C_{27}H_{23}N_2OPPd$: C, 61.32 (61.1); H, 4.38 (4.4); N, 5.30 (5.3). ^{1}H NMR: δ 7.86−7.37 (br m, 15H, PPh_3), 7.07 (d, J_{HH} = 7.5 Hz, 1H, H_3), 6.77 (t, J_{HH} = 7.0 Hz, 1H, H_5), 6.57 (s, 1H, *H*C=C), 6.14 (t, J_{HH} = 7.5 Hz, 1H, H_4), 5.82 (d, J_{HH} = 7.5 Hz, 1H, H_6), 1.95 (s, 3H, CH_3CO). ^{31}P NMR: δ 32.12 ppm. **4b**: yield 114 mg (61%). Anal. Calcd (found) for $C_{28}H_{25}N_2OPPd$: C, 61.94 (61.8); H, 4.64 (4.8); N, 5.16 (5.2). ^{1}H NMR: δ 7.86−7.37 (br m, 15H, PPh_3), 6.58 (d, J_{HH} = 7.0 Hz, 1H, H_4), 6.52 (s, 1H, *H*C=C), 6.06 (t, J_{HH} = 7.5 Hz, 1H, H_5), 5.68 (d, J_{HH} = 6.8 Hz, 1H, H_6), 2.35 (s, 3H, CH_3), 1.92 (s, 3H, CH_3C−O). ^{31}P NMR: δ 32.63 ppm. **4c**: yield 177 mg (95%). Anal. Calcd (found) for $C_{29}H_{27}N_2OPPd$: C, 62.54 (62.3); H, 4.88 (4.9); N, 5.03 (5.1). ^{1}H NMR: δ 7.86−7.37 (br m, 15H, PPh_3), 6.57 (m, 2H, *H*C=C, H_4), 6.07 (t, J_{HH} = 6.7 Hz, 1H, H_5), 5.67 (d, J_{HH} = 7.5 Hz, 1H, H_6), 2.68 (q, J_{HH} = 7.6 Hz, 2H, CH_2CH$_3$), 1.92 (s, 3H, CH_3C−O), 1.19 (t, J_{HH} = 7.6 Hz, 3H, CH_3CH$_2$). ^{31}P NMR: δ 33.4 ppm.

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Supporting Information Available: Tables of positional parameters, isotropic parameters, intermolecular and intramolecular bond lengths and angles, and anisotropic displacement parameters for **3b** and **4c** (34 pages).

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(14) *TEXSAN*: *Single-Crystal Structure Analysis Software*, version 5.0; Molecular Structure Corp.: The Woodlands, TX, 1989.

(15) González, A. *Synth. Commun.* **1988**, *18*, 1225.