

Nitrogen- vs Carbon-Coordination of the α -Cyano-Stabilized Phosphorus Ylide $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$. X-ray Crystal Structure of $\{\text{Pd}(\text{dmba})[\text{P}(\text{OMe})_3][\text{N}\equiv\text{C}-\text{C}(\text{H})=\text{PPh}_3]\}(\text{ClO}_4)$

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The reaction of the solvated complexes $[\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)(\text{THF})](\text{ClO}_4)$ [$\text{C}\hat{\text{N}} = 2-((\text{dimethylamino})\text{methyl})\text{phenyl}-\text{C}^1, \text{N}$ or dmba , $2-(1-(R)-(\text{dimethylamino})\text{ethyl})\text{phenyl}-\text{C}^1, \text{N}$ or $(R)\text{-dmphea}$; $\text{PR}'_3 = \text{PPh}_3, \text{P}(\text{OMe})_3$] with a stoichiometric amount of $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ (CPPY) (1:1 molar ratio), in THF at low temperature, gives the cationic derivatives $\{\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)[\text{N}\equiv\text{C}-\text{C}(\text{H})=\text{PPh}_3]\}(\text{ClO}_4)$, **4–6**, in which the ylide ligand is N-coordinated to the Pd^{II} center and *trans* to the *ortho*-metalated C_6H_4 group, in an “end-on nitrile” coordination mode that is unprecedented for this ylide. The reaction of $[\text{Pd}(\text{C}\hat{\text{N}})(\text{NCMe})_2](\text{ClO}_4)$ ($\text{C}\hat{\text{N}} = \text{dmba}, (R)\text{-dmphea}$) with $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ (1:2 molar ratio) gives the bis(ylide) complexes $[\text{Pd}(\text{C}\hat{\text{N}})(\text{Ph}_3\text{PCHCN})_2](\text{ClO}_4)$ (**7, 8**) in which one of the ylides is C-coordinated (*trans* to the NMe_2 group) and the other one is N-bonded (and *trans* to the C_6H_4 group). Either by reaction of $[\text{Pd}(\text{C}\hat{\text{N}})(\text{NCMe})_2](\text{ClO}_4)$ with $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ (1:1 molar ratio) or by reaction of the bis(ylide) complexes $[\text{Pd}(\text{C}\hat{\text{N}})(\text{Ph}_3\text{PCHCN})_2](\text{ClO}_4)$ with $[\text{Pd}(\text{C}\hat{\text{N}})(\text{NCMe})_2](\text{ClO}_4)$ (1:1 molar ratio), very insoluble materials of stoichiometry $[\text{Pd}(\text{C}\hat{\text{N}})(\text{Ph}_3\text{PCHCN})(\text{ClO}_4)]$ (**9, 10**) are obtained, which appear to be dinuclear derivatives with the ylide acting as a C,N-bridging group, $[(\text{C}\hat{\text{N}})\text{Pd}(\mu\text{-C}, \text{N}-\text{Ph}_3\text{PCHCN})_2\text{Pd}(\text{C}\hat{\text{N}})](\text{ClO}_4)_2$. At the same time, this ylide is shown to be sufficiently nucleophilic to promote the bridge-splitting of the dinuclear $[\text{Pd}(\mu\text{-Cl})(\text{C}\hat{\text{N}})]_2$ complexes, giving the mononuclear derivatives $[\text{PdCl}(\text{C}\hat{\text{N}})(\text{Ph}_3\text{PCHCN})]$ (**11, 12**) as a mixture of two isomers; in one of them, the ylide acts as a C-donor while in the other it acts as an N-donor. IR and NMR spectroscopies allow the unambiguous characterization of all of these products, and the X-ray crystal structure of $\{\text{Pd}(\text{dmba})[\text{P}(\text{OMe})_3][\text{N}\equiv\text{C}-\text{C}(\text{H})=\text{PPh}_3]\}(\text{ClO}_4)$ (**5**) is reported. Complex **5** crystallizes in the monoclinic system, space group $P2_1/c$, $a = 12.5690(10)$ Å, $b = 17.857(2)$ Å, $c = 14.729(2)$ Å, $\beta = 92.560(10)^\circ$, $Z = 4$, $V = 3302.5(6)$ Å³, 4881 reflections with $I > 2\sigma(I)$ for the refinement of 423 parameters and 30 restraints, $R1 = 0.0384$, $wR2 = 0.0961$, and $\text{GOF} = 1.044$.

Introduction

The carbonyl-stabilized phosphorus ylides $\text{R}_3\text{P}=\text{C}(\text{R}')\text{COR}''$ ($\text{R}, \text{R}', \text{R}'' = \text{alkyl, aryl, alkoxy, etc}$) have been shown to be very versatile ligands due to their ambidentate character, in addition to their applicability in organic synthesis.¹

In spite of the wide field of applications of the carbonyl-stabilized ylides, other α -stabilized ylides, such as the α -cyano-stabilized phosphorus ylide $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$, have received much less attention. In fact, for the latter, very few reports on its ability to act as a ligand² or as a synthetic tool in organic chemistry³ have been published.

As part of our current research in the α -stabilized phosphorus ylides,⁴ we have focused attention on the α -cyano-stabilized

ylide $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ (CPPY). In addition to the “usual” C-coordination (form **A**, Figure 1) one could expect for this ylide an end-on, N-linear coordination (as a nitrile, form **B**), an N-angular coordination (form **C**) or even a side-on π -coordination (form **D**). These coordination modes could be rationalized taking into account the electron delocalization through the resonance forms **a–c** shown in Figure 1.

We have studied the reactivity of $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ (CPPY) toward several C,N-cyclometalated complexes of Pd^{II} of stoichiometry $[\text{Pd}(\text{C}\hat{\text{N}})(\text{L})(\text{L}')](\text{ClO}_4)$ ($\text{C}\hat{\text{N}} = \text{dmba}, (R)\text{-dmphea}$; $\text{L} = \text{PPh}_3, \text{P}(\text{OMe})_3$, $\text{L}' = \text{THF}$; $\text{L} = \text{L}' = \text{NCMe}$) and $[\text{Pd}(\mu\text{-Cl})(\text{C}\hat{\text{N}})]_2$ ($\text{C}\hat{\text{N}} = \text{dmba}, (R)\text{-dmphea}$). This paper deals with the results obtained in this study and shows clearly the expected, but to date not reported, ambidentate character of the CPPY ylide.

Results and Discussion

Reactions of $[\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)(\text{THF})](\text{ClO}_4)$ with CPPY.

The starting solvated complexes $[\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)(\text{THF})](\text{ClO}_4)$ [$\text{C}\hat{\text{N}} = \text{dmba}, (R)\text{-dmphea}$; $\text{PR}'_3 = \text{PPh}_3, \text{P}(\text{OMe})_3$] were prepared by reaction of the corresponding chloride derivatives $[\text{PdCl}(\text{C}\hat{\text{N}})(\text{PR}'_3)]$ (**2–2'**, see Scheme 1) with AgClO_4 (1:1 molar ratio) in THF at room temperature. Once the AgCl had been eliminated by filtration, the freshly prepared solution of $[\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)(\text{THF})](\text{ClO}_4)$ was cooled to 0°C and allowed to react with CPPY (1:1 molar ratio), giving white solids of stoichiometry $[\text{Pd}(\text{C}\hat{\text{N}})(\text{PR}'_3)(\text{CPPY})](\text{ClO}_4)$ [$\text{C}\hat{\text{N}} = \text{dmba}, \text{PR}'_3 = \text{PPh}_3, 4, \text{P}(\text{OMe})_3, 5$; $\text{C}\hat{\text{N}} = (R)\text{-dmphea}$, $\text{PR}'_3 = \text{PPh}_3$,

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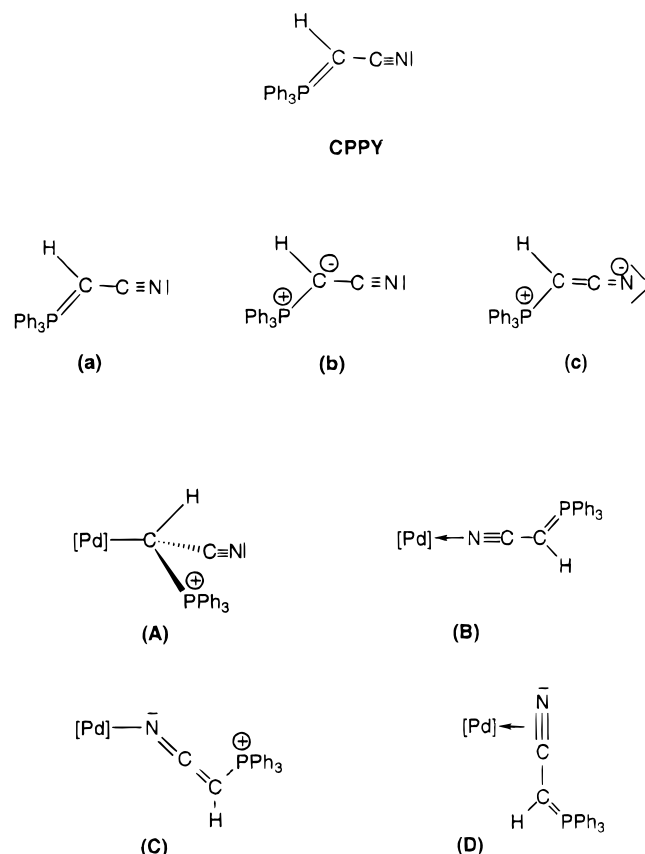


Figure 1

Figure 1. (a–c) Resonance forms of the CPPY ylide; (A–D) different coordination modes expected for the CPPY ylide as ligand.

6; see Scheme 1), as characterized by their elemental analyses and mass spectra (see Experimental Section).

The IR spectra of **4–6** show a sharp, very strong absorption in the 2150–2185 cm^{-1} range (see Table 1) which corresponds to the $\nu(\text{CN})$ absorption of the nitrile. This absorption is shifted to higher energies with respect to that in the free ylide (2136 cm^{-1}),^{2c} thus giving a positive $\Delta\nu$ value ($\Delta\nu = \nu_{\text{complex}} - \nu_{\text{free ylide}}$). The observation of this positive $\Delta\nu$ value implies that the ylide cannot be coordinated in forms **C** or **D** (Figure 1), since in these forms a negative $\Delta\nu$ value would be expected. Coordination in form **C** implies a major contribution of the resonance form **c** and a decrease in the CN multiple bond character; furthermore, a shift to lower frequencies of the $\nu(\text{CN})$ absorption has been considered characteristic of the side-on coordinated nitriles (form **D**).^{5,6} Both forms **A** and **B** in Figure 1 are in accord with the observed positive $\Delta\nu$ value. Coordination in form **A** implies a major contribution of the resonance form **b** and an increase in the $\nu(\text{CN})$ frequency^{2b,c} with respect to the free ylide, and it is sensible, furthermore, to assume that the end-on form **B** would give spectroscopic behavior similar to that usually observed for end-on coordinated nitriles,^{5–7} that is, an increase in the $\nu(\text{CN})$ frequency.

The ^1H NMR spectra of **4–6** show, in addition to the expected resonances for the dmbs (or the (*R*)-dmphea) and PPh_3 [or $\text{P}(\text{OMe})_3$] ligands (see Experimental Section), a doublet resonance at high field (ranging from 1.2 to 2.03 ppm, see Table 2) with a coupling constant of $^2J_{\text{P-H}}$ around 5 Hz, and attributed to the methine PCH proton. These values of $\delta(\text{CH})$ and $^2J_{\text{P-H}}$ are very close to those reported⁸ for the free ylide and are very

different from those found^{2b} in $[\text{Pd}(\mu\text{-Cl})\text{Cl}(\text{CPPY})]_2$ (for which C-coordination has been proposed). Moreover, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table 2) show the ylidic phosphorus resonance in a very short range of frequencies (24.17–24.68 ppm) and very close to that of the free ylide (23.75 ppm), and the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (Table 2) show the resonance attributed to the ylidic carbon atom as a doublet around 1.5 ppm with a coupling constant $^1J_{\text{P-C}}$ of 135 Hz, with values very similar to those found in the free ylide (–2.17 ppm/136 Hz). All these facts imply that no important structural and electronic changes have occurred in the neighborhood of the ylidic fragment $-\text{C}(\text{H})=\text{PPh}_3$ during the coordination process, thus strongly suggesting end-on N-coordination of the ylide. The ylide could be seen, then, as a functionalized nitrile $[\text{Pd}]\leftarrow\text{N}\equiv\text{C}-\text{R}$, $-\text{R}$ being the ylidic group $-\text{C}(\text{H})=\text{PPh}_3$.

The PR'_3 -*trans*-to- NMe_2 ligand arrangement in the starting products⁹ is preserved, after chlorine abstraction and ylide coordination, in complexes **4–6**, as can be inferred from the small, but significant, coupling constants $^4J_{\text{P-H}}$ (ranging from 1.8 to 3.9 Hz) of the NMe_2 and the CH_2N protons with the phosphorus atom.^{10,11} Thus, an $\text{N}(\text{ylide})$ -*trans*-to- $\text{C}(\text{ortho-metalated})$ ligand arrangement results, as has been depicted in Scheme 1, the reaction occurring with retention of the configuration at the palladium atom.

The crystal structure of $\{\text{Pd}(\text{dmbs})[\text{P}(\text{OMe})_3][\text{N}\equiv\text{C}-\text{C}(\text{H})=\text{PPh}_3]\}(\text{ClO}_4)$, **5**, provides further characterization. A drawing of the organometallic cationic fragment is shown in Figure 2, and selected bond distances and angles are collected in Table 4.

The palladium atom is located in a slightly distorted square-planar environment, surrounded by the C and N atoms of the *ortho*-metalated dmbs ligand, the P atom of the phosphite ligand and the N atom of the ylide ligand, with the latter showing its end-on N-coordination.

The structural parameters of the dmbs^{4,10,11} and $\text{P}(\text{OMe})_3$ ligands^{12,13} are similar to those found in other complexes containing these ligands. The $\text{Pd}(1)-\text{N}(2)$ bond distance [2.076 (3) Å] is similar to that found in other palladium-nitrile complexes,¹⁴ and the $\text{N}(2)-\text{C}(13)$ bond distance [1.156 (5) Å] is fairly typical of nitriles.^{14,15} The $\text{C}(13)-\text{C}(14)$ bond distance [1.379 (5) Å] is shorter than a $\text{C}(\text{sp}^2)-\text{C}(\text{sp}^1)$ bond distance [1.431 Å]¹⁵ and is similar to other C–C bond distances found in ylides for which resonance delocalization has been suggested: 1.407(8) and 1.399(8) Å for $\text{Ph}_3\text{P}=\text{C}(\text{H})-\text{COPh}$ ¹⁶ and 1.366(4) Å for $\{\text{Pd}(\text{dmbs})(\text{py})[\text{OC}(\text{Me})=\text{C}(\text{H})\text{PPh}_3]\}(\text{ClO}_4)$.⁴ This fact implies a partial multiple bond character for this bond. As was inferred from the NMR data in solution, the ylide fragment $-\text{C}(\text{H})=\text{PPh}_3$ remains almost unaltered; the $\text{P}(2)-\text{C}(14)$ bond distance [1.710 (4) Å] is similar, within experimental error, to those determined for the free ylide $\text{Ph}_3\text{P}=\text{CH}_2$ [1.697–(3), 1.688(3) Å]¹⁷ or other free keto stabilized ylides, such as

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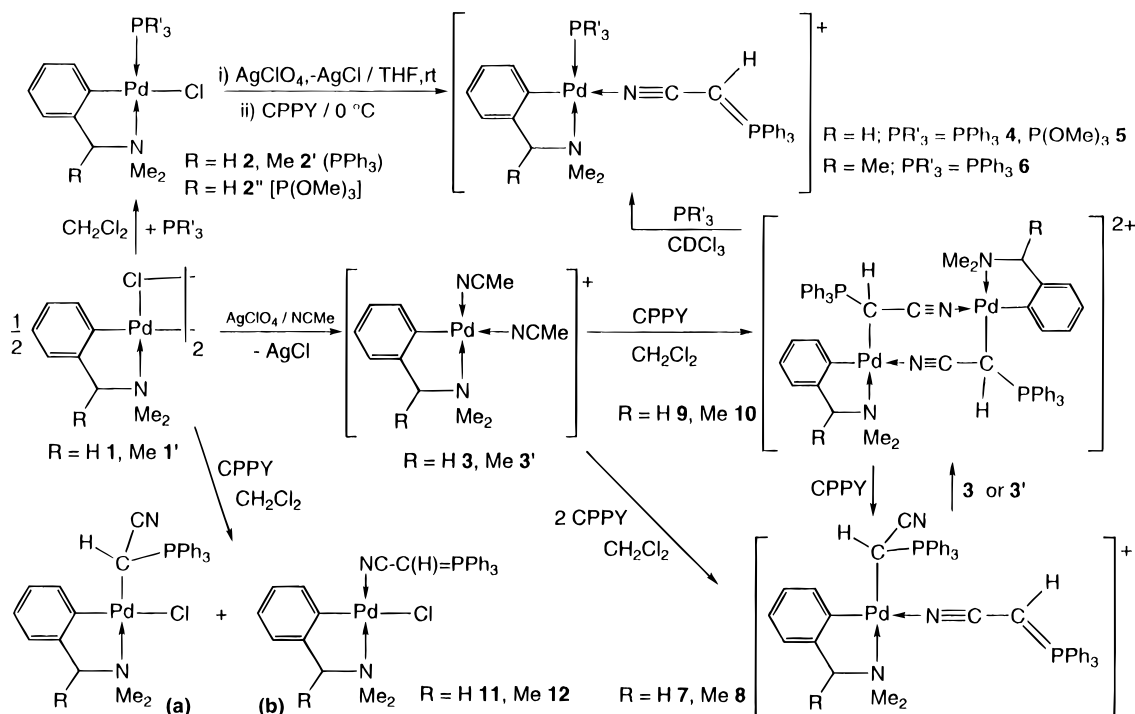
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Scheme 1

Table 1. Relevant IR Absorptions (ν , cm^{-1}) for Complexes 4–12

complex	$\nu(\text{CN})$	$\Delta\nu^a$
4	2158	+22
5	2181	+45
6	2166	+30
7	2174	+38
8	2172	+36
9	2224	+88
10	2229	+93
11	2178	+42
12	2187	+51
CPPY	2136	

^a $\Delta\nu = \nu(\text{CN})_{\text{complex}} - \nu(\text{CN})_{\text{free ylide}}$.

Table 2. Relevant NMR Data (δ , ppm; ²J, Hz) for Complexes 4–12

complex	$\delta(\text{CH})$	² J _{P-H}	$\delta(\text{P})$	$\delta(\text{CH})$	¹ J _{P-C}
4 (N) ^a	1.24	5.4	24.17	1.49	136
5 (N) ^a	2.03	5.2	24.68	1.64	135
6 (N) ^a	1.26	5.4	24.24	1.53	136
7 (N/C) ^a	1.45/3.05	6.0/13.8	24.35/26.80	1.88/−1.25	136/46
8 (N) ^a	1.41/1.38	5.9/5.9	24.28/24.52	2.20/1.94	136/136
9 (C) ^a	3.11/3.08	14.0/13.3	26.62/27.25	−1.48/−1.67	46/46
11a (C) ^a	4.37	14.3	28.07	−6.04	46
11b (N) ^a	1.92	6.5	23.66	1.94	137
12a (C) ^a	4.58/4.29	14.0/14.0	28.31/27.94	−7.07 ^b	45
12b (N) ^a	1.90	6.5	23.62	1.89	137
CPPY	1.61 ^c	7.8 ^c	23.75 ^d	−2.17 ^d	136 ^d

^a N = N-coordinated isomer; C = C-coordinated isomer, ^b Both isomers. ^c Determined by us at 203 K in CD₂Cl₂. Values for ¹H RMN in ref 8 are $\delta = 1.62$ ppm, $J_{\text{PCH}}^{-60^\circ\text{C}} = 7.5$ Hz. ^d CDCl₃, room temperature.

Ph₃P=C(H)COPh [1.716(5), 1.725(4) Å]¹⁶ and is notably shorter than the other P–C distances of the ylide in **5** [average: 1.802(4) Å].

The N-coordinated ylide shows an almost linear coordination, typical of end-on coordinated nitriles, as can be seen from the

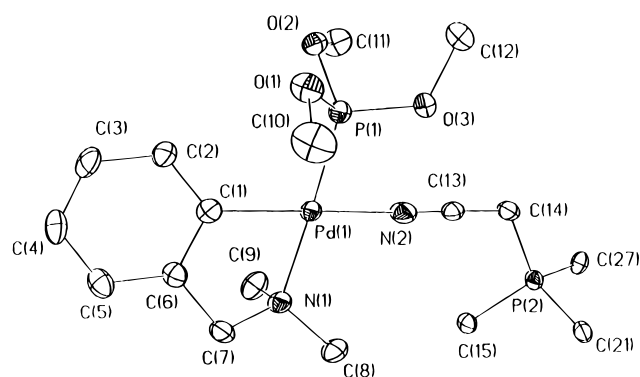


Figure 2. Thermal ellipsoid plot of the $\{\text{Pd}(\text{dmba})[\text{P}(\text{OMe})_3][\text{NC}-\text{C}(\text{H})=\text{PPh}_3]\}^+$ cation. Ph groups (except C_{ipso}) and H atoms are omitted for clarity. Atoms are drawn at the 50% probability level.

Table 3. Crystal Data for **5**

formula	C ₃₂ H ₃₇ ClN ₂ O ₇ P ₂ Pd	V, Å ³	3302.5 (6)
cryst syst	monoclinic	d _{calc} , g/cm ³	1.539
space group	P2 ₁ /c	cryst size, mm	0.40 × 0.35 × 0.30
fw	765.43	μ, mm ^{−1}	0.789
a, Å	12.5690(10)	no of unique rflns	5790
b, Å	17.857(2)	no of rflns with I > 2σ(I)	4881
c, Å	14.729(2)	no of variables/restraints	423/30
α, deg	90.0	R1 ^a	0.0384
β, deg	92.560(10)	wR2 ^a	0.0961
γ, deg	90.0	GOF ^a	1.044
Z	4	max. shift / σ	−0.087
F(000)	1568	res electron density, e/Å ³	0.864
T, °C	−123(2)	λ, Å	0.71073

^a R1 = $\sum ||F_o| - |F_c|| / \sum |F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. GOF = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{observs}} - n_{\text{params}})]^{1/2}$.

bond angles Pd(1)–N(2)–C(13) [177.1 (3)°] and N(2)–C(13)–C(14) [177.7 (4)°]. The environment at C(14) is planar [$\sum \text{angles} = 360.0^\circ$] and that of the P(2) is tetrahedral (average of angles: 109.44°).

The most striking feature of **4–6** is the selective N-coordination of the ylide, and these results could be easily explained by invoking the relative hardness and softness of the different donor atoms¹⁹ bonded to palladium and the antisym-

(18) The reaction of the solvated complexes $[\text{Pd}(\text{C}(\text{N})(\text{PPh}_3)(\text{THF}))(\text{ClO}_4)]$ (C = N = dmba, (R)-dmphea) with the ylides $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COR}$ (R = Me, Ph, OMe) gives products of stoichiometry $[\text{Pd}(\text{C}(\text{N})(\text{PPh}_3)(\text{ylide}))(\text{ClO}_4)]$ in which the ylide acts selectively as an O-donor ligand. Falvello, L. R.; Fernández, S.; Navarro, R.; Pascual, I.; Urriolabeitia, E. P. J. Chem. Soc., Dalton Trans., in press.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **5**

Bond Distances					
Pd(1)–C(1)	2.003 (4)	Pd(1)–N(1)	2.132 (3)	Pd(1)–N(2)	2.076 (3)
Pd(1)–P(1)	2.2070 (10)	N(2)–C(13)	1.156 (5)	C(13)–C(14)	1.379 (5)
P(2)–C(14)	1.710 (4)	P(2)–C(15)	1.796 (4)	P(2)–C(21)	1.814 (4)
P(2)–C(27)	1.795 (4)	P(1)–O(1)	1.589 (3)	P(1)–O(2)	1.590 (3)
P(1)–O(3)	1.575 (3)				
Bond Angles					
C(1)–Pd(1)–N(1)	82.17 (13)	N(1)–Pd(1)–N(2)	92.37 (12)		
N(2)–Pd(1)–P(1)	91.42 (9)	P(1)–Pd(1)–C(1)	94.34 (11)		
Pd(1)–N(2)–C(13)	177.1 (3)	N(2)–C(13)–C(14)	177.7 (4)		
C(13)–C(14)–P(2)	118.4 (3)				

biotic behavior of the Pd^{II} center.²⁰ Thus, the PR₃ ligand, which is a soft base, will be stabilized *trans* to the hard N atom (phosphines are very reluctant to bond *trans* to the carbon atom²¹) and the position *trans* to the soft *ortho*-metalated carbon atom would be occupied by the hardest donor atom of the CPPY ligand, that is, the N atom, with C-coordination of the ylide *trans* to the *ortho*-metalated carbon atom being unfavorable. Moreover, these results bear a strong resemblance to those obtained for the α -keto stabilized ylides Ph₃P=C(H)COR (R = Me, Ph, OMe).^{4,18} We will return to this point presently.

Reactions of [Pd(C[^]N)(NCMe)₂](ClO₄) with CPPY. The reaction of [Pd(C[^]N)(NCMe)₂](ClO₄) (**3**, **3'**; see Scheme 1) with CPPY (1:2 molar ratio) in CH₂Cl₂ at room temperature gives, after solvent evaporation and Et₂O addition, white solids of stoichiometry [Pd(C[^]N)(CPPY)₂](ClO₄) (C[^]N = dmbs **7**, (R)-dmphea **8**), as characterized by their elemental analyses and mass spectra (+FAB).

The IR spectra of **7** and **8** (Table 1) show strong absorptions at 2174 and 2172 cm⁻¹, respectively, corresponding to the ν -(CN) of the nitrile. The position of these absorptions indicates, as for **4**–**6**, that both the C-coordination and/or the N-coordination modes could account for the positive observed $\Delta\nu$ values. The NMR spectra are rather more informative about the structures of **7** and **8**.

The ¹H NMR spectrum (Table 2) of **7** shows, in addition to the low-field resonances of the Ph and C₆H₄ groups, an AB spin system for the CH₂N protons and two singlet resonances for the CH₃ protons of the NMe₂ group, showing that the molecular plane is not now a symmetry plane. Moreover, two doublet resonances of relative intensity 1:1 at 3.05 and 1.45 ppm also appear and are attributed to the methinic P=CH protons of the two coordinated ylides. The corresponding ²J_{P–H} values are 13.8 and 6.0 Hz, respectively. The ³¹P{¹H} NMR spectrum of **7** shows two singlet resonances of relative intensity 1:1 at 26.80 and 24.35 ppm, and in the ¹³C{¹H} NMR spectrum the ylidic P=CH carbons appear as two doublets, at δ 1.88 ppm (¹J_{P–C} = 136 Hz) and –1.25 ppm (¹J_{P–C} = 46 Hz).

The comparison of these sets of resonances with those obtained for **4**–**6** (which contain the ylide selectively N-coordinated) and with those shown by [PdCl₂(CPPY)₂]²² (which contains the ylide selectively C-coordinated) suggest that in **7**

we have the simultaneous presence of a C-coordinated ylide and another one N-coordinated to the same metal center. Other redistribution products, such as those containing both ylides C-coordinated or both N-coordinated, are not observed. In addition, of the two possible geometric isomers (C-*trans*-to-NMe₂ or N-*trans*-to-NMe₂), only one is observed. The elucidation of the coordination site of each ylide ligand comes from the observation of a very strong nOe interaction between the H₆ proton of the dmbs ligand (*ortho* to the cyclometalated position) at 6.27 ppm with the methine proton at 3.05 ppm, attributed to the C-bonded ylide. Thus, the C-bonded ylide is *trans* to the NMe₂ group and the N-coordinated ylide is *trans* to the *ortho*-metalated C₆H₄ group, as is depicted in Scheme 1.

It is expected that the C-bonded ylide would display very different spectroscopic parameters with respect to those observed in the free ylide or in the N-bonded ylide as a result of the hybridization change sp² → sp³ at the ylidic carbon atom.¹ Thus, the methine PCH signal has been shifted downfield by about 2 ppm and shows a notably higher value of ²J_{P–H} than the N-coordinated ylide (13.8 vs 6.0 Hz). In the same way, the ylidic phosphorus resonance PCH of the C-coordinated ylide has also been shifted downfield (approximately 2.5 ppm) while the ylidic carbon resonance PCH is shifted upfield with respect to the N-bonded form and has a coupling constant with one-third of the corresponding value seen in the free ylide or in the N-bonded form.

Similar conclusions can be derived from the NMR spectra of **8**, although in this case, due to the presence of a chiral center in the (R)-dmphea ligand, two sets of signals, corresponding to the two possible diastereoisomers (RR/RS) are observed. The two sets of signals (see Tables 1 and 2 and Experimental Section) show that a negligible diastereoselective induction has taken place, with the major/minor diastereomeric ratio being 1.2/1, although we have not determined the absolute configuration of each isomer.

The selectivity observed in the coordination modes of the ylides in **7** and **8** seems to be related to that observed in complexes **4**–**6**. Once again, consideration of the antisymbiotic behavior of the soft Pd^{II} center²⁰ provides a useful tool. Thus, the ylidic carbon atom of the C-linked ylide is a soft base, and it will be particularly stabilized when coordinated *trans* to the harder donor atom of the cyclometalated ligand, that is, the N atom. On the other hand, we have seen in **4**–**6** that the harder N atom of the ylide can be accommodated *trans* to the soft carbon of the *ortho*-metalated C₆H₄ group. This noteworthy isomerism of the ligand, similar to that observed in the well-known example of [Pd(Ph₂PCH₂CH₂CH₂NMe₂)(NCS)(SCN)],²³ has no precedent for ylides and clearly shows the ambidentate character of this ylide ligand.

Other reactions with the solvated complexes [Pd(C[^]N)(NCMe)₂](ClO₄) were attempted. The reaction of [Pd(C[^]N)(NCMe)₂](ClO₄) (**3**, **3'**; see Scheme 1) with CPPY (1:1 molar ratio) in CH₂Cl₂ at room temperature gives the immediate precipitation of white solids of stoichiometry [Pd(C[^]N)(CPPY)(ClO₄)] (C[^]N = dmbs **9**, (R)-dmphea **10**) as derived from their elemental analyses. The extremely low solubility of these compounds in the usual organic solvents precludes their analysis in solution; NMR data are not available, nor are conductivity measurements. In spite of this low solubility, mass spectra of **9** and **10** could be obtained. The mass spectrum of **9** shows the presence of a single peak at 541 a.m.u., corresponding to the stoichiometry [Pd(dmbs)(CPPY)]⁺. That of **10** shows a peak at 555 [Pd((R)-dmphea)(CPPY)]⁺ and another one at 1211, corresponding to the binuclear species [Pd₂((R)-dmphea)₂–

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(CPPY)₂(ClO₄)⁺ and suggesting that **9** and **10** are probably dinuclear in nature.

Excluding the chelation of the ligand because of the constraint imposed by the nitrile group, we can propose two possible structures for **9** and **10**; one is mononuclear with a covalent perchlorate ligand, and one is binuclear with the ylide acting as a bridging ligand. The IR spectra of **9** and **10** (Table 1) show two interesting features: the absorptions due to the ClO₄⁻ anion are not split, as expected for the low symmetry (C_{3v}) monodentate ligand^{24,25} —OCIO₃ group; on the other hand, the ν(CN) absorption appears as a strong, sharp band at 2224 cm⁻¹ (**9**) or 2229 cm⁻¹ (**10**), shifted to higher energies with respect to the values found in **7** or **8**. These facts suggest that the ClO₄⁻ anion is not included in the coordination sphere of the palladium (excluding a mononuclear structure), and the increase of the ν(CN) frequency strongly suggests that both the N- and the C-atoms of the ylide are bonded to the palladium center (both C- and N-coordination produce an increase of the ν(CN) frequency). A dimeric structure such as that depicted in Scheme 1 accounts for these observations.

Further evidence can be obtained from the observed reactivity (see Scheme 1). Thus, **9** can be obtained by reaction of **7** and [Pd(dmab)(NCMe)₂]⁺ (**3**) in equimolecular amounts, and inversely, the reaction of **9** with 2 equiv of CPPY gives **7** exclusively. Complex **9** also reacts with PPh₃ (1:2 molar ratio) producing bridge splitting and giving **4** in quantitative yield (see Experimental Section). However, while the free ylide or PPh₃ is able to produce bridge splitting in **9**, no reaction was observed between **9** and CO, Cl⁻, or pyridine, ligands which could easily replace a bound perchlorate.²⁶

Reactions of [Pd(μ-Cl)(C⁻N)]₂ with CPPY. The reactions of the binuclear chloride-bridged complexes [Pd(μ-Cl)(C⁻N)]₂ (**1**, **1'**; see Scheme 1) with CPPY (1:2 molar ratio) in CH₂Cl₂ at room temperature give, after solvent evaporation and Et₂O addition, pale yellow solids of stoichiometry [PdCl(C⁻N)(CPPY)] (C⁻N = dmab **11**, (R)-dmphea **12**) as characterized by elemental analysis. The neutral nature of these complexes is inferred from their nonconducting behavior in acetone solutions (see Experimental Section). Moreover, the determination of the molecular weight in solution for **12** (see Experimental Section) gives an excellent agreement between the measured and theoretical values.

The IR spectra of **11** and **12** (Table 1) show the expected ν(CN) absorption at 2178 (**11**) or 2187 (**12**) cm⁻¹. The increase of ν(CN) with respect to the free ylide indicates that the ligand is actually coordinated in **11** and **12** and that these products are not simply mixtures of the starting materials. The ¹H NMR spectrum of **11** gives additional information. Two sets of signals (relative intensity = 1.2/1) are observed, indicating the presence of two isomers. The major isomer shows singlet resonances for the CH₂N and NMe₂ protons, and a doublet for the methine PCH proton at 1.92 ppm (²J_{P-H} = 6.5 Hz). The minor isomer shows diastereotopic CH₂N protons, two singlets for the NMe₂ group and a doublet for the methine proton at 4.37 ppm (²J_{P-H} = 14.3 Hz). Using reasoning similar to that applied in our earlier discussion of the NMR of complexes **4**–**8**, we conclude that in the major isomer the ylide is N-bonded (**11b**) and that in the minor one the ylide is C-coordinated (**11a**), as has been depicted in Scheme 1. Thus, both C(ylide) and N(nitrile) atoms are able to produce bridge splitting in [Pd(μ-Cl)(C⁻N)]₂, giving an almost equimolar distribution of products. The ³¹P{¹H} and

¹³C{¹H} NMR data (Table 2) are in keeping with these conclusions. The molar ratio **11a**/**11b** remains unchanged in solution at room temperature; the same proportions of **11a** and **11b** are observed after 1 week in CDCl₃ solution. As expected, the NMR data of **12** show a similar behavior; the ylide breaks the chloride bridging system, giving isomeric mononuclear derivatives in which the ylide is C-coordinated (**12a**, obtained as a mixture of the corresponding two diastereoisomers) and N-bonded (**12b**, obtained as a single isomer since N-bonding of the ylide does not create a second chiral center).

Once again, the ¹H-¹H NOESY spectrum, performed on complex **11**, shows that the C-coordinated ylide in **11a** is *cis* to the C₆H₄ *ortho*-metalated group (and *trans* to the NMe₂ unit), as reflected by the strong nOe interaction between the resonance at 4.37 ppm (methine proton, **11a**) and the resonance at 6.68 ppm (H₆ of the dmab ligand). Less clear is the coordination site of the N-coordinated nitrile in **11b** (the NOESY spectrum is not informative in this respect, due to the remote location of the methine proton with respect to any proton of the dmab system). However, due to the fact that only one isomer has been detected for **11b** (and for **12b**), and by analogy with the splitting of the Pd(μ-Cl)₂Pd system by N-donor ligands,⁹ we propose an N-*trans*-to-N ligand arrangement (therefore, C-*trans*-to-Cl) for complexes **11b** and **12b**.

Conclusion

The ylide Ph₃P=C(H)CN (CPPY) behaves as an ambidentate ligand toward *ortho*-metalated derivatives of Pd^{II}. Depending on the starting material used, we have found examples in which the ylide is selectively N-coordinated, compounds with C-coordination, a mixture of isomers C- and N-coordinated isomers and even complexes containing two ylides, one of them C- and the other one N-coordinated—a fascinating example of ligand isomerism. Moreover, we have inferred the nature of products in which this ylide acts as a bridging ligand. This rich coordination chemistry, which has been almost exclusive by in the domain of classical polidentate ligands, is unprecedented for the α-stabilized ylide ligands and allows us to suspect that new and more interesting results may await study.

Experimental Section

Safety Note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See ref 27.

General Procedures. Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over sodium benzophenone ketyl; dichloromethane over P₂O₅ and *n*-hexane over sodium. Elemental analyses were carried out on a Perkin-Elmer 2400 microanalyzer. Infrared spectra (4000–200 cm⁻¹) were recorded on a Perkin-Elmer 883 infrared spectrophotometer in Nujol mulls between polyethylene sheets. ¹H (300.13 MHz), ¹³C{¹H} (75.47 MHz), and ³¹P{¹H} (121.49 MHz) NMR spectra were recorded in CDCl₃ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ¹H and ¹³C{¹H} were referenced using the solvent signal as internal standard and ³¹P{¹H} was externally referenced to H₃PO₄ (85%). The two dimensional ¹H-¹H NOESY experiments for complexes **7** and **11** were performed at a measuring frequency of 300.13 MHz. The data were acquired into a 512 × 1024 matrix, and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive ion FAB) were recorded on a V. G. Autospec spectrometer. Molecular weight determinations were made on a Knauer vapor pressure osmometer. Electrical conductivity measurements were performed in acetone solutions with concentrations around 5 × 10⁻⁴ M with a Philips PW 9509 conductivity cell. The starting complexes [Pd(μ-Cl)(C⁻N)]₂²⁸

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(C $\equiv$ N = dmbs **1** and (R)-dmphea **1'**), [PdCl(C $\equiv$ N)(PR'₃)]⁹ [PR'₃ = PPh₃; C $\equiv$ N = dmbs **2**, (R)-dmphea **2'**; PR'₃ = P(OMe)₃; C $\equiv$ N = dmbs **2''**], [Pd(C $\equiv$ N)(NCMe)₂](ClO₄)²⁹ [C $\equiv$ N = dmbs **3**, (R)-dmphea **3'**], and the ylide Ph₃P=C(H)CN (CPPY)^{3a} were prepared according to published methods.

{Pd(dmbsa)(PPh₃)[N≡C-C(H)=PPh₃]}(ClO₄), **4.** To a solution of PdCl(dmbsa)(PPh₃) **2** (0.129 g, 0.239 mmol) in THF (25 mL) was added AgClO₄ (0.049 g, 0.239 mmol), and the resulting suspension was stirred for 30 min at room temperature with exclusion of light. The insoluble AgCl was filtered off, and the freshly obtained pale yellow solution was cooled at 0 °C and then CPPY (0.072 g, 0.239 mmol) was added. After 30 min of stirring at 0 °C, the solvent was evaporated to dryness and the oily residue treated with 25 mL of Et₂O, giving complex **4** as a white solid, which was filtered and air-dried. Yield: 0.173 g (80% yield). Crude **4** was recrystallized from CH₂Cl₂/n-hexane. The white crystals of **4**·0.25CH₂Cl₂ were used for elemental analysis and NMR measurements. The amount of CH₂Cl₂ of crystallization was determined by ¹H NMR integration.

Anal. Calcd for C₄₇H₄₃ClN₂O₄P₂Pd·0.25CH₂Cl₂ (M_r = 924.90): C, 61.36; H, 4.74; N, 3.02. Found: C, 61.43; H, 4.58; N, 2.99. MS (+FAB) [m/z (%): 803 (21%) [M⁺]; 502 (100%) [(M - ylide)⁺]. IR (ν_{CN}, cm⁻¹): 2158. ¹H: δ 7.69–7.35 (m, 30H, Ph), 6.94 (d, 1H, C₆H₄, ³J_{H-H} = 7 Hz), 6.79 (false t, 1H, C₆H₄, ³J_{H-H} = 7 Hz), 6.33 (false t, 1H, C₆H₄), 6.19 (false t, 1H, C₆H₄, ³J_{H-H} = 7 Hz), 3.94 (d, 2H, CH₂N, ⁴J_{P-H} = 1.8 Hz), 2.30 (d, 6H, NMe₂, ⁴J_{P-H} = 2.5 Hz), 1.24 (d, 1H, CH ylide, ²J_{P-H} = 5.4 Hz). ³¹P{¹H}: δ 42.40 (Pd-PPh₃), 24.17 (≡PPh₃). ¹³C{¹H}: δ 149.18, 146.40, 137.95 (J_{P-C} = 11 Hz), 130.32, 125.20 (J_{P-C} = 15 Hz), 124.82 (C₆H₄), 134.86 (J_{P-C} = 12 Hz), 133.62, 132.68 (J_{P-C} = 10 Hz), 131.27, 129.55 (J_{P-C} = 13 Hz), 128.63 (J_{P-C} = 11 Hz), 125.07 (J_{P-C} = 93 Hz) (PPh₃), 123.00 (CN), 71.97 (CH₂N), 50.35 (NMe₂), 1.49 (CH ylide, ¹J_{P-C} = 136 Hz).

{Pd(dmbsa)[P(OMe)₃][N≡C-C(H)=PPh₃]}(ClO₄), **5.** Complex **5** was synthesized in a manner similar to that used for **4**: {Pd(dmbsa)-[P(OMe)₃](THF)}(ClO₄) (prepared from PdCl(dmbsa)[P(OMe)₃] **2''** (0.196 g, 0.489 mmol) and AgClO₄ (0.101 g, 0.489 mmol)) reacted, in THF at 0 °C, with CPPY (0.147 g, 0.489 mmol) to give **5** as a white solid. Yield: 0.246 g (65% yield).

Anal. Calcd for C₃₂H₃₇ClN₂O₇P₂Pd (M_r = 765.43): C, 50.21; H, 4.87; N, 3.66. Found: C, 49.80; H, 4.93; N, 3.64. MS (+FAB) [m/z (%): 665 (100%) [M⁺]; 541 (50%) [(M - phosphite)⁺]; 364 (100%) [(M - ylide)⁺]. IR (ν_{CN}, cm⁻¹): 2181. ¹H: δ 7.69–7.54 (m, 15H, Ph), 7.10 (m, 1H, C₆H₄), 6.95 (m, 2H, C₆H₄), 6.87 (m, 1H, C₆H₄), 3.94 (d, 2H, CH₂N, ⁴J_{P-H} = 2.7 Hz), 3.59 (d, 9H, -OMe, ³J_{P-H} = 13 Hz), 2.38 (d, 6H, NMe₂, ⁴J_{P-H} = 3.9 Hz), 2.03 (d, 1H, CH ylide, ²J_{P-H} = 5.2 Hz). ³¹P{¹H}: δ 118.84 (Pd-P(OMe)₃), 24.68 (≡PPh₃). ¹³C{¹H}: δ 149.03 (J_{P-C} = 4 Hz), 145.43, 136.40 (J_{P-C} = 12 Hz), 133.21 (J_{P-C} = 8 Hz), 126.27 (J_{P-C} = 7 Hz), 125.58 (C₆H₄), 133.66 (J_{P-C} = 2 Hz), 132.72 (J_{P-C} = 10 Hz), 129.63 (J_{P-C} = 13 Hz), 125.16 (J_{P-C} = 93 Hz) (PPh₃), 123.47 (CN), 71.51 (CH₂N, ³J_{P-C} = 4 Hz), 53.07 (OMe), 49.93 (NMe₂, ³J_{P-C} = 3 Hz), 1.64 (CH ylide, ¹J_{P-C} = 135 Hz).

{Pd((R)-dmphea)(PPh₃)[N≡C-C(H)=PPh₃]}(ClO₄), **6.** Complex **6** was synthesized in a manner similar to that used for **4**: [Pd((R)-dmphea)(PPh₃)(THF)](ClO₄) (prepared from PdCl((R)-dmphea)(PPh₃) **2'** (0.308 g, 0.556 mmol) and AgClO₄ (0.115 g, 0.556 mmol)) reacted, in THF at 0 °C, with CPPY (0.167 g, 0.556 mmol) to give **6** as a white solid. Yield: 0.420 g (82% yield).

Anal. Calcd for C₄₈H₄₅ClN₂O₄P₂Pd (M_r = 917.70): C, 62.82; H, 4.94; N, 3.05. Found: C, 62.54; H, 5.29; N, 2.90. MS (+FAB) [m/z (%): 817 (75%) [M⁺]; 555 (22%) [(M - phosphine)⁺]; 516 (100%) [(M - ylide)⁺]. IR (ν_{CN}, cm⁻¹): 2166. ¹H: δ 7.67–7.31 (m, 30H, Ph), 6.90 (dd, 1H, C₆H₄, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.3 Hz), 6.79 (false t, 1H, C₆H₄, ³J_{H-H} = 7 Hz), 6.33 (false t, 1H, C₆H₄), 6.19 (false t, 1H, C₆H₄, ³J_{H-H} = 7 Hz), 3.69 (q, 1H, CH-dmphea, ³J_{H-H} = 6 Hz), 2.43 (d, 3H, NMe₂, ⁴J_{P-H} = 1.8 Hz), 2.06 (d, 3H, NMe₂, ⁴J_{P-H} = 3.2 Hz), 1.62 (d, 3H, Me-dmphea), 1.26 (d, 1H, CH ylide, ²J_{P-H} = 5.4 Hz). ³¹P{¹H}: δ 41.70 (Pd-PPh₃), 24.24 (≡PPh₃). ¹³C{¹H}: δ 155.03, 145.97, 137.86 (J_{P-C} = 12 Hz), 130.41, 125.12 (J_{P-C} = 5 Hz), 124.85 (C₆H₄), 134.79 (J_{P-C} = 12 Hz), 133.60, 132.69 (J_{P-C} = 10 Hz), 131.23, 129.53 (J_{P-C} = 13 Hz), 128.63 (J_{P-C} = 10 Hz), 125.09 (J_{P-C} = 93 Hz) (PPh₃), 122.91 (CN), 74.43 (CH-dmphea), 50.53, 46.28 (NMe₂), 22.06 (Me-dmphea), 1.53 (CH ylide, ¹J_{P-C} = 136 Hz).

{Pd(dmbsa)[C(H)(C≡N)(PPh₃)](N≡C-C(H)=PPh₃)}(ClO₄), **7.**

To a solution of [Pd(dmbsa)(NCMe)₂](ClO₄) **3** (0.155 g, 0.367 mmol) in 25 mL of CH₂Cl₂ at room temperature was added CPPY (0.221 g, 0.734 mmol). A white cloudiness was immediately observed which, upon stirring, gradually dissipated. After 2 h of stirring at room temperature, a very small amount of white solid remained in suspension. This suspension was filtered, the solid discarded, and the clear solution evaporated to a small volume (ca. 3 mL). By addition of Et₂O (25 mL) and continuous stirring, **7** was obtained as a white solid, which was filtered and air-dried. Yield: 0.262 g (77% yield).

Anal. Calcd for C₄₉H₄₄ClN₃O₄P₂Pd (M_r = 942.71): C, 62.43; H, 4.70; N, 4.45. Found: C, 62.02; H, 4.84; N, 4.50. MS (+FAB) [m/z (%): 842 (28%) [M⁺]; 541 (100%) [(M - ylide)⁺]. IR (ν_{CN}, cm⁻¹): 2174. ¹H: δ 7.89–7.82 (m, Ph), 7.65–7.40 (m, Ph), 6.79 (m, 2H, C₆H₄), 6.79 (td, 1H, C₆H₄, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 2 Hz), 6.27 (d, 1H, C₆H₄), 3.72, 3.61 (AB spin system, 2H, CH₂N, ²J_{H-H} = 14 Hz), 3.05 (d, 1H, CH C-ylide, ²J_{P-H} = 13.8 Hz), 2.25 (s, 3H, NMe₂), 1.98 (s, 3H, NMe₂), 1.45 (d, 1H, CH N-ylide, ²J_{P-H} = 6.0 Hz). ³¹P{¹H}: δ 26.80 (–P⁺Ph₃, C-ylide), 24.35 (≡PPh₃, N-ylide). ¹³C{¹H}: δ 148.22, 147.25, 132.19, 125.16, 124.12, 122.55 (C₆H₄), 134.43, 134.15 (J_{P-C} = 10 Hz), 133.42, 132.76 (J_{P-C} = 10 Hz), 129.51 (J_{P-C} = 13 Hz), 125.15 (J_{P-C} = 92 Hz) (PPh₃), 121.71, 120.55 (CN), 72.14 (CH₂N), 51.21, 50.33 (NMe₂), 1.88 (CH N-ylide, ¹J_{P-C} = 136 Hz), –1.25 (CH C-ylide, ¹J_{P-C} = 46 Hz).

{Pd((R)-dmphea)[C(H)(C≡N)(PPh₃)](N≡C-C(H)=PPh₃)}(ClO₄), **8.**

Complex **8** was obtained in a manner similar to that for **7**: [Pd((R)-dmphea)(NCMe)₂](ClO₄) **3'** (0.146 g, 0.335 mmol) reacted in CH₂Cl₂ at room temperature with CPPY (0.202 g, 0.670 mmol) to give **8** as a white solid. Yield: 0.260 g (81% yield). Diastereomeric ratio: major/minor: 1.2/1. Complex **8** was recrystallized from CH₂Cl₂/n-hexane. The white microcrystalline solid of **8**·0.35CH₂Cl₂ was used for analytical and spectroscopic measurements. The amount of CH₂Cl₂ of crystallization was determined by ¹H NMR integration.

Anal. Calcd for C₅₀H₄₆ClN₃O₄P₂Pd·0.35CH₂Cl₂ (M_r = 986.46): C, 61.30; H, 4.77; N, 4.26. Found: C, 61.14; H, 4.93; N, 3.98. MS (+FAB) [m/z (%): 856 (31%) [M⁺]; 555 (100%) [(M - ylide)⁺]. IR (ν_{CN}, cm⁻¹): 2172. ¹H: δ 7.92–7.77 (m, Ph), 7.67–7.40 (m, Ph), 6.80–6.43 (m, 4H, C₆H₄, both isomers), 3.50 (q, 1H, CH-dmphea, major isomer, ³J_{H-H} = 6.5 Hz), 3.47 (q, 1H, CH-dmphea, minor isomer, ³J_{H-H} = 6.5 Hz), 3.11 (d, 1H, CH C-ylide, minor, ²J_{P-H} = 14.0 Hz), 3.08 (d, 1H, CH C-ylide, major, ²J_{P-H} = 13.3 Hz), 2.40 (s, 3H, NMe₂, major), 2.09 (s, 3H, NMe₂, minor), 1.99 (s, 3H, NMe₂, minor), 1.79 (s, 3H, NMe₂, major), 1.41 (d, 1H, CH N-ylide, major, ²J_{P-H} = 5.9 Hz), 1.38 (d, 1H, CH N-ylide, minor, ²J_{P-H} = 5.9 Hz), 1.34 (d, 3H, Me-dmphea, major), 1.28 (d, 3H, Me-dmphea, minor). ³¹P{¹H}: δ 27.25 (–P⁺Ph₃, C-ylide, minor), 26.62 (–P⁺Ph₃, C-ylide, major), 24.52 (≡PPh₃, N-ylide, major), 24.28 (≡PPh₃, N-ylide, minor). ¹³C{¹H}: δ 154.18, 154.03, 152.76, 146.83, 132.39, 132.26, 125.38, 125.16, 124.40, 124.13, 122.68, 122.58 (C₆H₄, both isomers), 134.84, 134.37 (J_{P-C} = 11 Hz), 134.08 (J_{P-C} = 13 Hz), 133.39, 132.76 (J_{P-C} = 10 Hz), 129.59 (J_{P-C} = 12 Hz), 129.49 (J_{P-C} = 13 Hz), 125.53 (J_{P-C} = 92 Hz) (PPh₃), 121.90, 120.74 (CN, minor), 121.68, 120.52 (CN, major), 74.36 (CH-dmphea, minor), 74.25 (CH-dmphea, major), 51.24, 45.82 (NMe₂, major), 50.65, 46.42 (NMe₂, minor), 20.43 (Me-dmphea, major), 20.12 (Me-dmphea, minor), 2.20 (CH N-ylide, minor, ¹J_{P-C} = 136 Hz), 1.94 (CH N-ylide, major, ¹J_{P-C} = 136 Hz), –1.48 (CH C-ylide, minor, ¹J_{P-C} = 46 Hz), –1.67 (CH C-ylide, major, ¹J_{P-C} = 46 Hz).

{Pd(dmbsa)[μ-C,N-Ph₃PCHCN]}₂(ClO₄)₂, **9.** To a solution of [Pd(dmbsa)(NCMe)₂](ClO₄) **3** (0.200 g, 0.473 mmol) in 25 mL of CH₂Cl₂ at room temperature was added CPPY (0.142 g, 0.473 mmol). A white solid precipitated immediately. The suspension was stirred for 30 min and filtered, and the solid **9** was washed with CH₂Cl₂ (20 mL) and air-dried. Yield: 0.240 g (80% yield). Complex **9** can also be obtained by reaction of **7** (0.045 g, 0.047 mmol) with [Pd(dmbsa)(NCMe)₂](ClO₄) **3** (0.020 g, 0.047 mmol) in CH₂Cl₂ (5 mL). After 24 h of stirring at room temperature, **9** precipitated as a white solid.

Anal. Calcd for C₅₈H₅₆Cl₂N₄O₈P₂Pd₂ (M_r = 1282.76): C, 54.31; H, 4.40; N, 4.37. Found: C, 53.92; H, 4.08; N, 4.30. MS (+FAB) [m/z (%): 541 (35%) {[Pd(dmbsa)(Ph₃PCHCN)]⁺}. IR (ν_{CN}, cm⁻¹): 2224. Further characterization was not possible due to its extremely low solubility in the usual organic solvents.

Reactions Performed in the NMR Tube. (a) Complex **9** and PPh₃ (molar ratio 1:2) were suspended in 0.4 mL of CDCl₃ and transferred

to an NMR tube. After 18 h at room temperature, the initial suspension had dissolved. The ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of this solution show the presence of **4** as the unique product of reaction. (b) To a suspension of **9** in CDCl_3 (0.4 mL) was added 2 equiv of CPPY. The initial suspension gradually dissolved, and after 12 h at room temperature, the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of this solution showed the presence of **7** as the unique product of reaction.

{Pd((R)-dmphea)[μ -C,N-Ph₃PCHCN]}₂(ClO₄)₂, **10.** To a solution of [Pd((R)-dmphea)(NCMe)₂](ClO₄) **3'** (0.200 g, 0.457 mmol) in 25 mL of CH_2Cl_2 at room temperature was added CPPY (0.137 g, 0.457 mmol). A white solid precipitated immediately. The suspension was stirred for 30 min and filtered, and the solid **10** was washed with CH_2Cl_2 (20 mL) and air-dried. Yield: 0.211 g (66% yield).

Anal. Calcd for $\text{C}_{60}\text{H}_{60}\text{Cl}_2\text{N}_4\text{O}_8\text{P}_2\text{Pd}_2$ (M_r = 1310.81): C, 54.98; H, 4.61; N, 4.27. Found: C, 54.62; H, 4.80; N, 4.25. MS (+FAB) [m/z (%): 1211 (10%) {[Pd₂(R-dmphea)₂(Ph₃PCHCN)₂(ClO₄)⁺]; 555 (35%) {[Pd(R-dmphea)(Ph₃PCHCN)]⁺}. IR (ν_{CN} , cm^{-1}): 2229. Further characterization was not possible due to its extremely low solubility in the usual organic solvents.

{PdCl(dmba)[C(H)(CN)(PPh₃)]}, **11a, {PdCl(dmba)[NC-C(H)=PPh₃]}, **11b**.** To a solution of [Pd(μ -Cl)(dmba)]₂ (**1**) (0.200 g, 0.362 mmol) in 25 mL of CH_2Cl_2 was added CPPY (0.218 g, 0.724 mmol). The resulting pale yellow solution was stirred at room temperature for 30 min and the solvent was then evaporated to dryness. By addition of Et₂O (25 mL) to the oily residue and continuous stirring, **11** (as a mixture of **11a** and **11b**) was obtained as a pale yellow solid, which was filtered and air-dried. Yield: 0.345 g (83% yield). Isomeric ratio: C-coordinated (**11a**)/N-coordinated (**11b**) = 1/1.2.

Anal. Calcd for $\text{C}_{29}\text{H}_{28}\text{ClN}_2\text{PPd}$ (M_r = 577.38): C, 60.32; H, 4.89; N, 4.85. Found: C, 60.38; H, 4.77; N, 4.66. Λ_M ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$): 2.64 (5×10^{-4} M in acetone solution). IR (ν_{CN} , cm^{-1}): 2178. ^1H : δ 7.92–7.85 (m, Ph), 7.63–7.40 (m, Ph), 6.79, 6.68, 6.46, 6.36 (m, 4H, C₆H₄, both isomers), 4.37 (d, 1H, CH ylide **11a**, $^2J_{\text{P-H}}$ = 14.3 Hz), 3.94, 3.42 (AX spin system, 2H, CH₂N **11a**, $^2J_{\text{H-H}}$ = 13 Hz), 3.79 (s, 2H, CH₂N **11b**), 2.78 (s, 6H, NMe₂, **11b**), 2.68 (s, 3H, NMe₂ **11a**), 2.48 (s, 3H, NMe₂ **11a**), 1.92 (d, 1H, CH-ylyde **11b**, $^2J_{\text{P-H}}$ = 6.5 Hz). $^{31}\text{P}\{^1\text{H}\}$: δ 28.07 (–P⁺Ph₃, **11a**), 23.66 (=PPh₃, **11b**). $^{13}\text{C}\{^1\text{H}\}$: δ 147.34, 147.17, 146.87, 146.22, 132.06, 131.93, 128.55, 128.39, 125.00, 124.68, 123.80, 123.05 (C₆H₄, both isomers), 134.37 ($J_{\text{P-C}}$ = 10 Hz), 133.75, 133.00, 132.86 ($J_{\text{P-C}}$ = 10 Hz), 129.31 ($J_{\text{P-C}}$ = 13 Hz), 129.03 ($J_{\text{P-C}}$ = 12 Hz), 126.06 ($J_{\text{P-C}}$ = 92 Hz) (PPh₃), 121.61, 121.04 (CN), 74.10, 73.09 (CH₂N), 52.60 (NMe₂ **11b**), 52.14, 50.13 (NMe₂ **11a**), 1.94 (CH-ylyde **11b**, $^1J_{\text{P-C}}$ = 137 Hz), –6.04 (CH-ylyde **11a**, $^1J_{\text{P-C}}$ = 46 Hz).

{PdCl((R)-dmphea)[C(H)(CN)(PPh₃)]}, **12a, {PdCl((R)-dmphea)[NC-C(H)=PPh₃]}, **12b**.** To a solution of [Pd(μ -Cl)((R)-dmphea)]₂ **1'** (0.236 g, 0.406 mmol) in 25 mL of CH_2Cl_2 was added CPPY (0.245 g, 0.813 mmol). The resulting pale yellow solution was stirred at room temperature for 30 min and the solvent was then evaporated to dryness. By addition of Et₂O (25 mL) to the oily residue and continuous stirring, **12** (as a mixture of **12a** and **12b**) was obtained as a pale yellow solid, which was filtered and air-dried. Yield: 0.359 g (75% yield). Isomeric ratio: C-coordinated (**12a**)/N-coordinated (**12b**) = 1/1. Diastereomeric ratio in **12a**: major/minor = 1.8/1.

Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{ClN}_2\text{PPd}$ (M_r = 591.41): C, 60.92; H, 5.11; N, 4.73. Found: C, 60.62; H, 5.24; N, 4.46. Λ_M ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$): 1.90 (5×10^{-4} M in acetone solution). Mol wt (CHCl₃): found, 592.41 (calcd, 591.41). IR (ν_{CN} , cm^{-1}): 2187. ^1H : δ 7.89–7.82 (m, Ph), 7.62–7.38 (m, Ph), 6.80–6.22 (m, C₆H₄, both isomers), 4.58 (d, 1H, CH-ylyde **12a**, major, $^2J_{\text{P-H}}$ = 14.0 Hz), 4.29 (d, 1H, CH-ylyde **12a**, minor, $^2J_{\text{P-H}}$ = 14.0 Hz), 3.80 (q, 1H, CH-dmphea **12a**, major, $^3J_{\text{H-H}}$ = 6.5 Hz), 3.67 (q, 1H, CH-dmphea **12b**, $^3J_{\text{H-H}}$ = 6 Hz), 3.22 (q, 1H, CH-dmphea **12a**, minor, $^3J_{\text{H-H}}$ = 6 Hz), 2.81, 2.59 (2s, 6H, NMe₂ **12b**), 2.75, 2.33 (2s, 6H, NMe₂ **12a**, minor), 2.54, 2.48 (2s, 6H, NMe₂ **12a**, major), 1.90 (d, 1H, CH-ylyde **12b**, $^2J_{\text{P-H}}$ = 6.5 Hz), 1.43 (d, 3H, Me-dmphea **12b**), 1.30 (d, 3H, Me-dmphea **12a**, major), 1.26 (d, 3H, Me-dmphea **12a**, minor). $^{31}\text{P}\{^1\text{H}\}$: δ 28.31 (–P⁺Ph₃, **12a**, minor), 27.94 (–P⁺Ph₃, **12a**, major), 23.62 (=PPh₃, **12b**). $^{13}\text{C}\{^1\text{H}\}$: δ 153.67, 152.38, 148.15, 146.32, 132.07, 131.91, 128.56, 128.49,

124.75, 123.76, 123.09, 122.95 (C₆H₄), 134.30 ($J_{\text{P-C}}$ = 10 Hz), 133.70, 133.59, 132.85 ($J_{\text{P-C}}$ = 10 Hz), 129.29 ($J_{\text{P-C}}$ = 12 Hz), 129.01 ($J_{\text{P-C}}$ = 11 Hz), 126.07 ($J_{\text{P-C}}$ = 93 Hz) (PPh₃), 122.17, 121.52, 121.20 (CN), 75.89 (2C), 75.34 (CH-dmphea), 52.15, 47.21 (NMe₂, **12b**), 51.25, 48.16 (NMe₂, **12a**, major), 50.39, 47.07 (NMe₂, **12a**, minor), 22.47 (Me-dmphea, **12a**, minor), 22.40 (Me-dmphea, **12a**, major), 19.25 (Me-dmphea, **12b**), 1.89 (CH-ylyde, **12b**, $^1J_{\text{P-C}}$ = 137 Hz), –7.07 (CH-ylyde, **12a**, both isomers, $^1J_{\text{P-C}}$ = 46 Hz).

X-ray Crystal Structure Determination of **5**. Data Collection.

Crystals suitable for X-ray analysis were grown by slow diffusion of *n*-hexane into a CH_2Cl_2 solution of **5** at –18 °C. A crystal of dimensions 0.40 × 0.35 × 0.30 mm was mounted at the end of a quartz fiber and covered with epoxy. Geometric and intensity data were taken at 150 K using normal procedures on an Enraf-Nonius CAD4 automated four-circle diffractometer. After initial indexing of the cell, axial photos were taken for the axes *a*, *b*, and *c* and [111] in order to check the lattice dimensions. The scan parameters for intensity data collection were chosen on the basis of two dimensional (ω – θ) plots of 25 reflections. Data were collected using a variable scan-speed technique in which the weakest data were measured at the slowest scan speed. That is to say, no measurement was skipped or measured rapidly because of weak diffraction. Azimuthal scans of 19 scattering vectors were used as the basis of an absorption correction. No intensity decay was observed in three monitor reflections that were remeasured every 3 h during data collection. Crystal orientation was checked by measuring three standard reflections every 400 reflections during data collection. The cell parameters were refined to the accurately determined positions of 25 reflections ($22.6 \leq 2\theta \leq 31.6^\circ$), each measured at four different positions.

Structure Solution and Refinement. After data reduction, the heavy atoms (Pd, P) of one asymmetric unit were located by an automated procedure that incorporates Patterson analysis, difference direct methods, and Fourier peaklist optimization.³⁰ The remaining non-hydrogen atoms and the hydrogen atom of the ylidic carbon were found from subsequent difference Fourier syntheses. The structure was refined to F_o^2 , and all positive data were used in the refinement.³¹ The remaining hydrogen atoms of the cation were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the O–C(methyl) or N–C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The perchlorate anion was found to be disordered and it was modeled as three equally populated congeners occupying the same interstice and with the chlorine atom common to the three components. During the final refinement, the bonded and 1–3 distances of all three perchlorate moieties were restrained to be similar. The refinement converged with the residuals shown in Table 3.³²

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Supporting Information Available: X-ray crystallographic files in CIF format for compound **5** are available on the Internet only. Access information is given on any current masthead page.

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