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Nitrogen- *vs* Carbon-Coordination of the α-Cyano-Stabilized Phosphorus Ylide $\mathrm{Ph_3P{=}C(H)CN}$. X-ray Crystal Structure of $\{\mathrm{Pd(dmba)[P(OMe)_3][N{\equiv}C{-}C(H){=}PPh_3]}\}(\mathrm{ClO_4})$

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The reaction of the solvated complexes $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})(\mathrm{THF})](\mathrm{ClO_4})$ [$\overset{\frown}{\mathrm{C\,N}}$ = 2-((dimethylamino)methyl)phenyl-C^1,N or dmba, 2-(1-(R)-(dimethylamino)ethyl)phenyl-C^1,N or (R)-dmphea; $\mathrm{PR'_3} = \mathrm{PPh_3}$, $\mathrm{P(OMe)_3}$] with a stoichiometric amount of $\mathrm{Ph_3P{=}C(H)CN}$ (CPPY) (1:1 molar ratio), in THF at low temperature, gives the cationic derivatives $\{\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})[\mathrm{N{\equiv}C{-}C(H){=}PPh_3}]\}(\mathrm{ClO_4})$, **4**−**6**, in which the ylide ligand is N-coordinated to the $\mathrm{Pd^{II}}$ center and *trans* to the *ortho*-metalated $\mathrm{C_6H_4}$ group, in an "end-on nitrile" coordination mode that is unprecedented for this ylide. The reaction of $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{NCMe})_2](\mathrm{ClO_4})$ ($\overset{\frown}{\mathrm{C\,N}}$ = dmba, (R)-dmphea) with $\mathrm{Ph_3P{=}C(H)CN}$ (1:2 molar ratio) gives the bis(ylide) complexes $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{Ph_3PCHCN})_2](\mathrm{ClO_4})$ (**7**, **8**) in which one of the ylides is C-coordinated (*trans* to the $\mathrm{NMe_2}$ group) and the other one is N-bonded (and *trans* to the $\mathrm{C_6H_4}$ group). Either by reaction of $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{NCMe})_2](\mathrm{ClO_4})$ with $\mathrm{Ph_3P{=}C(H)CN}$ (1:1 molar ratio) or by reaction of the bis(ylide) complexes $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{Ph_3PCHCN})_2](\mathrm{ClO_4})$ with $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{NCMe})_2](\mathrm{ClO_4})$ (1:1 molar ratio), very insoluble materials of stoichiometry $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{Ph_3PCHCN})(\mathrm{ClO_4})]$ (**9**, **10**) are obtained, which appear to be dinuclear derivatives with the ylide acting as a *C,N*-bridging group, $[(\overset{\frown}{\mathrm{C\,N}})\mathrm{Pd}(\mu\text{-C,N-Ph_3PCHCN})_2\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})](\mathrm{ClO_4})_2$. At the same time, this ylide is shown to be sufficiently nucleophilic to promote the bridge-splitting of the dinuclear $[\mathrm{Pd}(\mu\text{-Cl})(\overset{\frown}{\mathrm{C\,N}})]_2$ complexes, giving the mononuclear derivatives $[\mathrm{PdCl}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{Ph_3PCHCN})]$ (**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 $\{\mathrm{Pd(dmba)[P(OMe)_3][N{\equiv}C{-}C(H){=}PPh_3]}\}(\mathrm{ClO_4})$ (**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, $\beta = 92.560(10)°$, $Z = 4$, $V = 3302.5(6)$ Å^3, 4881 reflections with $I > 2\sigma(I)$ for the refinement of 423 parameters and 30 restraints, R1 = 0.0384, wR2 = 0.0961, and GOF = 1.044.

Introduction

The carbonyl-stabilized phosphorus ylides $\mathrm{R_3P{=}C(R')COR''}$ (R, R′, R″ = 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 $\mathrm{Ph_3P{=}C(H)CN}$, have received much less attention. In fact, for the latter, very few reports on its ability to act as a ligand[2] or as a synthetic tool in organic chemistry[3] 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 $\mathrm{Ph_3P{=}C(H)CN}$ (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 $\mathrm{Ph_3P{=}C(H)CN}$ (CPPY) toward several C,N-cyclometalated complexes of $\mathrm{Pd^{II}}$ of stoichiometry $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{L})(\mathrm{L'})](\mathrm{ClO_4})$ ($\overset{\frown}{\mathrm{C\,N}}$ = dmba, (R)-dmphea; L = $\mathrm{PPh_3}$, $\mathrm{P(OMe)_3}$, L′ = THF; L = L′ = NCMe) and $[\mathrm{Pd}(\mu\text{-Cl})(\overset{\frown}{\mathrm{C\,N}})]_2$ ($\overset{\frown}{\mathrm{C\,N}}$ = dmba, (R)-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 $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})(\mathrm{THF})](\mathrm{ClO_4})$ with CPPY. The starting solvated complexes $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})(\mathrm{THF})](\mathrm{ClO_4})$ [$\overset{\frown}{\mathrm{C\,N}}$ = dmba, (R)-dmphea; $\mathrm{PR'_3} = \mathrm{PPh_3}$, $\mathrm{P(OMe)_3}$] were prepared by reaction of the corresponding chloride derivatives $[\mathrm{PdCl}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})]$ (**2**−**2″**, see Scheme 1) with $\mathrm{AgClO_4}$ (1:1 molar ratio) in THF at room temperature. Once the AgCl had been eliminated by filtration, the freshly prepared solution of $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})(\mathrm{THF})](\mathrm{ClO_4})$ was cooled to 0 °C and allowed to react with CPPY (1:1 molar ratio), giving white solids of stoichiometry $[\mathrm{Pd}(\overset{\frown}{\mathrm{C\,N}})(\mathrm{PR'_3})(\mathrm{CPPY})](\mathrm{ClO_4})$ [$\overset{\frown}{\mathrm{C\,N}}$ = dmba, $\mathrm{PR'_3} = \mathrm{PPh_3}$, **4**, $\mathrm{P(OMe)_3}$, **5**; $\overset{\frown}{\mathrm{C\,N}}$ = (R)-dmphea, $\mathrm{PR'_3} = \mathrm{PPh_3}$,

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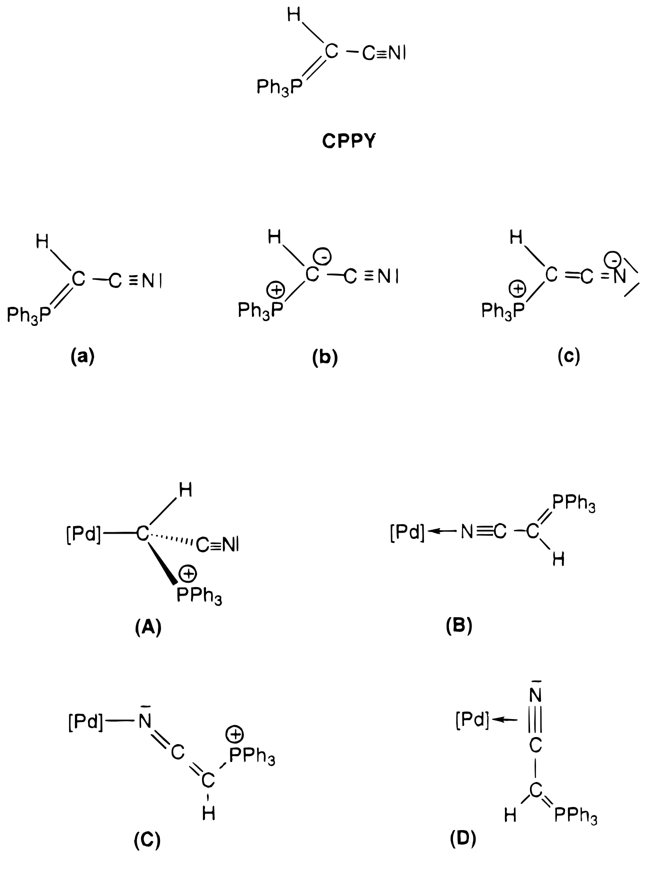

Figure 1

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 ν(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 ν(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 ν(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 ν(CN) frequency.

The ^{1}H NMR spectra of **4**−**6** show, in addition to the expected resonances for the dmba (or the (*R*)-dmphea) and PPh$_3$ [or P(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 PC*H* proton. These values of δ(C*H*) and $^2J_{\text{P-H}}$ are very close to those reported[8] for the free ylide and are very different from those found[2b] in [Pd(μ-Cl)Cl(CPPY)]$_2$ (for which C-coordination has been proposed). Moreover, the ^{31}P{^{1}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}C{^{1}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 similars to those found in the free ylide (−2.17 ppm/136 Hz). All these facts imply that no important structural and electronic changes have occured in the neighborhood of the ylidic fragment −C(H)═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 [Pd]←N≡C−R, −R being the ylidic group −C(H)═PPh$_3$.

The PR′$_3$-*trans*-to-NMe$_2$ ligand arrangement in the starting products[9] 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$_2$N protons with the phosphorus atom.[10,11] Thus, an N(ylide)-*trans*-to-C(*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 {Pd(dmba)[P(OMe)$_3$][N≡C−C(H)═PPh$_3$]}(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 dmba 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 dmba[4,10,11] and P(OMe)$_3$ ligands[12,13] are similar to those found in other complexes containing these ligands. The Pd(1)−N(2) bond distance [2.076 (3) Å] is similar to that found in other palladium-nitrile complexes,[14] and the N(2)−C(13) bond distance [1.156 (5) Å] is fairly typical of nitriles.[14,15] The C(13)−C(14) bond distance [1.379 (5) Å] is shorter than a C(sp^2)−C(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 Ph$_3$P═**C**(H)−**C**OPh[16] and 1.366(4) Å for {Pd(dmba)(py)[O**C**(Me)═**C**(H)PPh$_3$]}(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 −C(H)═PPh$_3$ remains almost unaltered; the P(2)−C(14) bond distance [1.710 (4) Å] is similar, within experimental error, to those determined for the free ylide Ph$_3$**P**═**C**H$_2$ [1.697(3), 1.688(3) Å][17] or other free keto stabilized ylides, such as

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Scheme 1

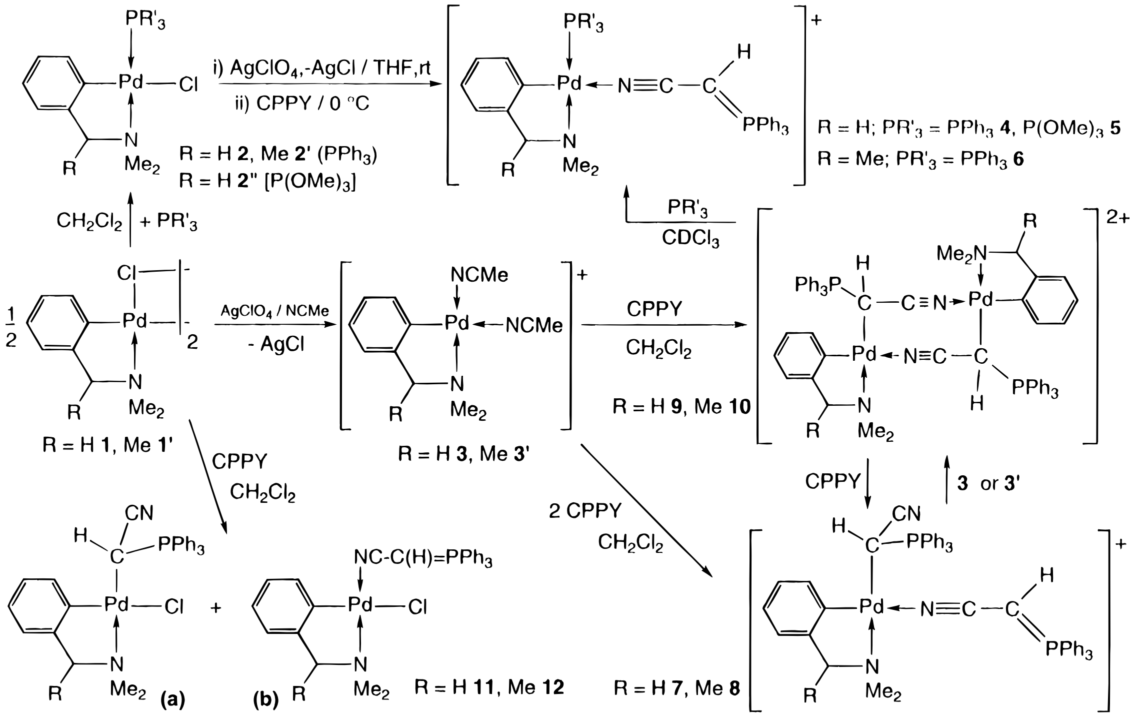

Table 1. Relevant IR Absorptions (ν, cm^{-1}) for Complexes **4**−**12**

complex	ν(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] $\Delta\nu = \nu(\mathrm{CN})_{\mathrm{complex}} - \nu(\mathrm{CN})_{\mathrm{free\ ylide}}$.

Table 2. Relevant NMR Data (δ, ppm; ^nJ, Hz) for Complexes **4**−**12**

complex	δ(C*H*)	$^2J_{\mathrm{P-H}}$	δ(P)	δ(*C*H)	$^1J_{\mathrm{P-C}}$
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
(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 CD_2Cl_2. Values for ^{1}H RMN in ref 8 are δ = 1.62 ppm, $J_{\mathrm{PCH}}{}^{-60\ °\mathrm{C}}$ = 7.5 Hz. [d] $CDCl_3$, room temperature.

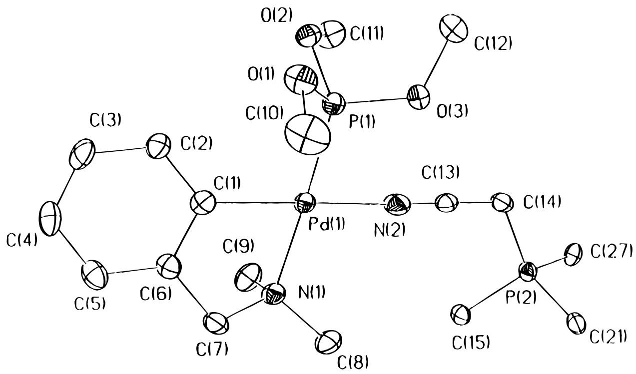

Figure 2. Thermal ellipsoid plot of the {Pd(dmba)[P(OMe)$_3$][NC−C(H)=PPh$_3$]}$^+$ cation. Ph groups (except C$_{\mathrm{ipso}}$) and H atoms are omitted for clarity. Atoms are drawn at the 50% probability level.

Table 3. Crystal Data for **5**

formula	$C_{32}H_{37}ClN_2O_7P_2Pd$	*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 rflcns	5790
b, Å	17.857(2)	no of rflcns with $I > 2\sigma(I)$	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] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. $GOF = [\sum w(F_o^2 - F_c^2)^2/(n_{\mathrm{observns}} - n_{\mathrm{params}})]^{1/2}$.

Ph$_3$**P=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 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 [∑angles = 360.0°] 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 atoms[19] bonded to palladium and the antisym-

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(18) The reaction of the solvated complexes [Pd(C$\frown$N)(PPh$_3$)(THF)](ClO$_4$) (C$\frown$N = dmba, (*R*)-dmphea) with the ylides Ph$_3$P=C(H)COR (R = Me, Ph, OMe) gives products of stoichiometry [Pd(C$\frown$N)(PPh$_3$)(ylide)](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 PR_3 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 atom[21]) 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 $Ph_3P{=}C(H)COR$ (R = Me, Ph, OMe).[4,18] We will return to this point presently.

Reactions of [Pd(C$^\frown$N)(NCMe)$_2$](ClO$_4$) with CPPY. The reaction of [Pd(C$^\frown$N)(NCMe)$_2$](ClO$_4$) (**3**, **3′**; see Scheme 1) with CPPY (1:2 molar ratio) in CH_2Cl_2 at room temperature gives, after solvent evaporation and Et_2O addition, white solids of stoichiometry [Pd(C$^\frown$N)(CPPY)$_2$](ClO$_4$) (C$^\frown$N = dmba **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 C_6H_4 groups, an AB spin system for the CH_2N protons and two singlet resonances for the CH_3 protons of the NMe_2 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 $^{31}P\{^1H\}$ NMR spectrum of **7** shows two singlet resonances of relative intensity 1:1 at 26.80 and 24.35 ppm, and in the $^{13}C\{^1H\}$ 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 $[PdCl_2(CPPY)_2]$[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-NMe_2 or N-*trans*-to-NMe_2), 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 H_6 proton of the dmba 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 NMe_2 group and the N-coordinated ylide is *trans* to the *ortho*-metalated C_6H_4 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 $sp^2 \rightarrow sp^3$ at the ylidic carbon atom.[1] Thus, the methine PC*H* 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 *P*CH of the C-coordinated ylide has also been shifted downfield (approximately 2.5 ppm) while the ylidic carbon resonance P*C*H 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} center[20] 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 C_6H_4 group. This noteworthy isomerism of the ligand, similar to that observed in the well-known example of [Pd(Ph$_2$PCH$_2$CH$_2$CH$_2$NMe$_2$)(*N*CS)(*S*CN)],[23] has no precedent for ylides and clearly shows the ambidentate character of this ylide ligand.

Other reactions with the solvated complexes [Pd(C$^\frown$N)(NCMe)$_2$](ClO$_4$) were attempted. The reaction of [Pd(C$^\frown$N)(NCMe)$_2$](ClO$_4$) (**3**, **3′**; see Scheme 1) with CPPY (1:1 molar ratio) in CH_2Cl_2 at room temperature gives the immediate precipitation of white solids of stoichiometry [Pd(C$^\frown$N)(CPPY)(ClO$_4$)] (C$^\frown$N = dmba **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 $[Pd(dmba)(CPPY)]^+$. That of **10** shows a peak at 555 [Pd((*R*)-dmphea)(CPPY)]$^+$ and another one at 1211, corresponding to the binuclear species [Pd$_2$((*R*)-dmphea)$_2$-

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(22) We prepared a sample of $PdCl_2(CPPY)_2$ in order to measure the chemical shift δ(PC*H*) and the coupling constants $^2J_{P-H}$ and $^1J_{P-C}$ of an authentic C-coordinated ylide.This complex has already been prepared by Burmeister *et al.*,[2c] but the NMR spectroscopic data were not reported. The product was obtained as a mixture of the *RR/SS* and *RS* diastereoisomers. Data ($CDCl_3$) are as follows: ^1H δ(PC*H*) = 3.74 ppm ($^2J_{P-H}$ = 12.7 Hz), 3.68 ppm ($^2J_{P-H}$ = 12.6 Hz); $^{31}P\{^1H\}$ δ(*P*CH) = 28.19 and 27.26 ppm; $^{13}C\{^1H\}$ δ(P*C*H) = −4.62 ppm ($^1J_{P-C}$ = 51.7 Hz), −5.84 ppm ($^1J_{P-C}$ = 52.0 Hz).

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$(CPPY)_2(ClO_4)]^+$ 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 ClO_4^- anion are not split, as expected for the low symmetry (C_{3v}) monodentate ligand[24,25] $-OClO_3$ 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 ClO_4^- 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 $[Pd(dmba)(NCMe)_2]^+$ (**3**) in equimolecular amounts, and inversely, the reaction of **9** with 2 equiv of CPPY gives **7** exclusively. Complex **9** also reacts with PPh_3 (1:2 molar ratio) producing bridge splitting and giving **4** in quantitative yield (see Experimental Section). However, while the free ylide or PPh_3 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 $[Pd(\mu\text{-}Cl)(C\frown N)]_2$ with CPPY. The reactions of the binuclear chloride-bridged complexes $[Pd(\mu\text{-}Cl)(C\frown N)]_2$ (**1**, **1′**; see Scheme 1) with CPPY (1:2 molar ratio) in CH_2Cl_2 at room temperature give, after solvent evaporation and Et_2O addition, pale yellow solids of stoichiometry $[PdCl(C\frown N)(CPPY)]$ ($C\frown N$ = dmba **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 CH_2N and NMe_2 protons, and a doublet for the methine PC*H* proton at 1.92 ppm ($^2J_{P-H}$ = 6.5 Hz). The minor isomer shows diastereotopic CH_2N protons, two singlets for the NMe_2 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 $[Pd(\mu\text{-}Cl)(C\frown N)]_2$, giving an almost equimolar distribution of products. The $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ 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 $CDCl_3$ 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 C_6H_4 *ortho*-metalated group (and *trans* to the NMe_2 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 (H_6 of the dmba 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 dmba 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 $Pd(\mu\text{-}Cl)_2Pd$ 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 $Ph_3P{=}C(H)CN$ (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 P_2O_5 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), $^{13}C\{^1H\}$ (75.47 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (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 $[Pd(\mu\text{-}Cl)(C\frown N)]_2$[28]

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(C$\frown$N = dmba **1** and (*R*)-dmphea **1′**), [PdCl(C$\frown$N)(PR′$_3$)][9] [PR′$_3$ = PPh$_3$; C$\frown$N = dmba **2**, (*R*)-dmphea **2′**; PR′$_3$ = P(OMe)$_3$; C$\frown$N = dmba **2″**), [Pd(C$\frown$N)(NCMe)$_2$](ClO$_4$)[29] [C$\frown$N = dmba **3**, (*R*)-dmphea **3′**], and the ylide Ph$_3$P=C(H)CN (CPPY)[3a] were prepared according to published methods.

{Pd(dmba)(PPh$_3$)[N≡C−C(H)=PPh$_3$]}(ClO$_4$), 4. To a solution of PdCl(dmba)(PPh$_3$) **2** (0.129 g, 0.239 mmol) in THF (25 mL) was added AgClO$_4$ (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 Et$_2$O, giving complex **4** as a white solid, which was filtered and air-dried. Yield: 0.173 g (80% yield). Crude **4** was recrystallized from CH$_2$Cl$_2$/*n*-hexane. The white crystals of **4**·0.25CH$_2$Cl$_2$ were used for elemental analysis and NMR measurements. The amount of CH$_2$Cl$_2$ of crystallization was determined by ^{1}H NMR integration.

Anal. Calcd for C$_{47}$H$_{43}$ClN$_2$O$_4$P$_2$Pd·0.25CH$_2$Cl$_2$ (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. ^{1}H: δ 7.69−7.35 (m, 30H, Ph), 6.94 (d, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}}$ = 7 Hz), 6.79 (false t, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}}$ = 7 Hz), 6.33 (false t, 1H, C$_6$H$_4$), 6.19 (false t, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}} \cong {}^{4}J_{\mathrm{P-H}}$ = 7 Hz), 3.94 (d, 2H, CH$_2$N, $^{4}J_{\mathrm{P-H}}$ = 1.8 Hz), 2.30 (d, 6H, NMe$_2$, $^{4}J_{\mathrm{P-H}}$ = 2.5 Hz), 1.24 (d, 1H, CH ylide, $^{2}J_{\mathrm{P-H}}$ = 5.4 Hz). ^{31}P{^{1}H}: δ 42.40 (Pd-PPh$_3$), 24.17 (=PPh$_3$). ^{13}C {^{1}H}: δ 149.18, 146.40, 137.95 ($J_{\mathrm{P-C}}$ = 11 Hz), 130.32, 125.20 ($J_{\mathrm{P-C}}$ = 15 Hz), 124.82 (C$_6$H$_4$), 134.86 ($J_{\mathrm{P-C}}$ = 12 Hz), 133.62, 132.68 ($J_{\mathrm{P-C}}$ = 10 Hz), 131.27, 129.55 ($J_{\mathrm{P-C}}$ = 13 Hz), 128.63 ($J_{\mathrm{P-C}}$ = 11 Hz), 125.07 ($^{1}J_{\mathrm{P-C}}$ = 93 Hz) (PPh$_3$), 123.00 (CN), 71.97 (CH$_2$N), 50.35 (NMe$_2$), 1.49 (CH ylide, $^{1}J_{\mathrm{P-C}}$ = 136 Hz).

{Pd(dmba)[P(OMe)$_3$][N≡C−C(H)=PPh$_3$]}(ClO$_4$), 5. Complex **5** was synthesized in a manner similar to that used for **4**: {Pd(dmba)[P(OMe)$_3$](THF)}(ClO$_4$) (prepared from PdCl(dmba)[P(OMe)$_3$] **2″** (0.196 g, 0.489 mmol) and AgClO$_4$ (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 C$_{32}$H$_{37}$ClN$_2$O$_7$P$_2$Pd (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. ^{1}H: δ 7.69−7.54 (m, 15H, Ph), 7.10 (m, 1H, C$_6$H$_4$), 6.95 (m, 2H, C$_6$H$_4$), 6.87 (m, 1H, C$_6$H$_4$), 3.94 (d, 2H, CH$_2$N, $^{4}J_{\mathrm{P-H}}$ = 2.7 Hz), 3.59 (d, 9H, −OMe, $^{3}J_{\mathrm{P-H}}$ = 13 Hz), 2.38 (d, 6H, NMe$_2$, $^{4}J_{\mathrm{P-H}}$ = 3.9 Hz), 2.03 (d, 1H, CH ylide, $^{2}J_{\mathrm{P-H}}$ = 5.2 Hz). ^{31}P{^{1}H}: δ 118.84 (Pd-P(OMe)$_3$), 24.68 (=PPh$_3$). ^{13}C {^{1}H}: δ 149.03 ($J_{\mathrm{P-C}}$ = 4 Hz), 145.43, 136.40 ($J_{\mathrm{P-C}}$ = 12 Hz), 133.21 ($J_{\mathrm{P-C}}$ = 8 Hz), 126.27 ($J_{\mathrm{P-C}}$ = 7 Hz), 125.58 (C$_6$H$_4$), 133.66 ($^{4}J_{\mathrm{P-C}}$ = 2 Hz), 132.72 ($^{3}J_{\mathrm{P-C}}$ = 10 Hz), 129.63 ($^{2}J_{\mathrm{P-C}}$ = 13 Hz), 125.16 ($^{1}J_{\mathrm{P-C}}$ = 93 Hz) (PPh$_3$), 123.47 (CN), 71.51 (CH$_2$N, $^{3}J_{\mathrm{P-C}}$ = 4 Hz), 53.07 (OMe), 49.93 (NMe$_2$, $^{3}J_{\mathrm{P-C}}$ = 3 Hz), 1.64 (CH ylide, $^{1}J_{\mathrm{P-C}}$ = 135 Hz).

{Pd((*R*)-dmphea)(PPh$_3$)[N≡C−C(H)=PPh$_3$]}(ClO$_4$), 6. Complex **6** was synthesized in a manner similar to that used for **4**: [Pd((*R*)-dmphea)(PPh$_3$)(THF)](ClO$_4$) (prepared from PdCl((*R*)-dmphea)(PPh$_3$) **2′** (0.308 g, 0.556 mmol) and AgClO$_4$ (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 C$_{48}$H$_{45}$ClN$_2$O$_4$P$_2$Pd (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. ^{1}H: δ 7.67−7.31 (m, 30H, Ph), 6.90 (dd, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}}$ = 7.5 Hz, $^{4}J_{\mathrm{H-H}}$ = 1.3 Hz), 6.79 (false t, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}}$ = 7 Hz), 6.33 (false t, 1H, C$_6$H$_4$), 6.19 (false t, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}} \cong {}^{4}J_{\mathrm{P-H}}$ = 7 Hz), 3.69 (q, 1H, CH−dmphea, $^{3}J_{\mathrm{H-H}}$ = 6 Hz), 2.43 (d, 3H, NMe$_2$, $^{4}J_{\mathrm{P-H}}$ = 1.8 Hz), 2.06 (d, 3H, NMe$_2$, $^{4}J_{\mathrm{P-H}}$ = 3.2 Hz), 1.62 (d, 3H, Me−dmphea), 1.26 (d, 1H, CH ylide, $^{2}J_{\mathrm{P-H}}$ = 5.4 Hz). ^{31}P{^{1}H}: δ 41.70 (Pd-PPh$_3$), 24.24 (=PPh$_3$). ^{13}C {^{1}H}: δ 155.03, 145.97, 137.86 ($J_{\mathrm{P-C}}$ = 12 Hz), 130.41, 125.12 ($J_{\mathrm{P-C}}$ = 5 Hz), 124.85 (C$_6$H$_4$), 134.79 ($J_{\mathrm{P-C}}$ = 12 Hz), 133.60, 132.69 ($J_{\mathrm{P-C}}$ = 10 Hz), 131.23, 129.53 ($J_{\mathrm{P-C}}$ = 13 Hz), 128.63 ($J_{\mathrm{P-C}}$ = 10 Hz), 125.09 ($^{1}J_{\mathrm{P-C}}$ = 93 Hz) (PPh$_3$), 122.91 (CN), 74.43 (CH−dmphea), 50.53, 46.28 (NMe$_2$), 22.06 (Me−dmphea), 1.53 (CH ylide, $^{1}J_{\mathrm{P-C}}$ = 136 Hz).

{Pd(dmba)[C(H)(C≡N)(PPh$_3$)][N≡C−C(H)=PPh$_3$]}(ClO$_4$), 7. To a solution of [Pd(dmba)(NCMe)$_2$](ClO$_4$) **3** (0.155 g, 0.367 mmol) in 25 mL of CH$_2$Cl$_2$ 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 Et$_2$O (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 C$_{49}$H$_{44}$ClN$_3$O$_4$P$_2$Pd (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. ^{1}H: δ 7.89−7.82 (m, Ph), 7.65−7.40 (m, Ph), 6.79 (m, 2H, C$_6$H$_4$), 6.79 (td, 1H, C$_6$H$_4$, $^{3}J_{\mathrm{H-H}}$ = 7.6 Hz, $^{4}J_{\mathrm{H-H}}$ = 2 Hz), 6.27 (d, 1H, C$_6$H$_4$), 3.72, 3.61 (AB spin system, 2H, CH$_2$N, $^{2}J_{\mathrm{H-H}}$ = 14 Hz), 3.05 (d, 1H, CH *C*-ylide, $^{2}J_{\mathrm{P-H}}$ = 13.8 Hz), 2.25 (s, 3H, NMe$_2$), 1.98 (s, 3H, NMe$_2$), 1.45 (d, 1H, CH *N*-ylide, $^{2}J_{\mathrm{P-H}}$ = 6.0 Hz). ^{31}P{^{1}H}: δ 26.80 (−P$^+$Ph$_3$, *C*-ylide), 24.35 (=PPh$_3$, *N*-ylide). ^{13}C {^{1}H}: δ 148.22, 147.25, 132.19, 125.16, 124.12, 122.55 (C$_6$H$_4$), 134.43, 134.15 ($J_{\mathrm{P-C}}$ = 10 Hz), 133.42, 132.76 ($J_{\mathrm{P-C}}$ = 10 Hz), 129.51 ($J_{\mathrm{P-C}}$ = 13 Hz), 125.15 ($^{1}J_{\mathrm{P-C}}$ = 92 Hz) (PPh$_3$), 121.71, 120.55 (CN), 72.14 (CH$_2$N), 51.21, 50.33 (NMe$_2$), 1.88 (CH *N*-ylide, $^{1}J_{\mathrm{P-C}}$ = 136 Hz), −1.25 (CH *C*-ylide, $^{1}J_{\mathrm{P-C}}$ = 46 Hz).

{Pd((*R*)-dmphea)[C(H)(C≡N)(PPh$_3$)][N≡C−C(H)=PPh$_3$]}(ClO$_4$), 8. Complex **8** was obtained in a manner similar to that for **7**: [Pd((*R*)-dmphea)(NCMe)$_2$](ClO$_4$) **3′** (0.146 g, 0.335 mmol) reacted in CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$/*n*-hexane. The white microcrystalline solid of **8**·0.35CH$_2$Cl$_2$ was used for analytical and spectrocopic measurements. The amount of CH$_2$Cl$_2$ of crystallization was determined by ^{1}H NMR integration.

Anal. Calcd for C$_{50}$H$_{46}$ClN$_3$O$_4$P$_2$Pd·0.35CH$_2$Cl$_2$ (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. ^{1}H: δ 7.92−7.77 (m, Ph), 7.67−7.40 (m, Ph), 6.80−6.43 (m, 4H, C$_6$H$_4$, both isomers), 3.50 (q, 1H, CH−dmphea, major isomer, $^{3}J_{\mathrm{H-H}}$ = 6.5 Hz), 3.47 (q, 1H, CH−dmphea, minor isomer, $^{3}J_{\mathrm{H-H}}$ = 6.5 Hz), 3.11 (d, 1H, CH *C*-ylide, minor, $^{2}J_{\mathrm{P-H}}$ = 14.0 Hz), 3.08 (d, 1H, CH *C*-ylide, major, $^{2}J_{\mathrm{P-H}}$ = 13.3 Hz), 2.40 (s, 3H, NMe$_2$, major), 2.09 (s, 3H, NMe$_2$, minor), 1.99 (s, 3H, NMe$_2$, minor), 1.79 (s, 3H, NMe$_2$, major), 1.41 (d, 1H, CH *N*-ylide, major, $^{2}J_{\mathrm{P-H}}$ = 5.9 Hz), 1.38 (d, 1H, CH *N*-ylide, minor, $^{2}J_{\mathrm{P-H}}$ = 5.9 Hz), 1.34 (d, 3H, Me−dmphea, major), 1.28 (d, 3H, Me−dmphea, minor). ^{31}P{^{1}H}: δ 27.25 (−P$^+$Ph$_3$, *C*-ylide, minor), 26.62 (-P$^+$Ph$_3$, *C*-ylide, major), 24.52 (=PPh$_3$, *N*-ylide, major), 24.28 (=PPh$_3$, *N*-ylide, minor). ^{13}C{^{1}H}: 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 (C$_6$H$_4$, both isomers), 134.84, 134.37 ($J_{\mathrm{P-C}}$ = 11 Hz), 134.08 ($J_{\mathrm{P-C}}$ = 13 Hz), 133.39, 132.76 ($J_{\mathrm{P-C}}$ = 10 Hz), 129.59 ($J_{\mathrm{P-C}}$ = 12 Hz), 129.49 ($J_{\mathrm{P-C}}$ = 13 Hz), 125.53 ($^{1}J_{\mathrm{P-C}}$ = 92 Hz) (PPh$_3$), 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 (NMe$_2$, major), 50.65, 46.42 (NMe$_2$, minor), 20.43 (Me−dmphea, major), 20.12 (Me−dmphea, minor), 2.20 (CH *N*-ylide, minor, $^{1}J_{\mathrm{P-C}}$ = 136 Hz), 1.94 (CH *N*-ylide, major, $^{1}J_{\mathrm{P-C}}$ = 136 Hz), −1.48 (CH *C*-ylide, minor, $^{1}J_{\mathrm{P-C}}$ = 46 Hz), −1.67 (CH *C*-ylide, major, $^{1}J_{\mathrm{P-C}}$ = 46 Hz).

{Pd(dmba)[*μ*-*C*,*N*-Ph$_3$PCHCN]}$_2$(ClO$_4$)$_2$, 9. To a solution of [Pd(dmba)(NCMe)$_2$](ClO$_4$) **3** (0.200 g, 0.473 mmol) in 25 mL of CH$_2$Cl$_2$ 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 CH$_2$Cl$_2$ (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(dmba)(NCMe)$_2$](ClO$_4$) **3** (0.020 g, 0.047 mmol) in CH$_2$Cl$_2$ (5 mL). After 24 h of stirring at room temperature, **9** precipitated as a white solid.

Anal. Calcd for C$_{58}$H$_{56}$Cl$_2$N$_4$O$_8$P$_2$Pd$_2$ (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(dmba)(Ph$_3$PCHCN)]$^+$}. 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 PPh$_3$ (molar ratio 1:2) were suspended in 0.4 mL of CDCl$_3$ and transferred

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(29) Forniés, J.; Navarro, R.; Sicilia, V. *Polyhedron* **1988**, *7*, 2659.

to an NMR tube. After 18 h at room temperature, the initial suspension had dissolved. The ^{1}H and ^{31}P{^{1}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 ^{1}H and ^{31}P{^{1}H} NMR spectra of this solution showed the presence of **7** as the unique product of reaction.

{Pd((*R*)-dmphea)[*μ*-*C*,*N*-Ph$_3$PCHCN]}$_2$(ClO$_4$)$_2$, 10. To a solution of [Pd((*R*)-dmphea)(NCMe)$_2$](ClO$_4$) **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 $C_{60}H_{60}Cl_2N_4O_8P_2Pd_2$ (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%) {[Pd$_2$(*R*-dmphea)$_2$(Ph$_3$PCHCN)$_2$(ClO$_4$)]$^+$}; 555 (35%) {[Pd(*R*-dmphea)(Ph$_3$PCHCN)]$^+$}. 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)(PPh$_3$)]}, 11a, {PdCl(dmba)[NC−C(H)=PPh$_3$]}, 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 Et_2O (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 $C_{29}H_{28}ClN_2PPd$ (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 (Ω^{-1} cm^2 mol^{-1}): 2.64 (5×10^{-4} M in acetone solution). IR (ν_{CN}, cm^{-1}): 2178. ^{1}H: δ 7.92−7.85 (m, Ph), 7.63−7.40 (m, Ph), 6.79, 6.68, 6.46, 6.36 (m, 4H, C_6H_4, both isomers), 4.37 (d, 1H, CH ylide **11a**, $^{2}J_{P-H}$ = 14.3 Hz), 3.94, 3.42 (AX spin system, 2H, CH_2N **11a**, $^{2}J_{H-H}$ = 13 Hz), 3.79 (s, 2H, CH_2N **11b**), 2.78 (s, 6H, NMe$_2$, **11b**), 2.68 (s, 3H, NMe$_2$ **11a**), 2.48 (s, 3H, NMe$_2$ **11a**), 1.92 (d, 1H, CH−ylide **11b**, $^{2}J_{P-H}$ = 6.5 Hz). ^{31}P{^{1}H}: δ 28.07 (−P$^+$Ph$_3$, **11a**), 23.66 (=PPh$_3$, **11b**). ^{13}C {^{1}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 (C_6H_4, both isomers), 134.37 (J_{P-C} = 10 Hz), 133.75, 133.00, 132.86 (J_{P-C} = 10 Hz), 129.31 (J_{P-C} = 13 Hz), 129.03 (J_{P-C} = 12 Hz), 126.06 ($^{1}J_{P-C}$ = 92 Hz) (PPh$_3$), 121.61, 121.04 (CN), 74.10, 73.09 (CH_2N), 52.60 (NMe$_2$ **11b**), 52.14, 50.13 (NMe$_2$ **11a**), 1.94 (CH−ylide **11b**, $^{1}J_{P-C}$ = 137 Hz), −6.04 (CH−ylide **11a**, $^{1}J_{P-C}$ = 46 Hz).

{PdCl((*R*)-dmphea)[C(H)(CN)(PPh$_3$)]}, 12a, {PdCl((*R*)-dmphea)[NC−C(H)=PPh$_3$]}, 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 Et_2O (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 $C_{30}H_{30}ClN_2PPd$ (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 (Ω^{-1} cm^2 mol^{-1}): 1.90 (5×10^{-4} M in acetone solution). Mol wt ($CHCl_3$): found, 592.41 (calcd, 591.41). IR (ν_{CN}, cm^{-1}): 2187. ^{1}H: δ 7.89−7.82 (m, Ph), 7.62−7.38 (m, Ph), 6.80−6.22 (m, C_6H_4, both isomers), 4.58 (d, 1H, CH−ylide **12a**, major, $^{2}J_{P-H}$ = 14.0 Hz), 4.29 (d, 1H, CH−ylide **12a**, minor, $^{2}J_{P-H}$ = 14.0 Hz), 3.80 (q, 1H, CH−dmphea **12a**, major, $^{3}J_{H-H}$ = 6.5 Hz), 3.67 (q, 1H, CH−dmphea, **12b**, $^{3}J_{H-H}$ = 6 Hz), 3.22 (q, 1H, CH−dmphea **12a**, minor, $^{3}J_{H-H}$ = 6 Hz), 2.81, 2.59 (2s, 6H, NMe$_2$ **12b**), 2.75, 2.33 (2s, 6H, NMe$_2$ **12a**, minor), 2.54, 2.48 (2s, 6H, NMe$_2$ **12a**, major), 1.90 (d, 1H, CH−ylide **12b**, $^{2}J_{P-H}$ = 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}P{^{1}H}: δ 28.31 (−P$^+$Ph$_3$, **12a**, minor), 27.94 (−P$^+$Ph$_3$, **12a**, major), 23.62 (=PPh$_3$, **12b**). ^{13}C{^{1}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 (C_6H_4), 134.30 (J_{P-C} = 10 Hz), 133.70, 133.59, 132.85 (J_{P-C} = 10 Hz), 129.29 (J_{P-C} = 12 Hz), 129.01 (J_{P-C} = 11 Hz), 126.07 ($^{1}J_{P-C}$ = 93 Hz) (PPh$_3$), 122.17, 121.52, 121.20 (CN), 75.89 (2C), 75.34 (CH−dmphea), 52.15, 47.21 (NMe$_2$, **12b**), 51.25, 48.16 (NMe$_2$, **12a**, major), 50.39, 47.07 (NMe$_2$, **12a**, minor), 22.47 (Me−dmphea, **12a**, minor), 22.40 (Me−dmphea, **12a**, major), 19.25 (Me−dmphea, **12b**), 1.89 (CH−ylide, **12b**, $^{1}J_{P-C}$ = 137 Hz), −7.07 (CH−ylide, **12a**, both isomers, $^{1}J_{P-C}$ = 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*, *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 ($\omega-\theta$) 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 ($22.6 \leq 2\theta \leq 31.6°$), 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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(31) Sheldrick, G. M., SHELXL-93: FORTRAN program for the refinement of crystal structures from diffraction data. Göttingen University, 1993.

(32) (a) Crystallographic calculations were done on a Local Area VAX-Cluster (VAX/VMS V5.5−2). (b) Data reduction was done by the program XCAD4B: Harms, K. Private communication, 1995. (c) Absorption corrections and molecular graphics were done using the commercial package: SHELXTL-PLUS, Release 4.21/V; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.