Synthesis and Structure of Pd^{II} Complexes Containing the C,C-Chelating Bis-Ylide Ligand [Ph$_3$P=C(H)]$_2$CO. X-ray Crystal Structure of {Pd(μ-Cl){[C(H)PPh$_3$]$_2$CO}}$_2$(ClO$_4$)$_2$·CH$_2$Cl$_2$

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The reaction of Pd(OAc)$_2$ with the bis(phosphonium) salt [Ph$_3$PCH$_2$COCH$_2$PPh$_3$]Cl$_2$ (1:1 molar ratio) results in the formation of the *cis*-dichlorobis(ylide) derivative Cl$_2$Pd{[C(H)PPh$_3$]$_2$CO}, **1**, in which the bis(ylide) ligand [C(H)PPh$_3$]$_2$CO acts as a chelating group through the two ylide carbon atoms. Complex **1** reacts with TlClO$_4$ (1:1 molar ratio) to give [Pd(μ-Cl){[C(H)PPh$_3$]$_2$CO}]$_2$(ClO$_4$)$_2$, **2**, which reacts with two further equivalents of TlClO$_4$ in NCMe to give [Pd{[C(H)PPh$_3$]$_2$CO}(NCMe)$_2$](ClO$_4$)$_2$ **3**. The reactivity of **2** and **3** has been explored. Compound **2** reacts with pyridine, 3,5-lutidine, or Ph$_3$P=C(H)CN (1:2 molar ratio), resulting in the rupture of the chlorine bridging system and formation of [PdCl{[C(H)PPh$_3$]$_2$CO}(L)](ClO$_4$) (L = py (**4**), 3,5-lu (**5**), *N*C−C(H)= PPh$_3$ (**6**)), and with Tlacac (1:2 molar ratio) with formation of the acetylacetonate [Pd(acac){[C(H)PPh$_3$]$_2$CO}]- (ClO$_4$), **7**. On the other hand, complex **3** reacts with the ylide Ph$_3$P=C(H)CN (1:2 molar ratio) giving [Pd{[C(H)PPh$_3$]$_2$CO}[NC−C(H)=PPh$_3$]$_2$](ClO$_4$)$_2$, **8**, which contains two N-coordinated ylides, and with NBu$_4$- OH (1:1) to give [Pd(μ-OH){[C(H)PPh$_3$]$_2$CO}]$_2$(ClO$_4$)$_2$, **9**. The reaction of Pd(OAc)$_2$ with the ylide phosphonium salt [Ph$_3$P=C(H)COCH$_2$PPh$_3$](ClO$_4$) (1:1) gives the acetate dimer [Pd(μ-OOCCH$_3$){[C(H)PPh$_3$]$_2$CO}]$_2$(ClO$_4$)$_2$, **10**. The structures of complexes **1**−**10** were deduced from their spectroscopic data and from the resolution of the molecular structure of complex **2**·CH$_2$Cl$_2$.

Introduction

Ylides of phosphorus are now recognized as a class of extremely powerful ligands that form complexes with both main group elements and transition metals.[1] In recent papers, we have described a part of the chemistry of Pd^{II} and Pt^{II} with α-stabilized ylides, such as Ph$_3$P=C(H)COR (R = Me, Ph, OMe, NMe$_2$) and Ph$_3$P=C(H)CN.[2−7] Throughout these studies, we have observed the ability of these ylides to behave as ambidentate ligands (except for the NMe$_2$ derivative[7]). Moreover, we have obtained evidence about the possibility of controlling the binding modes—that is, given an organometallic substrate to predict the coordination mode of a given ylide and, conversely, to design a substrate to drive a given binding mode.

A bis-ylide such as Ph$_3$P=C(H)COC(H)=PPh$_3$ offers new synthetic possibilities. First, it has three potential coordinating atoms (two carbons and one oxygen). Second, it can behave as a chelating or bridging ligand through the same or different donor atoms due to its multifuctionality. However, as far as we know, only one report on this bis-ylide has appeared in the literature[8] (polynuclear gold and silver complexes), and very few reports of related ylides containing the CCC skeleton have been published.[9,10]

In this report we present our first results on the previously unexplored chemistry of Pd^{II} with this bis-ylide. A series of new complexes with the ylide coordinated as a C,C-chelate are described, together with the crystal structure of a representative example.

Results and Discussion

The reaction of Pd(OAc)$_2$ with the bis-phosphonium salt [Ph$_3$- PCH$_2$COCH$_2$PPh$_3$]Cl$_2$ (1:1 molar ratio) in CH$_2$Cl$_2$ at room temperature results in the deprotonation of the two methylene groups of the bis-phosphonium salt and formation of a solid of stoichiometry Cl$_2$Pd{[C(H)PPh$_3$]$_2$CO}, **1**, as deduced from its elemental analysis and mass spectrum (see Experimental Section and Scheme 1). The IR spectrum clearly shows the cis- disposition of the chlorine ligands[11]—two absorptions at 293 and 278 cm^{-1}—and the location of these bands at low wave- numbers suggests a Cl-*trans*-to-C arrangement.[12] The ν(CO)

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Scheme 1
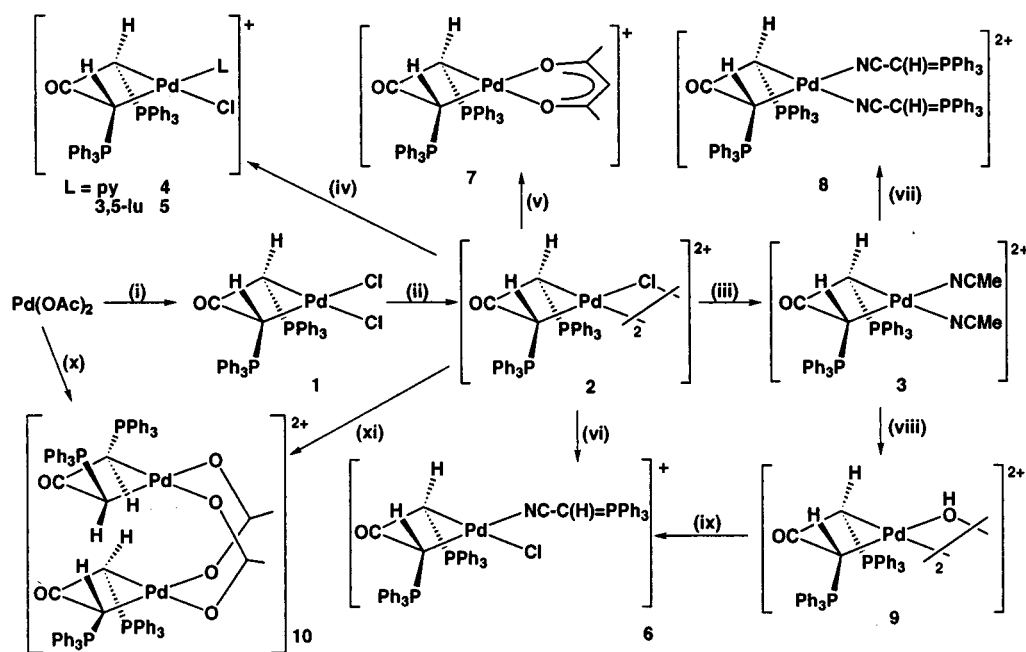
Legend for Scheme 1:
(i): + [Ph₃PCH₂COCH₂PPh₃]Cl₂, - 2 HOAc, CH₂Cl₂, r.t.
(ii): + TlClO₄, - TlCl, CH₂Cl₂, r.t.
(iii): + 2 TlClO₄, - 2 TlCl, NCMe, r.t.
(iv): + 2 L, CH₂Cl₂, r.t.
(v): + 2 NC-C(H)=PPh₃, CH₂Cl₂, r.t.
(vi): + 2 Tl(acac), - 2 TlCl, CH₂Cl₂, r.t.
(vii): + 2 NC-C(H)=PPh₃, CH₂Cl₂, r.t.
(viii): + 2 NBu₄OH, MeOH / H₂O, r.t.
(ix): + 2 [Ph₃PCH₂CN]Cl, - H₂O, CH₂Cl₂, r.t. (see text)
(x): + [Ph₃P=C(H)COCH₂PPh₃](ClO₄), - HOAc, CH₂Cl₂, r.t.
(xi): + 2 Tl(OOCCH₃), - 2 TlCl, CH₂Cl₂, r.t.

absorption appears at 1587 cm⁻¹, shifted to lower energies with respect to the free phosphonium (1712 cm⁻¹)[13,14] and indicating C-coordination of the ylide.[2-7]

The ¹H NMR spectrum of **1** shows, in additon to complex resonances at low field due to Ph groups, a doublet centered at 3.70 ppm, with a coupling constant $^2J_{P-H}$ of 7 Hz, which is attributed to the ylide proton. The ³¹P{¹H} NMR spectrum of **1** shows a singlet at 25.15 ppm. These spectral parameters suggest that the bis-ylide is coordinated through both carbon atoms, although we cannot deduce from these data if the bis-ylide acts as a chelate (mononuclear) or as a bridging (dinuclear) ligand. The measurement of the molecular weight in CHCl₃ solution was inconclusive, although the value obtained was closer to that of a mononuclear complex. The reactivity of **1** was more informative.

Thus, 1 equiv of complex **1** reacts with 1 equiv of TlClO₄ resulting in the precipitation of TlCl and formation of a yellow solid of stoichiometry [PdCl{[C(H)PPh₃]₂CO}](ClO₄) **2**, according to its elemental analysis. The mass spectrum of this solid shows a weak peak at 1541 amu, which corresponds to the stoichiometry [PdCl{[C(H)PPh₃]₂CO}]₂(ClO₄)⁺ and strongly suggests a dinuclear nature for complex **2**. The molar conductivity of **2** in acetone is $\Lambda_M = 177\ \Omega^{-1}\ cm^2\ mol^{-1}$, which agrees with the average value reported[15] for 2:1 electrolytes (180 Ω^{-1} cm² mol⁻¹) in the range of concentration employed (6 × 10⁻⁴ M). Thus, complex **1** is concluded to be a mononuclear

compound which, after abstraction of one chlorine, dimerizes following a well-known pathway for the formation of dinuclear complexes.[16] These facts imply that the bis-ylide group acts as a chelating ligand in **1**.

Other possible routes to complex **2** were tested, for example the transmetalation of the bis-ylide from the silver complex [Ag{[C(H)PPh₃]₂CO}]₂(ClO₄)₂ to the palladium derivative PdCl₂(NCMe)₂ or the transylidation reaction (exchange of ylide ligands) of PdCl₂[C(H)COMe(PPh₃)]₂ with [Ph₃PCH₂COCH₂-PPh₃](ClO₄)₂. However, the low solubility of the silver derivative in the first case and the difficulty of completely eliminating the phosphonium salt [Ph₃PCH₂COCH₃]Cl in the second case resulted in low yields of pure **2**, and these methods are not described in the Experimental Section. On the other hand, all attempts to obtain complexes with the bis-ylide coordinated through only one carbon atom ([M]−C(H)PPh₃−COCH=PPh₃) or complexes containing the mono-ylide unit ([M]−C(H)PPh₃−COCH₂PPh₃) were unsuccessful, even for the more obvious processes (e.g. reaction of PdCl₂(NCMe)₂ with the ylide-phosphonium salt [Ph₃P=C(H)COCH₂PPh₃](ClO₄)).

The IR spectrum of **2** shows the expected changes. The *ν*-(Pd−Cl) stretch is shifted to lower energies with respect to **1**, in accord with the change of Cl from terminal to bridging and *ν*(CO) shows a value similar to that in **1**. The NMR spectral parameters show the presence of a single product, as can be inferred from the observation of only one doublet in the ¹H NMR spectrum (4.32 ppm, $^2J_{P-H} = 5.4$ Hz) and a singlet in the ³¹P{¹H} NMR spectrum (23.75 ppm).

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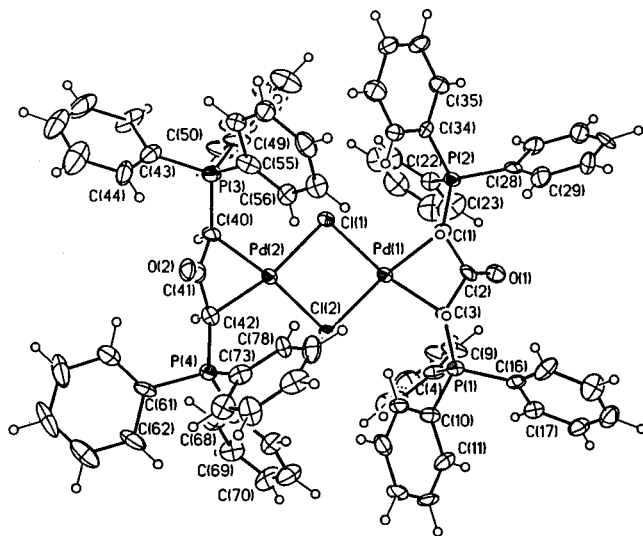
Figure 1. Thermal ellipsoid plot of the [Pd(μ-Cl){[C(H)PPh$_3$]$_2$CO}]$_2^{2+}$ cation. Atoms are drawn at the 50% probability level.

Due to the presence of two chiral centers in **1**, two diastereoisomers would be expected (*RR* or *SS* and *RS* or *SR*) along with two sets of signals in the NMR spectrum. However, only one set is observed and hence only one diastereoisomer is obtained (no splitting or broadening of the signals was observed in the NMR spectrum at low temperature—CD$_2$Cl$_2$, 183 K— ruling out a fast interconversion equilibrium between the two isomers). The same holds for **2**, in which four chiral centers are present, but only one set of resonances is observed. The elucidation of the stereochemistry of complexes **1** and **2** comes from the X-ray structure determination of compound **2·**CH$_2$-Cl$_2$.

Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a CH$_2$Cl$_2$ solution of **2** at room temperature. A drawing of the organometallic dinuclear cation is shown in Figure 1, selected bond distances and angles are collected in Table 1 and relevant crystallographic parameters are given in Table 2.

The complex crystallizes in the paramorphic orthorhombic space group $P2_12_12_1$, with one molecule in the asymmetric unit. Thus, just one diastereoisomer is present. Each palladium atom is located in a distorted square-planar environment, surrounded by the two bridging chlorine atoms and the two ylide carbon atoms. This confirms the dinuclear nature of this complex and the C,C-chelating coordination mode of the bis-ylide ligand. The atom Pd(2) deviates 0.026 (5) Å from the best least-squares plane defined by C(40), C(42), Cl(1), and Cl(2), and Pd(1) deviates −0.046 (5) Å from the plane defined by C(1), C(3), Cl(1), and Cl(2).

The basic skeleton C(40)−C(42)−Pd(2)−Cl(1)−Cl(2)−Pd-(1)-C(1)−C(3) is not planar, and the dihedral angle between the coordination planes is 145.38 (27)°. The coordination planes are defined as the best least-squares planes formed with C(40)−C(42)−Cl(1)−Cl(2)−Pd(2) and C(1)−C(3)−Cl(1)−Cl(2)−Pd-(1). The value of this angle is similar to those reported in some other dinuclear palladium(II) complexes with halide bridges; for di-μ-bromobis-π-cycloheptenyldipalladium(II) the value reported[17a] is 139°, for di-μ-chlorobis-π-1,3-dimethylallyldi-palladium(II)[17b] this value is 150°, and for di-μ-chlorobis{[2,6-dimethyl-*N*-(benzylidene)phenylaminato-*C*$^{2'}$,*N*]pallad-

Table 1. Selected Bond Lengths [Å] and Angles [deg] for **2·**CH$_2$Cl$_2$

Pd(1)−C(3)	2.053(11)	Pd(1)−C(1)	2.060(11)
Pd(1)−Cl(1)	2.372(3)	Pd(1)−Cl(2)	2.389(3)
Pd(2)−C(40)	2.061(12)	Pd(2)−C(42)	2.078(11)
Pd(2)−Cl(1)	2.389(3)	Pd(2)−Cl(2)	2.390(3)
P(1)−C(3)	1.774(11)	P(1)−C(16)	1.774(12)
P(1)−C(4)	1.789(12)	P(1)−C(10)	1.810(13)
P(2)−C(1)	1.766(11)	P(2)−C(22)	1.779(12)
P(2)−C(34)	1.789(13)	P(2)−C(28)	1.795(13)
C(1)−C(2)	1.468(16)	C(2)−O(1)	1.243(15)
C(2)−C(3)	1.471(16)	P(3)−C(40)	1.779(12)
P(3)−C(43)	1.800(14)	P(3)−C(55)	1.822(13)
P(3)−C(49)	1.825(15)	P(4)−C(42)	1.772(12)
P(4)−C(73)	1.784(13)	P(4)−C(67)	1.792(13)
P(4)−C(61)	1.803(13)	C(40)−C(41)	1.460(18)
C(41)−O(2)	1.234(15)	C(41)−C(42)	1.471(17)

C(3)−Pd(1)−C(1)	68.8(4)	C(3)−Pd(1)−Cl(1)	169.2(3)
C(1)−Pd(1)−Cl(1)	101.0(3)	C(3)−Pd(1)−Cl(2)	102.6(3)
C(1)−Pd(1)−Cl(2)	171.3(3)	Cl(1)−Pd(1)−Cl(2)	87.49(10)
C(40)−Pd(2)−C(42)	68.0(5)	C(40)−Pd(2)−Cl(1)	101.1(3)
C(42)−Pd(2)−Cl(1)	169.0(3)	C(40)−Pd(2)−Cl(2)	171.4(3)
C(42)−Pd(2)−Cl(2)	103.9(3)	Cl(1)−Pd(2)−Cl(2)	87.06(11)
Pd(1)−Cl(1)−Pd(2)	87.82(10)	Pd(1)−Cl(2)−Pd(2)	87.40(10)
C(2)−C(1)−Pd(1)	83.4(7)	P(2)−C(1)−Pd(1)	125.1(6)
O(1)−C(2)−C(1)	125.5(11)	O(1)−C(2)−C(3)	127.4(11)
C(1)−C(2)−C(3)	104.5(11)	C(2)−C(3)−Pd(1)	83.6(7)
P(1)−C(3)−Pd(1)	123.8(6)	C(41)−C(40)−Pd(2)	83.4(8)
P(3)−C(40)−Pd(2)	126.5(7)	O(2)−C(41)−C(40)	128.0(12)
O(2)−C(41)−C(42)	126.2(12)	C(40)−C(41)−C(42)	104.2(11)
C(41)−C(42)−Pd(2)	82.5(7)	P(4)−C(42)−Pd(2)	128.5(6)

Table 2. Crystallographic Data for **2·**CH$_2$Cl$_2$^{a}

empirical formula	C$_{79}$H$_{66}$Cl$_6$O$_{10}$P$_4$Pd$_2$
fw	1724.70
T	−123(1) °C
λ	0.71073 Å
space group	$P2_12_12_1$ (No. 19)
a	19.247(5) Å
b	19.521(4) Å
c	19.757(4) Å
V	7423(3) Å^3
Z	4
ρ_{calcd}	1.543 g cm^{-3}
μ	8.46 cm^{-1}
R1 [*I* > 2σ(*I*)]^a	0.0578
wR2 [*I* > 2σ(*I*)]^b	0.1216

^{a} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

ium(II)}[18] the reported value is 143.3(1)°. However, this feature is rather unusual in palladium(II) complexes, where the normal arrangement of the ligands results in planar dinuclear complexes, that is, the two coordination planes are coplanar. One of the facts which gives significant deviations from the planarity is the presence of metal−metal interactions, but there is no reason to suppose that these molecules are affected by metal−metal bonding. The Pd−C (ylide) bond distances [range 2.053(11)− 2.078(11) Å] are similar, within experimental error, to those found in other C-coordinated ylide Pd complexes[2,19] and the palladium−chlorine bond distances [range 2.372(3)−2.390(3) Å] are also similar to those found in related dinuclear di-μ-chlorine Pd complexes.[18,20]

The environment of each ylide carbon [C(1), C(3), C(40), and C(42)] is tetrahedral, with the PPh$_3$ substituents on the same

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side of the coordination plane within each fragment [PdCl(bis-ylide)] and on opposite sides at the two ends of the molecule. That gives absolute configurations for the ylide carbon atoms $S_{C(1)}$, $R_{C(3)}$, $S_{C(40)}$, and $R_{C(42)}$. Thus, the molecule crystallizes in one of the *meso* forms. Due to the fact that only one stereoisomer is observed in solution for **2** (within the range of detection of the NMR spectrometer), we can conclude that the *RS* configuration for the ylide carbon atoms of the chelating bis-ylide ligand is preseved in solution, and that for complex **1** these, and not the *RR/SS* configurations, are the absolute configurations for the carbon atoms. These facts are depicted in Scheme 1. A similar disposition of the substituents around the ylide carbon atoms has been found in the gold(I) derivative[8] [Au₂{μ-{{CH(PPh₃)}₂CO}}₂](ClO₄)₂.

Finally, there is a short metal−hydrogen contact C(56)−H(56)···Pd(2) [M−H = 2.71(2) Å], similar to that found in [Pd-(H1-nabz)₂][21] [2.66(7) Å]. We have not been able to isolate the solution ¹H NMR signal of this proton among the aromatic protons,[22] and thus we cannot positively characterize this as an intramolecular three-center four-electron or three-center two-electron interaction.[21]

The reactivity of complex **2** is as expected for a dinuclear system with chlorine bridges. Thus, treatment of **2** with TlClO₄ (1:2 molar ratio) in NCMe results in the formation of the bis-solvate [Pd{[C(H)PPh₃]₂CO}(NCMe)₂](ClO₄)₂, **3**. In these syntheses we have avoided the use of AgClO₄ as halide abstracting agent because of the formation of the very insoluble salt [Ag₂{μ-{{CH(PPh₃)}₂CO}}₂](ClO₄)₂[8] as a consequence of a lateral transmetalation process. For the same reason, the synthesis of **2** starting from **1** was carried out with the thallium salt instead of the silver. The IR spectrum of **3** shows the expected absorptions corresponding to the presence of coordinated NCMe, and the ¹H NMR and ³¹P{¹H} NMR spectra show a doublet at 4.51 ppm ($^2J_{P-H}$ = 3.1 Hz), and a singlet at 25.00 ppm, respectively, corresponding to the ylide proton and to the phosphorus. The stereochemistry for the chelate bis-ylide moiety in **3** is likely to be similar to that described for **2** (see Scheme 1), assuming that the Pd−C bonds remain unbroken in the reaction.

Treatment of **2** with bases such as pyridine or 3,5-lutidine (1:2.5 molar ratio) in CH₂Cl₂ promotes the symmetrical cleavage of the bridging system and formation of the corresponding complexes of stoichiometry [PdCl{[C(H)PPh₃]₂CO}(L)](ClO₄) (L = pyridine (**4**), 3,5-lutidine (**5**)). The IR spectra of **4** and **5** show a slight increase in energy of the Pd−Cl stretch, corresponding to the change from bridging to terminal coordination, in addition to the absorptions attributed to the bis-ylide and to the pyridine ligands. The ¹H NMR spectrum of **4** shows the presence of two doublet resonances attributed to the two nonequivalent ylide proton atoms, one at 4.80 ppm ($^2J_{P-H}$ = 6 Hz) and the other at 4.51 ppm ($^2J_{P-H}$ = 4.5 Hz), together with characteristic resonances of coordinated pyridine (see Experimental Section). The ³¹P{¹H} NMR spectrum shows the presence of an AB spin sytem (25.75 and 24.55 ppm) with a coupling constant of $^4J_{P-P}$ = 12 Hz. These observations are in accord with the structure depicted in Scheme 1. Similar

conclusions can be inferred from the analysis of the spectra of complex **5**.

The cleavage of the halide bridge system in **2** can also be carried out with other ligands. We have tried reactions with α-stabilized phosphoylide ligands Ph₃P=C(H)COR (R = Me, Ph, OMe) and Ph₃P=C(H)CN. Surprisingly, the keto-stabilized ylides do not produce the cleavage of the chloride bridge, and the starting products can be recovered unaltered. The reaction with the cyano-stabilized ylide Ph₃P=C(H)CN (1:2 molar ratio) gives a product of stoichiometry [PdCl{[C(H)PPh₃]₂CO}(Ph₃-PCHCN)](ClO₄), **6**, according to its elemental analysis and mass spectrum (see Experimental Section). The cleavage of the bridging system can be inferred from the observation in the ¹H NMR spectrum of **6** of two doublets attributed to the ylide protons (3.96 ppm, $^2J_{P-H}$ = 6 Hz; 3.86 ppm, $^2J_{P-H}$ = 4 Hz) and the coordination mode of the ylide from the appearance of a doublet in the high field region (1.02 ppm, $^2J_{P-H}$ = 6.3 Hz), which is indicative of N-coordination of the ylide.[4] The ³¹P-{¹H} NMR spectrum shows the expected resonances; an AB spin system for the ylide phosphorus (25.90 and 24.20 ppm, $^4J_{P-P}$ = 11 Hz) and a singlet for the N-bonded ylide (22.84 ppm). It is worth noting the selective N-coordination of the ylide in **6**. In similar reactions performed with the halide bridged [Pd(dmba)(μ-Cl)]₂ (dmba = C₆H₄CH₂NMe₂-2), the reaction product contained a mixture of the C- and N-bonded forms, probably in thermal equilibrium, and both of them were postulated to be trans to the N atom of the cyclometalated ligand.[4] Here, complex **6** shows a single coordination form, and this fact could be rationalized by two factors. The first is the antisymbiotic behavior of the Pd(II) center,[23] which results in a higher stability of the N-bonded ylide ("borderline" base[24]) trans to the ylide carbon atom (soft base) than of a C-*trans*-to-C arrangement. The second factor is the low steric requirement of the N-bonded ylide, compared to the C-form, in a cis position to the bulky C(H)PPh₃ fragment.

Complex **2** also undergoes other reactions typical of halide bridges, such as substitution by anionic chelating ligands. Thus, **2** reacts with Tl(acac) (1:2 molar ratio) to give the acetylacetonato derivative [Pd(acac-O,O′){[C(H)PPh₃]₂CO}](ClO₄) **7**. The characterization of **7** results from the same considerations as those used previously; the key indicators are the ν(CO) in the IR spectrum and the chemical shifts of the ylide proton and the phosphorus in the NMR spectra (see Experimental Section).

The reactivity of the bis-solvate **3** has also been explored. Thus, complex **3** reacts with the ylide Ph₃P=C(H)CN (1:2) to give [Pd{[C(H)PPh₃]₂CO}(NC−C(H)=PPh₃)₂](ClO₄)₂, **8** (see Scheme 1), in which both NCMe ligands have been replaced by the ylide Ph₃P=C(H)CN as characterized by the elemental analysis and mass spectrum. The IR spectrum of **8** shows the expected absorptions corresponding to the bis-ylide (ν(CO) = 1615 cm⁻¹) and to the cyano-ylide (ν(CN) = 2175 cm⁻¹). The most interesting feature of this complex is the presence of two cyano-ylides N-bonded to the Pd(II) center, as can be inferred from the ¹H NMR. The resonance attributed to the bis-ylide appears at 4.48 ppm ($^2J_{P-H}$ = 3.6 Hz) while the resonance attributed to the cyano-ylide appears at 0.86 ppm ($^2J_{P-H}$ = 5.4 Hz), typical for N-coordination of this ylide.[4] The relative intensity of these resonances is 1:1, confirming the complete substitution of the NCMe ligand. Further evidence for the proposed structure (see Scheme 1) can be obtained from the ³¹P{¹H} NMR spectrum, which shows two resonances of relative intensity 1:1 (24.65 ppm for the bis-ylide and 22.92 ppm for

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the N-coordinated ylide).[4] This behavior is rather different from that observed for this ylide in C,N-cyclometalated complexes.[4] There, the reaction of the cationic complex [Pd(dmba)-(NCMe)₂]⁺ with 2 equiv of Ph₃P=C(H)CN gave [Pd(dmba)-{C(H)PPh₃(CN)}{NC−C(H)=PPh₃}]⁺ in which the C-bonded ylide was trans to the N atom of the dmba and the N-bonded ylide was trans to the orthometalated atom of the dmba group.[4] Taking into account the preceding discussion for complex **6**, the structure of complex **8** can be easily explained in terms of the antisymbiotic effect (the hardest atom of the cyano-ylide, that is, the N atom, would be more stabilized trans to the carbon atom of the bis-ylide) and of the steric interactions (due to the large volume of the bis-ylide, the low steric requirements of the N-bonded ylide are preferred).

It is interesting to note that all similar complexes described to date possess, trans to the bis-ylide, ligands with donor atoms which behave as borderline or hard bases (Cl⁻, NCMe, pyridine, N-bonded ylides, acac⁻).[24] We have decided to explore other interesting "hard" O-donor ligands, such as the hydroxy group OH⁻, which is scarcely represented in palladium(II) chemistry,[25−27] and which shows a very interesting reactivity.[28,29] The reaction of **3** with a methanolic solution of NBu₄OH (1:2.1 molar ratio) results in the immediate precipitation of the dinuclear complex [Pd(μ-OH){[C(H)PPh₃]₂CO}]₂(ClO₄)₂, **9**, as deduced from its elemental analysis and mass spectrum. The presence of the OH ligand is inferred from the observation in the IR spectrum of **9** of an absorption at 3602 cm⁻¹. The ¹H NMR spectrum shows the resonances attributed to the ylide proton at 3.78 ppm ($^2J_{P−H}$ = 6.6 Hz), and the resonance due to the OH group at −4.44 ppm as a singlet. The relative intensities of these resonances (2:1) confirm the bridging nature of the OH group. The ³¹P{¹H} NMR spectrum shows a single resonance at 23.99 ppm. Further treatment of **9** with NBu₄OH does not promote the formation of the bis-hydroxo derivative [Pd(OH)₂{[C(H)PPh₃]₂CO}], and the reaction of **3** with an excess of NBu₄OH (1:6 molar ratio) gives **9** as the only reaction product. It seems that the bridging arrangement confers a special stability to this ligand. However, **9** reacts with the phosphonium salt [Ph₃PCH₂CN]Cl to give a (1:1) mixture of **2** and **6**. The reactivity of **9** in other processes is presently under study.

Finally, the reaction of Pd(OAc)₂ with the mixed ylide-phosphonium salt [Ph₃P=C(H)COCH₂PPh₃](ClO₄) (1:1 molar ratio) results in the formation of the acetate bridged dimer [Pd-(μ-OOCCH₃){[C(H)PPh₃]₂CO}]₂(ClO₄)₂, **10**. The elemental analyses and mass spectrum are in good agreement with the proposed stoichiometry, and the conductivity data in acetone solution (Λ_M = 217 Ω⁻¹ cm² mol⁻¹) confirms the dicationic character of **10**. Complex **10** can also be obtained by reaction of **2** with TlOOCCH₃ (1:2 molar ratio), although in this case the yield is notably lower. We are unaware of the reasons of this low yield, and for this reason this synthetic method has not been included in the Experimental Section.

The IR spectrum of **10** shows two strong absorptions in the carbonyl region; one at 1611 cm⁻¹ and attributed to the bis-

ylide ligand and the other one at 1557 cm⁻¹ and attributed to the asymmetric stretch of the acetate ligand[30] (the symmetric stretch falls in the polyethylene region, precluding its observation). The NMR spectra show high symmetry in the molecule. Thus, in the ¹H NMR the resonance attributed to the ylide proton appears as a doublet at 4.92 ppm ($^2J_{P−H}$ = 5.6 Hz) and the methyl group of the acetate ligand as a singlet at 1.41 ppm. The ³¹P{¹H} NMR shows a single resonance at 26.41 ppm. Several dinuclear structures are consistent with these data: (i) the bis-ylide and the acetate bridge two palladium atoms, (ii) the bis-ylide acts as a chelate and the acetate as bridge, and (iii) the bis-ylide acts as a bridge and the acetate as a chelate.

We propose the second possibility as the most plausible, since in complexes **1−9** the bis-ylide acts as a chelate and shows good stability. Moreover, the spectral parameters (IR, NMR) of the coordinated chelating bis-ylide in **1−9** and those of **10** are very similar. Moreover, the acetate group is a very good bridging ligand, giving "open-book" structures.[31] The high symmetry of the molecule shown in the NMR spectra allows us to propose the structure shown in Scheme 1. We think that this disposition of the ligands, with the ylide H atoms on the inner side of the "book", is less sterically hindered and accounts for the symmetry.

Conclusion

A series of new complexes with the bis-ylide {[Ph₃P=C(H)]₂-CO} has been prepared and one of the new products has been structurally characterized by X-ray diffraction. In all of the complexes the bis-ylide acts as a C,C-chelate. The presence of two soft carbon atoms on the palladium center appears to stabilize the coordination of hard ligands, such as the OH group, and is able to drive the selective coordination of ambidentate ligands through their hardest atoms. The results derived so far from this chemistry suggest that further novel, interesting systems 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.*

General Procedures. Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane, and chloroform over P₂O₅, acetonitrile over CaH₂, methanol over magnesium and *n*-hexane over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Infrared spectra (4000−200 cm⁻¹) were recorded on a Perkin-Elmer 883 Infrared spectrophotometer from Nujol mulls between polyethylene sheets. ¹H (300.13 MHz) and ³¹P{¹H} (121.49 MHz) NMR spectra were recorded in CDCl₃ or CD₂Cl₂ solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ¹H was referenced using the solvent signal as internal standard and ³¹P{¹H} was externally referenced to H₃PO₄ (85%). Mass spectra (positive ion FAB) were recorded on a V. G. Autospec. 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 compounds Pd(OAc)₂,[32] Ph₃P=C(H)CN,[33] [Ph₃PCH₂COCH₂PPh₃]Cl₂,[13,14] and [Ph₃P=C(H)COCH₂-PPh₃]ClO₄[8] were prepared according to published methods.

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Preparations. Cl₂Pd[{C(H)PPh₃}₂CO], 1. To a solution of Pd-(OAc)₂ (0.200 g, 0.890 mmol) in CH₂Cl₂ (20 mL) at room temperature, [Ph₃PCH₂COCH₂PPh₃]Cl₂ (0.580 g, 0.890 mmol) was added. The resulting orange solution was stirred for 5 h at room temperature, then evaporated to dryness. By addition of Et₂O (40 mL) to the oily residue and continuous stirring **1** was obtained as an orange solid, which was filtered, washed with additional Et₂O (20 mL) and air-dried. The crude solid was recrystallized from CH₂Cl₂/*n*-hexane, giving orange crystals of **1**·0.5CH₂Cl₂. Obtained: 0.553 g (82% yield). The crystals of **1**·0.5CH₂Cl₂ were used for elemental analyses and NMR measurements. The amount of CH₂Cl₂ was determined by ¹H NMR integration. Anal. Found for $C_{39}H_{32}Cl_2OP_2Pd \cdot 0.5CH_2Cl_2$: C, 58.51; H, 4.24. Calcd: C, 59.42; H, 4.16. MS (+ FAB) [*m/z* (%)]: 721 [(M − Cl)⁺, 6%]. IR (cm⁻¹): 1587 (ν_{CO}), 293, 278 (ν_{Pd-Cl}). ¹H NMR (CDCl₃): δ 8.08−6.96 (m, 15H, Ph), 3.70 (d, CH ylide, 1H, $^2J_{P-H}$ = 7 Hz). ³¹P{¹H} NMR (CDCl₃): δ 25.15.

{Pd(μ-Cl)[{C(H)PPh₃}₂CO]}₂(ClO₄)₂, 2. To a solution of **1** (0.200 g, 0.264 mmol) in CH₂Cl₂ (30 mL) at room temperature, TlClO₄ (0.080 g, 0.26 mmol) was added and the resulting suspension was stirred overnight at room temperature, then filtered. The clear yellow solution was evaporated to dryness and the residue treated with Et₂O (30 mL) giving **2** as a yellow solid, which was filtered, washed with additional Et₂O (30 mL) and air-dried. The crude solid was recrystallized from CH₂Cl₂/*n*-hexane, giving orange crystals of **2**·CH₂Cl₂. Obtained: 0.177 g (83% yield). The crystals of **2**·CH₂Cl₂ were used for elemental analysis, NMR and X-ray measurements. The amount of CH₂Cl₂ was determined by ¹H NMR integration. Anal. Found for $C_{78}H_{64}Cl_4O_{10}P_4$-$Pd_2 \cdot CH_2Cl_2$: C, 54.27; H, 3.74. Calcd: C, 55.01; H, 4.05. MS (+ FAB) [*m/z* (%)]: 1541 [(M₂ − ClO₄)⁺, 20%]. Λ_M = 177 Ω^{-1} cm² mol⁻¹ (6 × 10⁻⁴ M in acetone). IR (cm⁻¹): 1617 (ν_{CO}), 278 (ν_{Pd-Cl}). ¹H NMR (CDCl₃): δ 8.07−6.95 (m, 15H, Ph), 4.32 (d, CH ylide, 1H, $^2J_{P-H}$ = 5.4 Hz). ³¹P{¹H} NMR (CDCl₃): δ 23.75.

{Pd[{C(H)PPh₃}₂CO](NCMe)₂}(ClO₄)₂, 3. To a solution of **2** (1.000 g, 0.610 mmol) in NCMe (60 mL) at room temperature, TlClO₄ (0.371 g, 1.220 mmol) was added and the resulting suspension was stirred overnight at room temperature, then filtered. The clear yellow solution was evaporated to dryness and the residue treated with Et₂O (30 mL) giving **3** as a yellow solid, which was filtered, washed with additional Et₂O (30 mL) and air-dried. Obtained: 0.955 g (82% yield). Anal. Found for $C_{43}H_{38}Cl_2N_2O_9P_2Pd$: C, 53.55; H, 3.58; N, 2.89. Calcd: C, 53.46; H, 3.96; N, 2.51. MS (+ FAB) [*m/z* (%)]: 785 [(M − 2NCMe − ClO₄)⁺, 100%]. IR (cm⁻¹): 2327, 2315, 2300, 2288 (ν_{CN}), 1634 (ν_{CO}). ¹H NMR (CD₂Cl₂, 218 K): δ 7.93−7.41 (m, 15H, Ph), 4.51 (d, CH ylide, 1H, $^2J_{P-H}$ = 3.1 Hz), 1.72 (s, 3H, NCMe). ³¹P{¹H} NMR (CD₂Cl₂, 218 K): δ 25.00.

{PdCl(py)[{C(H)PPh₃}₂CO]}(ClO₄), 4. To a solution of **2** (0.200 g, 0.122 mmol) in CH₂Cl₂ (30 mL) at room temperature, pyridine (50 μL, 0.624 mmol) was added. The resulting solution was stirred for 3 h, then evaporated to dryness. The oily residue was treated with Et₂O (30 mL) giving **4** as a yellow solid, which was filtered, washed with additional Et₂O (30 mL) and air-dried. Obtained: 0.185 g (84% yield). Anal. Found for $C_{44}H_{37}Cl_2NO_5P_2Pd$: C, 58.47; H, 3.80; N, 1.72. Calcd: C, 58.78; H, 4.15; N, 1.56. MS (+ FAB) [*m/z* (%)]: 798 [M⁺, 12%], 719 [(M − py)⁺, 50%]. IR (cm⁻¹): 1601 (br, ν_{CO}), 302 (ν_{Pd-Cl}). ¹H NMR (CDCl₃): δ 8.75 (m, 2H, H₂ and H₆, py), 8.20 (m, 1H, H₄, py), 7.97−6.98 (m, 30H, Ph), 6.74 (m, 2H, H₃ and H₅, py), 4.80 (d, CH ylide, 1H, $^2J_{P-H}$ = 6 Hz), 4.51 (d, CH ylide, 1H, $^2J_{P-H}$ = 4.5 Hz). ³¹P{¹H} NMR (CDCl₃): δ 25.75, 24.55 (AB spin system, $^4J_{P-P}$ = 12 Hz).

{PdCl(3,5-lu)[{C(H)PPh₃}₂CO]}(ClO₄), 5. Complex **5** was synthesized similarly to **4**. Complex **2** (0.300 g, 0.182 mmol) was reacted with 3,5-lutidine (41.7 μL, 0.365 mmol) in CH₂Cl₂ (30 mL) to give **5** as a yellow solid. Obtained: 0.295 g (87% yield). Anal. Found for $C_{46}H_{41}Cl_2NO_5P_2Pd$: C, 59.10; H, 4.01; N, 1.68. Calcd: C, 59.59; H, 4.46; N, 1.51. MS (+ FAB) [*m/z* (%)]: 826 [M⁺, 20%], 719 [(M − lu)⁺, 65%]. IR (cm⁻¹): 1601 (br, ν_{CO}), 284 (ν_{Pd-Cl}). ¹H NMR (CDCl₃): δ 8.51 (m, 2H, H₂ and H₆, lu), 8.12−6.98 (m, 31H, Ph+H₄), 4.67 (d, CH ylide, 1H, $^2J_{P-H}$ = 6 Hz), 4.43 (d, CH ylide, 1H, $^2J_{P-H}$ = 4.2 Hz), 1.91 (s, 6H, CH₃, lu). ³¹P{¹H} NMR (CDCl₃): δ 25.75, 24.40 (AB spin system, $^4J_{P-P}$ = 12 Hz).

{PdCl[NC−C(H)=PPh₃][{C(H)PPh₃}₂CO]}(ClO₄), 6. To a solution of **2** (0.163 g, 0.100 mmol) in CH₂Cl₂ (25 mL) at room temperature, Ph₃P=C(H)CN (0.090 g, 0.30 mmol) was added. The resulting solution was stirred for 1 h, then evaporated to dryness. The oily residue was treated with Et₂O (30 mL) giving **6** as a pale yellow solid, which was filtered, washed with additional Et₂O (30 mL) and air-dried. The crude product was recrystallized from CH₂Cl₂/*n*-hexane, giving pale yellow crystals of **6**·0.5CH₂Cl₂. Obtained: 0.191 g (85% yield). These crystals were used for analytical and spectroscopic purposes. The amount of CH₂Cl₂ was established by ¹H NMR integration. Anal. Found for $C_{59}H_{48}ClN_O_5P_3Pd \cdot 0.5CH_2Cl_2$: C, 61.82; H, 4.18; N, 0.94. Calcd: C, 61.41; H, 4.24; N, 1.20. MS (+ FAB) [*m/z* (%)]: 1020 [M⁺, 10%]. IR (cm⁻¹): 2166 (ν_{CN}), 1621 (ν_{CO}), 299 (ν_{Pd-Cl}). ¹H NMR (CDCl₃): δ 7.88−7.32 (m, 45H, Ph), 3.96 (d, CH ylide, 1H, $^2J_{P-H}$ = 6 Hz), 3.86 (d, CH ylide, 1H, $^2J_{P-H}$ = 4 Hz), 1.02 (d, CH ylide N-coordinated, 1H, $^2J_{P-H}$ = 6.3 Hz). ³¹P{¹H} NMR (CDCl₃): δ 25.90, 24.20 (AB spin system, 2P, bis-ylide C-coordinated, $^4J_{P-P}$ = 11 Hz), 22.84 (s, 1P, ylide N-coordinated).

{Pd(acac-O,O′)[{C(H)PPh₃}₂CO]}(ClO₄), 7. To a solution of **2** (0.200 g, 0.122 mmol) in CH₂Cl₂ (25 mL) at room temperature, Tl-(acac) (0.107 g, 0.354 mmol) was added and the resulting suspension was stirred for 2 h at room temperature and then filtered. The clear pale yellow solution was evaporated to dryness and the residue treated with Et₂O (30 mL) giving **7** as a yellow solid, which was filtered, washed with additional Et₂O (30 mL), filtered and air-dried. Obtained: 0.146 g (67% yield). Anal. Found for $C_{44}H_{39}ClO_7P_2Pd$: C, 59.12; H, 4.53. Calcd: C, 59.81; H, 4.44. MS (+ FAB) [*m/z* (%)]: 783 [M⁺, 100%]. IR (cm⁻¹): 1610 ($\nu_{CO-ylide}$), 1568, 1517 ($\nu_{CO-acac}$). ¹H NMR (CDCl₃): δ 7.63−7.34 (m, 30H, Ph), 4.97 (s, 1H, CH-acac), 4.05 (d, CH ylide, 2H, $^2J_{P-H}$ = 5.7 Hz), 1.29 (s, 6H, CH₃-acac). ³¹P{¹H} NMR (CDCl₃): δ 25.26.

{Pd[{C(H)PPh₃}₂CO][NC−C(H)=PPh₃]₂}(ClO₄)₂, 8. To a solution of **3** (0.115 g, 0.119 mmol) in CH₂Cl₂ (25 mL) at room temperature, Ph₃P=C(H)CN (0.072 g, 0.24 mmol) was added. The resulting solution was stirred for 2 h at room temperature, then evaporated to dryness. The residue was treated with Et₂O (30 mL) giving **8** as a pale yellow solid, which was filtered, washed with additional Et₂O (30 mL), filtered, and air-dried. The crude product was recrystallized from CH₂Cl₂/*n*-hexane, giving pale yellow crystals of **8**·CH₂Cl₂. Obtained: 0.100 g (56% yield). These crystals were used for analytical and spectroscopic purposes. The amount of CH₂Cl₂ was assayed by ¹H NMR integration. Anal. Found for $C_{79}H_{64}Cl_2N_2O_9P_4Pd \cdot CH_2Cl_2$: C, 61.48; H, 4.21; N, 1.54. Calcd: C, 61.14; H, 4.23; N, 1.78. MS (+ FAB) [*m/z* (%)]: 984 [(M − 2ClO₄ − NCCHPPh₃ + H)⁺, 20%]. IR (cm⁻¹): 2175 (ν_{CN}), 1615 ($\nu_{CO-ylide}$). ¹H NMR (CDCl₃): δ 7.58−7.12 (m, 15H, Ph), 4.48 (d, CH ylide C-coordinated, 1H, $^2J_{P-H}$ = 3.6 Hz), 0.86 (d, CH ylide N-coordinated, 1H, $^2J_{P-H}$ = 5.4 Hz). ³¹P{¹H} NMR (CDCl₃): δ 24.65 (bis-ylide C-coordinated), 22.92 (ylide N-coordinated).

{Pd(μ-OH)[{C(H)PPh₃}₂CO]}₂(ClO₄)₂, 9. To a solution of **3** (0.173 g, 0.179 mmol) in MeOH (30 mL) at room temperature, NBu₄-OH (0.097 g, 0.38 mmol) was added. A yellow solid precipitated almost instantaneously. This suspension was stirred for 30 min at room temperature and then filtered. The yellow solid of **9** was washed with MeOH (5 mL) and Et₂O (30 mL) and then air-dried. The product was recrystallized as usual from CH₂Cl₂/*n*-hexane giving yellow crystals of **9**·1.5CH₂Cl₂. Obtained: 0.100 g (69% yield). Anal. Found for $C_{78}H_{66}Cl_2O_{12}P_4Pd_2 \cdot 1.5CH_2Cl_2$: C, 55.03; H, 3.90. Calcd: C, 55.18; H, 4.02. MS (+ FAB) [*m/z* (%)]: 1503 [(M₂ − ClO₄)⁺, 5%]. IR (cm⁻¹): 3602 (ν_{OH}), 1594 ($\nu_{CO-ylide}$). ¹H NMR (CDCl₃): δ 8.21−6.90 (m, 30H, Ph), 3.78 (d, CH ylide, 2H, $^2J_{P-H}$ = 6.6 Hz), − 4.44 (s, 1H, μ-OH). ³¹P{¹H} NMR (CDCl₃): δ 23.99.

{Pd(μ-OOCCH₃)[{C(H)PPh₃}₂CO]}₂(ClO₄)₂, 10. To a solution of Pd(OAc)₂ (0.139 g, 0.619 mmol) in CH₂Cl₂ (25 mL), [Ph₃P=C(H)-COCH₂PPh₃]ClO₄ (0.421 g, 0.619 mmol) was added. The resulting orange solution was stirred for 5 h at room temperature and then evaporated to dryness. The residue was treated with CHCl₃ (20 mL) giving **10** as an orange solid, which was collected and air-dried. Obtained: 0.187 g (36% yield). The solution was evaporated to dryness and the residue was treated with Et₂O (20 mL). An orange solid was obtained, which was identified as **10** contaminated with very small amounts of an unidentified compound. A second recrystallization

carried out in CHCl$_3$ (5 mL) gave a second fraction of pure **10**. Obtained: 0.197 g (38% yield; net yield of **10**: 74%). Anal. Found for C$_{82}$H$_{70}$Cl$_2$O$_{14}$P$_4$Pd$_2$: C, 58.78; H, 3.80. Calcd: C, 58.38; H, 4.18. MS (+ FAB) [m/z (%)]: 1587 [(M$_2$ − ClO$_4$)$^+$, 10%]. Λ_M = 217 Ω^{-1} cm^2 mol^{-1} (acetone solution, 5 × 10^{-4} M). IR (cm^{-1}): 1611 ($\nu_{CO-ylide}$), 1557 ($\nu_{CO2-asym}$). ^{1}H NMR (CD$_2$Cl$_2$): δ 7.78−7.71 (m, 9H, Ph), 7.52−7.46 (m, 6H, Ph), 4.92 (d, CH ylide, 1H, $^2J_{P-H}$ = 5.6 Hz), 1.41 (s, 3H, CH$_3$−acetate). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 26.41.

Crystal Structure Determination of 2·CH$_2$Cl$_2$. A yellow crystal of **2**·CH$_2$Cl$_2$ was mounted on a quartz fiber and covered with epoxy. Normal procedures were used for the determination of the unit cell constants and for the measurement of intensity data. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*, *b*, and *c* axes to verify the lattice dimensions and symmetry. Unit cell dimensions were determined from 25 centered reflections in the range 22.0 ≤ 2θ ≤ 30.1°. For intensity data collection, pure ω-scans were used with $\Delta\omega$ = 1.00 + 0.35 tan θ. Three monitor reflections measured after every 3 h of beam time showed a decay of 16% over the period of data collection. The orientation of the crystal was checked after every 700 intensity measurements. Absorption corrections[34] were based on azimuthal scans of 10 reflections which had the Eulerian angle χ near 90°.

The structure was solved and developed by Patterson and Fourier methods.[35] All non-hydrogen atoms were assigned anisotropic displacement parameters. All hydrogen atoms of compound **2** (including those of the ylide groups, which were observed in a difference map) were placed at idealized positions and treated as riding atoms with isotropic displacement parameters set to 1.2 times the equivalent isotropic displacement parameters of their respective parent atoms. Five

atomic sites in an interstitial zone were modeled as a disordered CH$_2$Cl$_2$ molecule. One of the chlorine atoms [Cl(5)] of this group is disordered over three positions with partial occupancies of 0.600, 0.200, and 0.200. The hydrogens atoms of this molecule were omitted from the model. At the end of the refinement, there was only one difference Fourier peak with ρ > 1.00 e/Å^3, in the area of the disordered CH$_2$Cl$_2$ molecule. The data-to-parameter ratio in the final refinement was 7.7. The structure was refined to $F_o{}^2$, and all reflections were used in the least-squares calculation.[36a] To determine the correct absolute structure the Flack *x* parameter was refined.[36b,c] Once the enantiomorph had been established, the Flack parameter was not refined again, but rather estimated following the least-squares calculations. The residuals and other pertinent parameters are summarized in Table 2. Crystallographic calculations were done on a Local Area VAXCluster (VAX/VMS V5.5−2). Data reduction was done by the program XCAD4B.[37]

Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of **2**·CH$_2$Cl$_2$ is available on the Internet only. Access information is given on any current masthead page.

(34) 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.

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