

Synthesis and Structure of Pd^{II} Complexes Containing the C,C-Chelating Bis-Ylide Ligand [Ph₃P=C(H)]₂CO. X-ray Crystal Structure of {Pd(μ -Cl){[C(H)PPh₃]₂CO}}₂(ClO₄)₂·CH₂Cl₂

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The reaction of Pd(OAc)₂ with the bis(phosphonium) salt [Ph₃PCH₂COCH₂PPh₃]₂Cl₂ (1:1 molar ratio) results in the formation of the *cis*-dichlorobis(ylide) derivative Cl₂Pd{[C(H)PPh₃]₂CO}, **1**, in which the bis(ylide) ligand [C(H)PPh₃]₂CO acts as a chelating group through the two ylide carbon atoms. Complex **1** reacts with TiClO₄ (1:1 molar ratio) to give [Pd(μ -Cl){[C(H)PPh₃]₂CO}]₂(ClO₄)₂, **2**, which reacts with two further equivalents of TiClO₄ in NCMe to give [Pd{[C(H)PPh₃]₂CO}(NCMe)₂](ClO₄)₂, **3**. The reactivity of **2** and **3** has been explored. Compound **2** reacts with pyridine, 3,5-lutidine, or Ph₃P=C(H)CN (1:2 molar ratio), resulting in the rupture of the chlorine bridging system and formation of [PdCl{[C(H)PPh₃]₂CO}(L)](ClO₄) (L = py (**4**), 3,5-lu (**5**), NC-C(H)=PPh₃ (**6**)), and with TlAcac (1:2 molar ratio) with formation of the acetylacetonate [Pd(acac){[C(H)PPh₃]₂CO}](ClO₄), **7**. On the other hand, complex **3** reacts with the ylide Ph₃P=C(H)CN (1:2 molar ratio) giving [Pd{[C(H)PPh₃]₂CO}[NC-C(H)=PPh₃]₂](ClO₄)₂, **8**, which contains two N-coordinated ylides, and with NBu₄-OH (1:1) to give [Pd(μ -OH){[C(H)PPh₃]₂CO}]₂(ClO₄)₂, **9**. The reaction of Pd(OAc)₂ with the ylide phosphonium salt [Ph₃P=C(H)COCH₂PPh₃](ClO₄) (1:1) gives the acetate dimer [Pd(μ -OOCCH₃){[C(H)PPh₃]₂CO}]₂(ClO₄)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**·CH₂Cl₂.

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 Ph₃P=C(H)COR (R = Me, Ph, OMe, NMe₂) and Ph₃P=C(H)CN.^{2–7} Throughout these studies, we have observed the ability of these ylides to behave as ambidentate ligands (except for the NMe₂ derivative⁷). 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 Ph₃P=C(H)COC(H)=PPh₃ 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 multifunctionality. However, as far as we know, only one report on this bis-ylide has appeared in the literature⁸ (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.

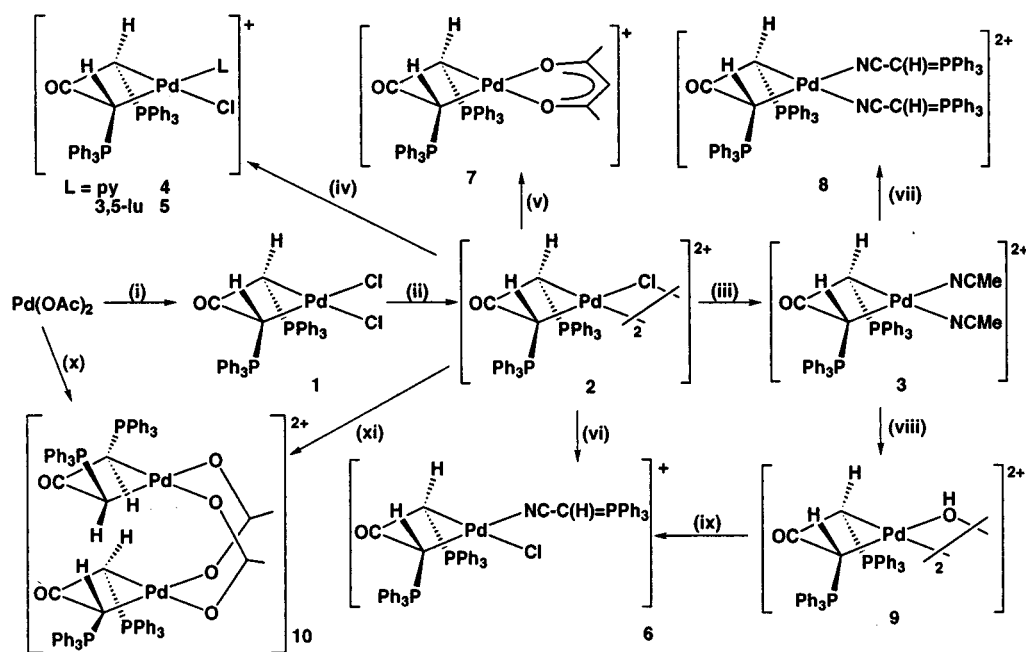
Results and Discussion

The reaction of Pd(OAc)₂ with the bis-phosphonium salt [Ph₃PCH₂COCH₂PPh₃]₂Cl₂ (1:1 molar ratio) in CH₂Cl₂ at room temperature results in the deprotonation of the two methylene groups of the bis-phosphonium salt and formation of a solid of stoichiometry Cl₂Pd{[C(H)PPh₃]₂CO}, **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 ligands¹¹—two absorptions at 293 and 278 cm^{–1}—and the location of these bands at low wavenumbers suggests a Cl-*trans*-to-C arrangement.¹² The ν (CO)

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Scheme 1



Legend for Scheme 1:

- (i): + $[\text{Ph}_3\text{PCH}_2\text{COCH}_2\text{PPh}_3]\text{Cl}_2$, - 2 HOAc, CH_2Cl_2 , r.t.
(ii): + TiClO_4 , - TiCl , CH_2Cl_2 , r.t.
(iii): + 2 TiClO_4 , - 2 TiCl , NCMe, r.t.
(iv): + 2 L, CH_2Cl_2 , r.t.
(v): + 2 NC-C(H)=PPh₃, CH_2Cl_2 , r.t.
(vi): + 2 $\text{Ti}(\text{acac})$, - 2 TiCl , CH_2Cl_2 , r.t.
(vii): + 2 NC-C(H)=PPh₃, CH_2Cl_2 , r.t.
(viii): + 2 NBu_4OH , MeOH / H_2O , r.t.
(ix): + 2 $[\text{Ph}_3\text{PCH}_2\text{CN}]\text{Cl}$, - H_2O , CH_2Cl_2 , r.t. (see text)
(x): + $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COCH}_2\text{PPh}_3](\text{ClO}_4)$, - HOAc, CH_2Cl_2 , r.t.
(xi): + 2 $\text{Ti}(\text{OOCCH}_3)_3$, - 2 TiCl , CH_2Cl_2 , 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 addition to complex resonances at low field due to Ph groups, a doublet centered at 3.70 ppm, with a coupling constant $^2J_{\text{P-H}}$ of 7 Hz, which is attributed to the ylide proton. The $^{31}\text{P}\{^1\text{H}\}$ 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 CHCl_3 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 TiClO_4 resulting in the precipitation of TiCl and formation of a yellow solid of stoichiometry $[\text{PdCl}\{\text{C}(\text{H})\text{PPh}_3\}_2\text{CO}]\text{ClO}_4$ **2**, according to its elemental analysis. The mass spectrum of this solid shows a weak peak at 1541 amu, which corresponds to the stoichiometry $[\text{PdCl}\{\text{C}(\text{H})\text{PPh}_3\}_2\text{CO}]\text{ClO}_4^+$ and strongly suggests a dinuclear nature for complex **2**. The molar conductivity of **2** in acetone is $\Lambda_{\text{M}} = 177\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$, which agrees with the average value reported¹⁵ for 2:1 electrolytes ($180\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) in the range of concentration employed ($6 \times 10^{-4}\text{ M}$). 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 $[\text{Ag}\{\text{C}(\text{H})\text{PPh}_3\}_2\text{CO}]\text{ClO}_4$ to the palladium derivative $\text{PdCl}_2\text{-(NCMe)}_2$ or the transylidation reaction (exchange of ylide ligands) of $\text{PdCl}_2[\text{C}(\text{H})\text{COMe}(\text{PPh}_3)]_2$ with $[\text{Ph}_3\text{PCH}_2\text{COCH}_2\text{PPh}_3](\text{ClO}_4)_2$. However, the low solubility of the silver derivative in the first case and the difficulty of completely eliminating the phosphonium salt $[\text{Ph}_3\text{PCH}_2\text{COCH}_3]\text{Cl}$ 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 $[\text{M}]\text{-C}(\text{H})\text{PPh}_3\text{-COCH}=\text{PPh}_3$ or complexes containing the mono-ylide unit $[\text{M}]\text{-C}(\text{H})\text{PPh}_3\text{-COCH}_2\text{PPh}_3$ were unsuccessful, even for the more obvious processes (e.g. reaction of $\text{PdCl}_2(\text{NCMe})_2$ with the ylide-phosphonium salt $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COCH}_2\text{PPh}_3](\text{ClO}_4)$).

The IR spectrum of **2** shows the expected changes. The $\nu(\text{Pd-Cl})$ stretch is shifted to lower energies with respect to **1**, in accord with the change of Cl from terminal to bridging and $\nu(\text{CO})$ 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, $^2J_{\text{P-H}} = 5.4\text{ Hz}$) and a singlet in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (23.75 ppm).

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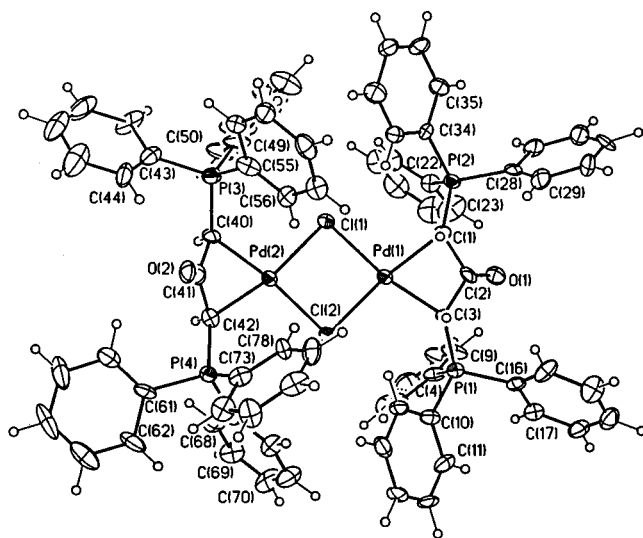


Figure 1. Thermal ellipsoid plot of the $[\text{Pd}(\mu\text{-Cl})\{[\text{C}(\text{H})\text{PPh}_3]_2\text{CO}\}]_2^{2+}$ cation. Atoms are drawn at the 50% probability level.

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_2Cl_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_2Cl_2 .

Crystals suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a CH_2Cl_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 -cycloheptyldipalladium(II) the value reported^{17a} is 139°, for di- μ -chlorobis- π -1,3-dimethylallyldipalladium(II)^{17b} this value is 150°, and for di- μ -chlorobis{[2,6-dimethyl-*N*-(benzylidene)phenylamino]-C^{2'},*N*}pallad-

Table 1. Selected Bond Lengths [Å] and Angles [deg] for **2**· CH_2Cl_2

Pd(1)–C(3)	2.053(11)	Pd(1)–Cl(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_2Cl_2 ^a

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

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

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 preserved 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) derivative⁸ $[Au_2\{\mu-\{CH(PPh_3)_2CO\}\}_2](ClO_4)_2$.

Finally, there is a short metal–hydrogen contact $C(56)\cdots H(56)\cdots Pd(2)$ [$M-H = 2.71(2)$ 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 $TiClO_4$ (1:2 molar ratio) in NCMe results in the formation of the bis-solvate $[Pd\{[C(H)PPh_3]_2CO\}(NCMe)_2](ClO_4)_2$, **3**. In these syntheses we have avoided the use of $AgClO_4$ as halide abstracting agent because of the formation of the very insoluble salt $[Ag_2\{\mu-\{CH(PPh_3)_2CO\}\}_2](ClO_4)_2$ 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 $^{31}P\{^1H\}$ 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 CH_2Cl_2 promotes the symmetrical cleavage of the bridging system and formation of the corresponding complexes of stoichiometry $[PdCl\{[C(H)PPh_3]_2CO\}(L)](ClO_4)$ (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 $^{31}P\{^1H\}$ NMR spectrum shows the presence of an AB spin system (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 $Ph_3P=C(H)COR$ (R = Me, Ph, OMe) and $Ph_3P=C(H)CN$. 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 $Ph_3P=C(H)CN$ (1:2 molar ratio) gives a product of stoichiometry $[PdCl\{[C(H)PPh_3]_2CO\}(Ph_3PCHCN)](ClO_4)$, **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 $^{31}P\{^1H\}$ 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 $[Pd(dmba)(\mu-Cl)]_2$ ($dmba = C_6H_4CH_2NMe_2-2$), 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" base²⁴) *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 $C(H)PPh_3$ 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 $[Pd(acac-O,O')\{[C(H)PPh_3]_2CO\}](ClO_4)$, **7**. The characterization of **7** results from the same considerations as those used previously; the key indicators are the $\nu(CO)$ 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 $Ph_3P=C(H)CN$ (1:2) to give $[Pd\{[C(H)PPh_3]_2CO\}(NC-C(H)=PPh_3)_2](ClO_4)_2$, **8** (see Scheme 1), in which both NCMe ligands have been replaced by the ylide $Ph_3P=C(H)CN$ as characterized by the elemental analysis and mass spectrum. The IR spectrum of **8** shows the expected absorptions corresponding to the bis-ylide ($\nu(CO) = 1615$ cm^{-1}) and to the cyano-ylide ($\nu(CN) = 2175$ 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 $^{31}P\{^1H\}$ 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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(22) However, the positioning of this proton atom leaves it ideally located to undergo an orthometalation process, and, in fact, compound **2** can be transformed into its orthometalated isomer $[Pd(\mu-Cl)(C_6H_4-PPh_2C(H)COCH_2PPh_3)_2](ClO_4)_2$ in an intramolecular acid–base reaction: Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics*, in press.

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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 $[\text{Pd}(\text{dmba})\text{-(NCMe)}_2]^+$ with 2 equiv of $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$ gave $[\text{Pd}(\text{dmba})\text{-}\{\text{C}(\text{H})\text{PPh}_3(\text{CN})\}\{\text{NC}-\text{C}(\text{H})=\text{PPh}_3\}]^+$ 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 NBu_4OH (1:2.1 molar ratio) results in the immediate precipitation of the dinuclear complex $[\text{Pd}(\mu\text{-OH})\{[\text{C}(\text{H})\text{PPh}_3]_2\text{CO}\}]_2(\text{ClO}_4)_2$, **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 ($^2J_{\text{P-H}} = 6.6\text{ Hz}$), 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 $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a single resonance at 23.99 ppm . Further treatment of **9** with NBu_4OH does not promote the formation of the bis-hydroxo derivative $[\text{Pd}(\text{OH})_2\{[\text{C}(\text{H})\text{PPh}_3]_2\text{CO}\}]$, and the reaction of **3** with an excess of NBu_4OH (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 $[\text{Ph}_3\text{PCH}_2\text{CN}]\text{Cl}$ 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 $\text{Pd}(\text{OAc})_2$ with the mixed ylide-phosphonium salt $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COCH}_2\text{PPh}_3](\text{ClO}_4)$ (1:1 molar ratio) results in the formation of the acetate bridged dimer $[\text{Pd}(\mu\text{-OOCCH}_3)\{[\text{C}(\text{H})\text{PPh}_3]_2\text{CO}\}]_2(\text{ClO}_4)_2$, **10**. The elemental analyses and mass spectrum are in good agreement with the proposed stoichiometry, and the conductivity data in acetone solution ($\Lambda_{\text{M}} = 217\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$) confirms the dicationic character of **10**. Complex **10** can also be obtained by reaction of **2** with TiOOCCH_3 (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 ligand³⁰ (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 ($^2J_{\text{P-H}} = 5.6\text{ Hz}$) and the methyl group of the acetate ligand as a singlet at 1.41 ppm . The $^{31}\text{P}\{^1\text{H}\}$ 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 $\{[\text{Ph}_3\text{P}=\text{C}(\text{H})]_2\text{CO}\}$ 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 P_2O_5 , acetonitrile over CaH_2 , methanol over magnesium and *n*-hexane over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Infrared spectra ($4000\text{--}200\text{ cm}^{-1}$) were recorded on a Perkin-Elmer 883 Infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^1H (300.13 MHz) and $^{31}\text{P}\{^1\text{H}\}$ (121.49 MHz) NMR spectra were recorded in CDCl_3 or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H was referenced using the solvent signal as internal standard and $^{31}\text{P}\{^1\text{H}\}$ was externally referenced to H_3PO_4 (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 $5 \times 10^{-4}\text{ M}$ with a Philips PW 9509 conductivity cell. The starting compounds $\text{Pd}(\text{OAc})_2$,³² $\text{Ph}_3\text{P}=\text{C}(\text{H})\text{CN}$,³³ $[\text{Ph}_3\text{PCH}_2\text{COCH}_2\text{PPh}_3]\text{Cl}_2$,^{13,14} and $[\text{Ph}_3\text{P}=\text{C}(\text{H})\text{COCH}_2\text{PPh}_3]\text{ClO}_4$ 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]₂Cl₂ (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 C₃₉H₃₂Cl₂OP₂Pd·0.5CH₂Cl₂: 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}[(C(H)PPh₃)₂CO]·2(CIO₄)₂, 2. To a solution of **1** (0.200 g, 0.264 mmol) in CH₂Cl₂ (30 mL) at room temperature, TiCl₄ (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 C₇₈H₆₄Cl₄O₁₀P₄·Pd₂·CH₂Cl₂: C, 54.27; H, 3.74. Calcd: C, 55.01; H, 4.05. MS (+ FAB) [*m/z* (%): 1541 [(M₂ - ClO₄)⁺, 20%]. Δ_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}(CIO₄)₂, 3. To a solution of **2** (1.000 g, 0.610 mmol) in NCMe (60 mL) at room temperature, TiCl₄ (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 C₄₃H₃₈Cl₂N₂O₉P₂Pd: 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}[(C(H)PPh₃)₂CO]·2(CIO₄)₂, 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 C₄₄H₃₇Cl₂N₂O₉P₂Pd: 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}[(C(H)PPh₃)₂CO]·2(CIO₄)₂, 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 C₄₆H₄₁Cl₂N₂O₉P₂Pd: 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}[(C(H)PPh₃)₂CO]·2(CIO₄)₂, 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 C₅₉H₄₈Cl₂N₂O₉P₃Pd·0.5CH₂Cl₂: 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]·2(CIO₄)₂, 7. To a solution of **2** (0.200 g, 0.122 mmol) in CH₂Cl₂ (25 mL) at room temperature, Ti(acac)₃ (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 C₄₄H₃₉ClO₇P₂Pd: C, 59.12; H, 4.53. Calcd: C, 59.81; H, 4.44. MS (+ FAB) [*m/z* (%): 783 [M⁺, 100%]. IR (cm⁻¹): 1610 (ν_{CO-ylide}), 1568, 1517 (ν_{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}(CIO₄)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 C₇₉H₆₄Cl₂N₂O₉P₄Pd·CH₂Cl₂: 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 (ν_{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}[(C(H)PPh₃)₂CO]·2(CIO₄)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 C₇₈H₆₆Cl₂O₁₂P₄Pd₂·1.5CH₂Cl₂: 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 (ν_{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}[(C(H)PPh₃)₂CO]·2(CIO₄)₂, 10. To a solution of Pd(OAc)₂ (0.139 g, 0.619 mmol) in CH₂Cl₂ (25 mL), [Ph₃P=C(H)-COCH₂PPh₃]₂ClO₄ (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 $\text{C}_{82}\text{H}_{70}\text{Cl}_2\text{O}_{14}\text{P}_4\text{Pd}_2$: C, 58.78; H, 3.80. Calcd: C, 58.38; H, 4.18. MS (+ FAB) $[m/z (\%)]$: 1587 $[(\text{M}_2 - \text{ClO}_4)^+]$, 10%. $\Lambda_{\text{M}} = 217 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (acetone solution, $5 \times 10^{-4} \text{ M}$). IR (cm^{-1}): 1611 ($\nu_{\text{CO-ylide}}$), 1557 ($\nu_{\text{CO}_2\text{-asym}}$). ^1H NMR (CD_2Cl_2): δ 7.78–7.71 (m, 9H, Ph), 7.52–7.46 (m, 6H, Ph), 4.92 (d, CH ylide, 1H, $^2J_{\text{P-H}} = 5.6 \text{ Hz}$), 1.41 (s, 3H, $\text{CH}_3\text{-acetate}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 26.41.

Crystal Structure Determination of $2\cdot\text{CH}_2\text{Cl}_2$. A yellow crystal of $2\cdot\text{CH}_2\text{Cl}_2$ 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 $22.0 \leq 2\theta \leq 30.1^\circ$. For intensity data collection, pure ω -scans were used with $\Delta\omega = 1.00 + 0.35 \tan \theta$. 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 corrections³⁴ 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 $\text{CH}_2\text{-Cl}_2$ 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 $\rho > 1.00 \text{ e/\AA}^3$, in the area of the disordered CH_2Cl_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

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

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(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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