Reactivity of Palladium(II) Complexes Containing the Orthometalated C,C-Chelating Ligand C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$ toward Deprotonating Reagents

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The dinuclear complex $[Pd(\mu\text{-Cl})(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ reacts with $Hg(OOCCH_3)_2$ (1:1 molar ratio, CH_2Cl_2, room temperature) giving the trinuclear derivative $[Pd_2Hg(\mu\text{-Cl})_2(C_6H_4\text{-2-}PPh_2C(H)COC(H)PPh_3)_2](ClO_4)_2$ (**1**). The X-ray structure of **1** has been determined: $C_{78}H_{62}Cl_4HgO_{10}P_4Pd_2$, monoclinic, *I*2/*a*, $a = 20.205(3)$ Å, $b = 11.7529(9)$ Å, $c = 30.905(3)$ Å, $\beta = 90.333(10)°$, $V = 7339.0(14)$ Å^3, $Z = 4$. The structure shows two Pd atoms bridged by two Cl atoms and also shows weak Pd−Hg contacts. Both orthometalated ylide groups $[C_6H_4\text{-2-}PPh_2C(H)COC(H)(PPh_3)]^-$ in **1** act as C,C,C-tridentate ligands, coordinated to the palladium center through the arylic carbon atom and the ylidic carbon atom adjacent to the PPh_2 group and to the mercury center through the ylidic carbon atom adjacent to the PPh_3 group. The reaction of $[Pd(\mu\text{-Cl})(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ with (acac)$AuPPh_3$ (acac = acetylacetonate; 1:2 molar ratio) affords $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)(acac\text{-}O,O')](ClO_4)$ (**2**) by transmetalation of the acac group. Further treatment of **2** with (acac)$AuPPh_3$ gives the dinuclear derivative $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH(AuPPh_3)(PPh_3))(acac\text{-}O,O')](ClO_4)$ (**3**) in which the orthometalated ylide fragment acts as a C,C,C-tridentate ligand. The reaction of $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)Cl(PPh_3)](ClO_4)$ with NBu_4OH (1:1 molar ratio) affords $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH{=}PPh_3)Cl(PPh_3)]$ as a mixture of the cis and trans isomers (**4a**/**4b**), while the reaction of the same cationic precursor $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)Cl(PPh_3)](ClO_4)$ with (acac)$AuPPh_3$ results in the formation of $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH(AuPPh_3)(PPh_3))Cl(PPh_3)](ClO_4)$ (**5**). The reaction of $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)(L{-}L)](ClO_4)_2$ (L−L = dppe, phen) with $Na[N(SiMe_3)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane and phen = 1,10-phenanthroline; 1:1 molar ratio, THF, room temperature) results in the formation of the cationic species $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH{=}PPh_3)(L{-}L)](ClO_4)$ (L−L = dppe (**6**), phen (**7**)), which contain a free ylidic fragment. Complex **6** reacts with ClAu(tht) (tht = tetrahydrothiophene; 1:1 molar ratio) giving $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH(AuCl)(PPh_3))(dppe)](ClO_4)$ (**8**), while $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH_2PPh_3)(phen)](ClO_4)_2$ reacts with (acac)$AuPPh_3$ (1:1 molar ratio) affording $[Pd(C_6H_4\text{-2-}PPh_2C(H)COCH(AuPPh_3)(PPh_3))(phen)](ClO_4)_2$ (**9**).

Introduction

We have recently reported the synthesis and characterization of several palladium(II) complexes containing the bis-ylide ligand $Ph_3P{=}C(H)COC(H){=}PPh_3$ coordinated as a C,C-chelate.[1a] This bis-ylide group is scarcely represented as a ligand toward transition metals,[1b] and, as far as we know, the chemistry of palladium with this ylide remains unexplored.[1c−e]

We have also recently reported that, under certain experimental conditions, complexes containing the $Pd\{[C(-)(H)P(+)Ph_3]_2C{=}O\}$ unit undergo an intramolecular rearrangement which transforms the C,C-chelating ligand $[C(H)PPh_3]C{=}O$ into a new C,C-chelating orthometalated ligand $C_6H_4(-)$-2-$P(+)Ph_2C(-)(H)C(O)CH_2P(+)Ph_3$.[2a] This ligand contains two markedly different moieties—the orthometalated C,C-chelating unit $C_6H_4(-)$-2-$P(+)Ph_2C(-)(H)$- and the free phosphonium fragment $-C(O)CH_2P(+)Ph_3$. The deprotonation of this phosphonium fragment would generate a "free ylide" unit $-C(O)C(H){=}PPh_3$ which in turn could be coordinated to the same or to another metal center, acting now as a tridentate ligand.

Our aim at the beginning of this work was to determine how this deprotonation could be realized and the nature of the obtained products. In addition, the reactivity of the generated free ylide unit toward electrophilic reagents would lead to the formation of a second chiral carbon atom in the resulting molecule, whose absolute configuration could be related with that already present in the starting compound. A diastereoselective induction can be envisaged in this point.

Concerning the nature of the deprotonating reagents, the use of $(NBu_4)[Au(acac)_2]$ (acac = acetylacetonate), [(acac)$AuPPh_3$] and $Hg(OAc)_2$ as deprotonating agents is already known in ylide chemistry and facilitates the synthesis of ylide- and bridging-

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(1) (a) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Inorg. Chem.* **1998**, *37*, 6007−6013. (b) Vicente, J.; Chicote, M. T.; Sauras-Llamas, I.; Jones, P. G.; Meyer-Bäse, K.; Erdbrügger, C. F. *Organometallics*, **1988**, *7*, 997−1006. (c) Johnson, A. W.; Kaska, W. C.; Starzewski, K. A. O.; Dixon, D. A. *Ylides and Imines of Phosphorous*; John Wiley & Sons: New York, 1993; Chapter 14, and references cited therein. (d) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62. (e) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907.

(2) (a) Falvello, L. R.; Fernández, S.; Navarro, R.; Rueda, A.; Urriolabeitia, E. P. *Organometallics* **1998**, *18*, 5887−5900. Selected references of previous work on orthopalladated ylide complexes: (b) Baldwin, J. C.; Kaska, W. C. *Inorg. Chem.* **1979**, *18*, 686−691. (c) Illingsworth, M. L.; Teagle, J. A.; Burmeister, J. L.; Fultz, W. C.; Rheingold, A. L. *Organometallics* **1983**, *2*, 1364−1369. (d) Teagle, J. A.; Burmeister, J. L. *Inorg. Chim. Acta* **1986**, *118*, 65−72. (e) Albanese, J. A.; Rheingold, A. L.; Burmeister, J. L. *Inorg. Chim. Acta* **1988**, *150*, 213−216. (f) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J. *J. Organomet. Chem.* **1989**, *364*, 407−414. (g) Albanese, J. A.; Staley, D. L.; Rheingold, A. L.; Burmeister, J. L. *J. Organomet. Chem.* **1989**, *375*, 265−272.

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carbene complexes.[3−5] However, as far as we know, only one example of an orthometalated tridentate ylide has been reported.[6]

In this paper we report the results obtained in studies of the reactivity of several precursors containing the $[C_6H_4(-)\text{-}2\text{-}P(+)\text{-}Ph_2C(-)(H)C(O)CH_2P(+)Ph_3]$ ligand (formal charges will be omitted throughout the text by reason of simplicity) toward different deprotonating agents such as $Hg(OOCCH_3)_2$, [(acac)-$AuPPh_3$], $(NBu_4)[Au(acac)_2]$, $Na[N(SiMe_3)_2]$, and NBu_4OH. These reactions yield two different classes of compounds—one containing the free ylide unit $-C(H)=PPh_3$ and one with the metalated ylide unit $-C(H)(ML_n)(PPh_3)$. In the last case, the ylide acts as a C,C,C-tridentate ligand, the reaction occurring with a high stereoselectivity.

Results and Discussion

The reaction of $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ with $Hg(OOCCH_3)_2$ (1:1 molar ratio, CH_2Cl_2, room temperature) results in the formation of a mixture of two products—the trinuclear $[Pd_2Hg(\mu\text{-}Cl)_2(C_6H_4\text{-}2\text{-}PPh_2C(H)CO C(H)\text{-}PPh_3)_2](ClO_4)_2$ (**1**) and the dinuclear acetate bridging $\{(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Pd(\mu\text{-}OAc)_2Pd[C(H)PPh_3]_2CO\}^{2+}$. The molar ratio of these compounds in the mixture is 5:1. The formation of the bridging acetate dimer can be rationalized in the same way as that described[2a] for the reaction of $[Pd(\mu\text{-}Cl)\text{-}(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ with $Ag(OOCCH_3)$, that is, chelation of one acetate ligand, deprotonation of the phosphonium fragment, generation of a new ylide group, and concomitant formation of acetic acid; finally, the protonation of the C(aryl)−Pd bond generates the bis-ylide ligand. Complex **1** can be purified by treatment of the mixture of products with MeOH (see Experimental Section) in which **1** remains insoluble. Further recrystallization of this complex from CH_2Cl_2/*n*-hexane affords yellow single crystals of **1**, which are of adequate quality for X-ray measurements.

A drawing of the trinuclear organometallic cation is shown in Figure 1, relevant crystallographic data are presented in Table 1, and selected bond distances and angles are collected in Table 2. Complex **1** crystallizes in the centrosymmetric space group *I*2/*a*. The asymmetric unit consists of half a molecule of the complex and one perchlorate anion. The complete molecule possesses crystallographic 2-fold symmetry, and the 2-fold axis passes through the Hg center. The molecule is chiral and contains four chiral centers. Figure 1 shows the *R*[C(19)]-*S*[C(21)] molecule, but the crystal as a whole is a racemate. The skeleton of the molecule comprises two palladium atoms bridged by two chlorine atoms, each palladium showing weak interactions with the mercury center, probably of dative Pd → Hg nature. The distance Pd−Hg [3.0716(9) Å] is greater than the Pd−Hg bond distances found in the clusters $Pd_4Hg_2Br_2\text{-}(CO)_4(PEt_3)_4$ [ranging from 2.704(1) to 2.993(1) Å][7] and $[Hg_2\text{-}Pd(AuPPh_3)_8](NO_3)_2$ [2.91, 2.98 Å][8] and is shorter than that found in the dinuclear derivative $[PdBr(S_2COEt)\{\mu\text{-}P(o\text{-}tolyl)_2C_6H_4CH_2-\}HgBr]\cdot 0.5HgBr_2\cdot C_2H_4Cl_2$ [3.098(1) Å][9] and also shorter than the sum of the van der Waals radii (3.1 Å).[10]

Each palladium atom completes its square-planar coordination environment by bonding to the orthometalated carbon atom C(1)/C(1A) and to the ylidic carbon atom C(19)/C(19A). The mercury center is bonded to the ylidic carbon atoms C(21) and C(21A), and its environment is—excluding the weak dative interactions with the Pd centers—essentially linear. The Pd−C(1) bond distance [2.012(10) Å] and the Pd−C(19) bond

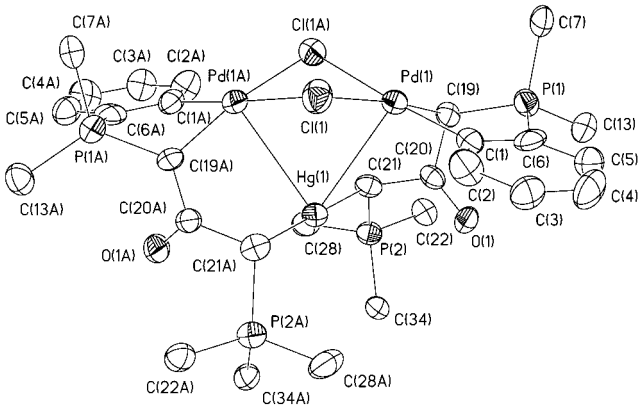


Figure 1. Thermal ellipsoid plot of the cationic organometallic $[Pd_2\text{-}Hg(\mu\text{-}Cl)_2(C_6H_4\text{-}2\text{-}PPh_2C(H)COC(H)(PPh_3))_2]^{2+}$ (**1**). H atoms and Ph groups have been omitted for clarity. Atoms are drawn at the 50% probability level. Hg(1) lies on a crystallographic 2-fold axis.

Table 1. Crystal Data and Structure Refinement for **1**

empirical formula	$C_{78}H_{62}Cl_4HgO_{10}P_4Pd_2$	β	90.333(10)°
fw	1838.35	V	7339.0(14) Å^3
T	297(2) K	Z	4
λ	0.71073 Å	ρ_{calc}	1.664 g cm^{-3}
space group	*I*2/*a* (No. 15)	μ	2.863 mm^{-1}
a	20.205(3) Å	$R_1{}^a$ [$I > 2\sigma(I)$]	0.0591
b	11.7529(9) Å	$R_{w2}{}^a$ [$I > 2\sigma(I)$]	0.1116
c	30.905(3) Å		

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $R_{w2} = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2)^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Hg(1)−C(21)	2.159(9)	Hg(1)−Pd(1)	3.0716(9)	Pd(1)−C(1)	2.012(10)
Pd(1)−C(19)	2.083(9)	Pd(1)−Cl(1)	2.360(3)	Pd(1)−Cl(1)^a	2.454(3)
P(1)−C(6)	1.779(12)	P(1)−C(7)	1.788(12)	P(1)−C(19)	1.793(9)
P(1)−C(13)	1.802(10)	C(19)−C(20)	1.468(13)	C(20)−O(1)	1.220(11)
C(20)−C(21)	1.533(13)	C(21)−P(2)	1.808(10)	P(2)−C(22)	1.786(10)
P(2)−C(28)	1.789(11)	P(2)−C(34)	1.802(10)		

C(21)^a−Hg(1)−C(21)	179.7(6)	C(21)^a−Hg(1)−Pd(1)^a	72.7(3)
C(21)−Hg(1)−Pd(1)^a	107.6(3)	C(21)^a−Hg(1)−Pd(1)	107.6(3)
C(21)−Hg(1)−Pd(1)	72.7(3)	Pd(1)^a−Hg(1)−Pd(1)	65.65(3)
C(1)−Pd(1)−C(19)	87.2(4)	C(1)−Pd(1)−Cl(1)	96.3(3)
C(19)−Pd(1)−Cl(1)	172.4(3)	C(1)−Pd(1)−Cl(1)^a	176.6(3)
C(19)−Pd(1)−Cl(1)^a	92.3(3)	Cl(1)−Pd(1)−Cl(1)^a	84.65(11)
C(1)−Pd(1)−Hg(1)	103.0(3)	C(19)−Pd(1)−Hg(1)	90.8(3)
Cl(1)−Pd(1)−Hg(1)	81.79(7)	Cl(1)^a−Pd(1)−Hg(1)	80.36(7)
Pd(1)−Cl(1)−Pd(1)^a	87.52(9)	C(20)−C(19)−P(1)	114.0(7)
C(20)−C(19)−Pd(1)	98.4(6)	P(1)−C(19)−Pd(1)	103.2(4)
O(1)−C(20)−C(19)	125.8(9)	O(1)−C(20)−C(21)	120.0(9)
C(19)−C(20)−C(21)	114.2(9)	C(20)−C(21)−P(2)	110.8(7)
C(20)−C(21)−Hg(1)	104.1(6)	P(2)−C(21)−Hg(1)	116.3(5)

^{a} Symmetry transformations used to generate equivalent atoms: $-x + {}^3/_2, y, -z + 1$.

(3) (a) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G. *J. Chem. Soc., Dalton Trans.* **1991**, 2579−2583, and references cited therein. (b) Vicente, J.; Chicote, M. T.; Cayuelas, J. A.; Fernández-Baeza, J.; Jones, P. G. Sheldrick, G. M.; Espinet, P. *J. Chem. Soc., Dalton Trans.* **1985**, 1163−1168.
(4) Lusser, M.; Peringer, P. *Organometallics* **1984**, *3*, 1916−1917.
(5) (a) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M. *Organometallics* **1995**, *14*, 2918−2922, and references cited therein. (b) Fernández, E. J.; Gimeno, M. C.; Jones, P. G.; Laguna, A.; Laguna, M.; López-de-Luzuriaga, J. M.; Rodríguez, M. A. *Chem. Ber.* **1995**, *128*, 121−124.
(6) Vicente, J.; Chicote, M. T.; Lagunas, M. C.; Jones, P. G.; Bembenek, E. *Organometallics* **1994**, *13*, 1243−1250.
(7) Mednikov, E. G.; Bashilov, V. V.; Sokolov, V. I.; Slovokhotov, Y. L.; Struchkov, Y. T. *Polyhedron* **1983**, *2*, 141−144.
(8) Gould, R. A. T.; Craighead, K. L.; Wiley: J. S.; Pignolet, L. H. *Inorg. Chem.* **1995**, *34*, 2902−2913.
(9) Falvello, L. R.; Forniés, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroya, P. *Inorg. Chem.* **1997**, *36*, 6166−6171.
(10) (a) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. (b) Allinger, N. L.; et al. *J. Am. Chem. Soc.* **1968**, *90*, 1199−1210.

distance [2.083(9) Å] are slightly longer than the respective mean values reported for Pd−C_{aryl} bonds (1.981 Å) and Pd−C_{alkyl} bonds (2.027 Å).[11] The Hg−C(21) bond distance [2.159(9) Å] is shorter than that found in [$HgCl_2$·Ph_3PCHCOPh]$_2$·$2CH_3OH$ [2.208(8) Å].[12] The Pd−Cl bond distances are slightly different [Pd(1)−Cl(1) = 2.360(3) Å and Pd(1)−Cl(1A) = 2.454(3) Å], with the longer one corresponding to the chlorine atom trans to the orthometalated carbon atom. This fact is in good agreement with the higher trans influence of an arylic carbon as compared to an ylidic carbon atom. Finally, the relative disposition of the two orthometalated rings is anti in the molecule shown. This disposition coincides with the presence of a 2-fold axis in **1** but probably also exists in the dinuclear starting compound.[2a]

Thus, the crystal structure of **1** shows clearly that deprotonation of the phosphonium moiety in the starting compound [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$(ClO_4)$_2$ has taken place with concomitant formation of HOAc and that the resulting ylide has reacted with the Hg center with a C-bonded mode.

Complex **1** has also been characterized through analytic and spectroscopic methods. The mass spectrum of **1** shows an intense peak at 1739 amu which corresponds to the trinuclear cation plus one ClO_4^- group. The IR spectrum of **1** shows the carbonyl stretch at 1619 cm^{-1}, that is, shifted to lower energy with respect to the corresponding absorption in the starting compound (1648 cm^{-1}).[2a] This shift follows the observed trend in the sequence ν_{CO}(phosphonium) > ν_{CO}(C-bonded ylide) > ν_{CO}(free ylide) > ν_{CO}(O-bonded ylide) for the carbonyl absorption in keto-stabilized ylides.[13]

The NMR data of **1** are temperature independent and reveal the presence of only one diastereoisomer in solution (the racemic mixture of the two enantiomers), since only one set of signals is observed in the ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectra. It is interesting to note that the NMR spectrum of the crude product precipitated in MeOH (see Experimental Section) is exactly the same and shows the same temperature independence as that of the product recrystallized from CH_2Cl_2/hexane. On the other hand, the monitoring of the reaction by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy shows resonances corresponding exclusively to **1** and to the dinuclear byproduct {(C_6H_4-2-PPh_2C(H)$COCH_2$-PPh_3)Pd(μ-OAc)$_2$Pd[C(H)PPh_3]$_2$CO}$^{2+}$, showing that there are not resolution or selective crystallization during precipitation and purification of **1**. That is, the stereoselective induction occurs at reaction time, and there are no other kinds of resolution.

As we will see, the structural results obtained for compound **1** indicate that a given chirality at the ylidic carbon bonded to the palladium induces a specific chirality at the ylidic carbon bonded to mercury. Thus, in complex **1** if C(19)—bonded to palladium—has the *R* configuration, then C(21)—the resulting ylidic carbon atom bonded to mercury—has the *S* configuration and the molecule exists as the mixture $C_R(19)C_S(21)/C_S(19)$-$C_R(21)$. This stereoselective induction (*R* induces *S* and *S* induces *R*) resembles that found in palladium complexes with the C,C-chelating bis-ylide [C(H)PPh_3]$_2$CO[1] and also that described by Vicente et al. in gold complexes with the bridging bis-ylide.[1b] The only exception we have found in the course of this study is the dinuclear complex [Pd(C_6H_4-2-PPh_2C(H)$COCH$(AuPPh$_3$)-(PPh_3))(acac)](ClO_4) (**3**), which is obtained as a mixture of the two diastereoisomers (see below).

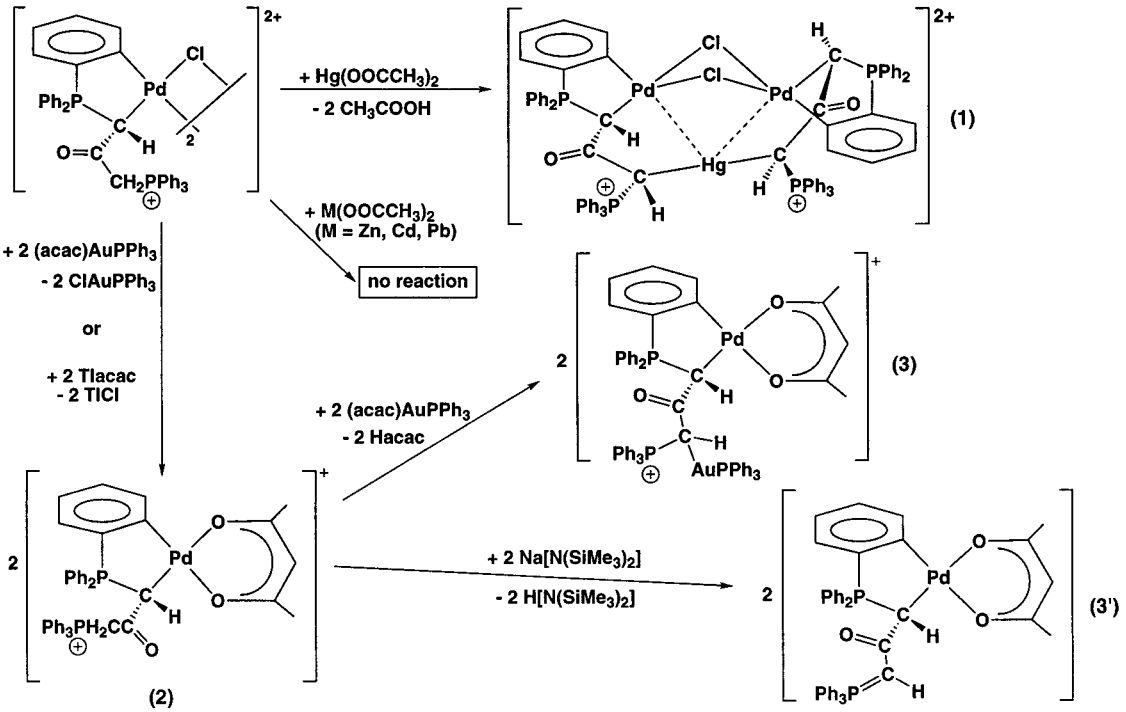
The ^{1}H NMR spectrum of **1** shows the methine proton Pd−C(H)P as a doublet at 4.82 ppm and the methine proton of the group Hg−C(H)P as a doublet of doublets at 5.66 ppm, while the ^{13}C{^{1}H} NMR spectrum shows the ylidic carbon bonded to palladium as a doublet of doublets at 43.16 ppm and the ylidic carbon bonded to mercury as a doublet of doublets at 55.86 ppm. Neither in the ^{1}H NMR spectrum nor in the ^{13}C spectrum have we observed ^{199}Hg satellites. The ^{31}P{^{1}H} NMR spectrum shows an AB spin system with resonances centered at 23.93 and 21.52 ppm and in which the signal at 23.93 ppm shows the ^{199}Hg satellites with a coupling constant of $^2J_{Hg-P}$ = 87 Hz. The δ value is very similar to that found in [$HgCl_2$·Ph_3-PCHCOPh][12] (23.41 ppm); the latter does not show mercury satellites, probably because of a fast exchange with the metal. However, in our case, the presence of an observable coupling constant indicates that the molecule is static on the NMR time scale and that the observation of a single set of signals is due exclusively to the presence of a single diastereoisomer in solution and not to the presence of several isomers in fast exchange equilibrium. The value of the $^2J_{Hg-P}$ coupling constant is smaller than other reported values (ranging from 106 to 160 Hz).[14] The diminution of the coupling constant could indicate that the hybridization of the mercury atom is not sp but rather something with a lower percentage of "s" character[15] (probably dsp^3) and which could be responsible for the weak dative interactions with the two palladium atoms.

We have also performed reactions between the starting dinuclear derivative [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$-(ClO_4)$_2$ and other acetate salts, such as M($OOCCH_3$)$_2$ (M = Zn, Cd, Pb; see Scheme 1), but under the same experimental conditions, no reaction takes place and the mixture of the starting compounds is recovered. Other deprotonating reagents have also been tested. The reaction of the dinuclear derivative [Pd(μ-Cl)-(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$(ClO_4)$_2$ with (acac)$AuPPh_3$ (1:2 molar ratio) results in the formation of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(acac)](ClO_4) (**2**) and $ClAuPPh_3$. A transmetalation reaction of the acac ligand from the gold center to palladium has taken place. The same transmetalation process is observed when (NBu_4)[Au(acac)$_2$] (1:1 molar ratio) is employed as deprotonating agent, and the reaction products are in this case **2** and (NBu_4)[$AuCl_2$]. Obviously, complex **2** can be obtained in a more convenient (and less expensive) way by treatment of [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$(ClO_4)$_2$ with Tl(acac) (1:2 molar ratio), and this latter method is described in the Experimental Section.

Complex **2** reacts with 1 equiv of (acac)$AuPPh_3$ to give a pale yellow solid of stoichiometry [Pd(acac)(C_6H_4-2-PPh_2C-(H)$COCH$(AuPPh$_3$)PPh_3)](ClO_4) (**3**) as deduced from its elemental analysis, mass spectrum, IR, and NMR data (see Experimental Section). The IR spectrum of **3** shows the carbonyl absorption attributed to the ylide at 1614 cm^{-1} and those of the acac group at 1580 and 1515 cm^{-1}. The positions of the acac absorptions indicate that this ligand is acting as a chelate, and the position of the ylidic carbonyl band is very close to that found in **1** and is shifted to lower energy with respect to that in **2** (1642 cm^{-1}). These facts mean that the (acac)$AuPPh_3$ has reacted with **2**, producing the deprotonation of the phosphonium

(11) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
(12) Kalyanasundari, M.; Panchanatheswaran, K.; Robinson, W. T.; Wen, H. *J. Organomet. Chem.* **1995**, *491*, 103−109.
(13) Falvello, L. R.; Fernández, S.; Navarro, R.; Pascual, I.; Urriolabeitia, E. P. *J. Chem. Soc., Dalton Trans.* **1997**, 763−771, and references cited therein.
(14) Mason, J. *Multinuclear NMR*; Plenum Press: New York, 1987; p 583, and references cited therein.
(15) (a) Schmidbaur, H.; Gasser, O.; Fraser, T. E.; Ebsworth, E. A. V. *J. Chem. Soc., Chem. Commun.* **1977**, 334−335. (b) Colquhoun, I. J.; McFarlane, W. *J. Chem. Soc., Dalton Trans.* **1981**, 658−660.

Scheme 1



fragment, liberation of Hacac, incorporation of the $[AuPPh_3]^+$ unit into the resulting ylide, and C-coordination of this ylide to the gold center.

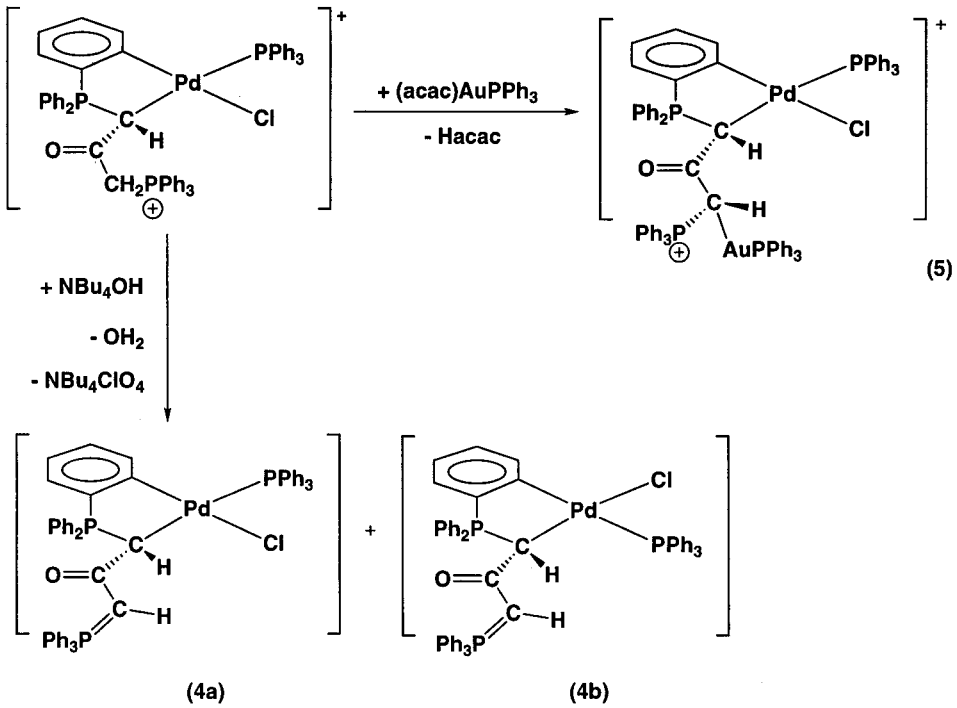
The NMR spectra of **3** show two sets of signals each (1:2 molar ratio) with the same pattern, corresponding to the presence of the two possible diastereoisomers (*RR*/*SS* and *RS*/*SR*), although we have not been able to determine unambiguously the absolute configurations of each isomer. Tentatively, we assign the absolute configurations (*RS*/*SR*) to the major isomer, in accord with the discussion given for **1**. The presence of the $-C(O)C(H)(AuPPh_3)(PPh_3)$ unit is clearly reflected in the NMR spectra. The ^1H NMR spectrum shows the methine resonance $C(H)(AuPPh_3)(PPh_3)$ as a doublet of triplets, signifying that this proton is coupled to three P atoms. The measurement of the $^1H\{^{31}P\}$ spectrum confirms this and permits the determination of the values of the coupling constants (see Experimental Section). Similarly, the $^{13}C\{^1H\}$ NMR spectrum of **3** shows the ylidic carbon $-C(H)(AuPPh_3)(PPh_3)$ as a doublet of triplets and the ylidic carbonyl resonance also as a doublet of triplets (see Experimental Section). Finally, the $^{31}P\{^1H\}$ NMR spectrum shows the presence of three chemically inequivalent phosphorus atoms, centered at about 39 ppm (typical for $AuPPh_3$) and 20−25 ppm ($C(H)PPh_3$ and C_6H_4-2-PPh_2).

We have also attempted the synthesis of the intermediate orthometalated−free ylide compound $[Pd(acac)(C_6H_4\text{-}2\text{-}PPh_2C(H)COC(H)=PPh_3)]$ by direct deprotonation of **2** with $Na[N(SiMe_3)_2]$, a strong and nonnucleophilic base.[16] The treatment of a tetrahydrofuran (THF) solution of **2** with $Na[N(SiMe_3)_2]$ (1:1 molar ratio) affords an orange solution from which, after workup in order to eliminate the byproduct $NaClO_4$, a yellow solid was obtained. The ^1H NMR of this solid shows the presence of a single set of resonances; signals attributed to the acac ligand appear at 5.16 (s, 1H, CH) and 1.97 and 1.64 (2s, 6H, Me) ppm, and signals attributed to the ylide appear at 4.03 (d, 1H, C(H)Pd) and 3.77 (dd, 1H) ppm. This last resonance shows coupling constants of $^2J_{P-H} = 26$ Hz and $^4J_{P-H} = 2$ Hz, with the value of 26 Hz clearly indicating the presence of the unit $-C(H)=PPh_3$.[13] Additional evidence for the existence of the free ylide moiety can be inferred from the $^{31}P\{^1H\}$ NMR spectrum, since it shows an AX spin system centered at 25.45 ppm (C_6H_4-2-PPh_2) and at 15.19 ppm (typical for $-C(H)=PPh_3$). In addition, the IR spectrum shows only two absorptions in the carbonyl region (1583 and 1515 cm^{-1}), in the typical range for the chelating acac ligand. The presence of the $-C(O)C(H)=PPh_3$ unit should shift the ylidic CO stretch to lower energy, at least lower than that found for **3** (1614 cm^{-1}); thus, this absorption should be obscured by those of the acac ligand. With all of these data, it is sensible to assume that the yellow solid obtained should have a stoichiometry $[Pd(acac)(C_6H_4\text{-}2\text{-}PPh_2C(H)COC(H)=PPh_3)]$ (**3′**) and a structure such as that depicted in Scheme 1. However, the IR spectrum again shows the presence of ClO_4 (probably as the Na^+ salt), and the microanalytical data found are much lower than expected. All attempts at recrystallization were unsuccessful, and a chromatographic purification resulted in the protonation of the product. Although in this case the obtention of the pure free ylide intermediate has not been possible, we have had more success using other ancillary ligands and/or other deprotonating agents.

The treatment of $[Pd(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)Cl(PPh_3)](ClO_4)$ with $Na[N(SiMe_3)_2]$ in THF (1:1 molar ratio) results in the formation of a very complex mixture of products, which we were not able to separate and identify. However, the treatment of a methanolic suspension of the same starting compound with a solution of NBu_4OH in MeOH (1:1 molar ratio) gives, after several extractions in $CHCl_3$ and toluene, a pale yellow solid of stoichiometry $[Pd(C_6H_4PPh_2C(H)COCHPPh_3)Cl(PPh_3)]$ (**4**; see Scheme 2) as deduced from its elemental analysis. The IR spectrum of **4** shows the presence of a strong absorption at 1504 cm^{-1}, attributed to the ylidic carbonyl stretch. The position of this absorption strongly suggests the presence of the $-C(O)C(H)=PPh_3$ fragment, since it is located in the same region as the carbonyl absorption of the ylides $Ph_3P=C(H)COR$ (R = Me, Ph, OMe).[13]

(16) Al-Jibori, S.; Shaw, B. L. *Inorg. Chim. Acta* **1982**, *65*, L123−L124.

Scheme 2



The ^{1}H NMR spectrum of **4** shows the presence of two sets of resonances with the same pattern but different intensities (integral ratio = 1.6/1), indicating the presence of two isomers. The presence of the free ylide unit −C(H)=PPh_3 in both isomers of **4** can be inferred from the observation of doublets of doublets centered at 4.28 ppm ($^2J_{P-H}$ = 28 Hz) and 3.33 ppm ($^2J_{P-H}$ = 27 Hz). Thus, only one chiral center is present in each molecule of **4**, and the presence of isomers could have two different reasons—geometrical isomerism and formation of cis and trans isomers or isomerism internal to the −C(O)C(H)=PPh_3 fragment with formation of the cisoid and transoid isomers.[13] The first possibility seems more plausible, since the resonances attributed to the methine proton appear as a doublet of doublets in one isomer (4.93 ppm) and as a doublet of doublets of doublets (3.50 ppm) in the other. The latter splitting could be due to the presence of the ylidic carbon trans to a PPh_3 ligand (isomer **4a**) while the former should possess the phosphine ligand trans to the orthometalated carbon (isomer **4b**) (see Scheme 2).

The ^{13}C{^{1}H} NMR spectrum of **4** confirms this hypothesis. The resonance attributed to the orthometalated carbon C_1 in each isomer appears as a doublet of doublets but shows very different values of the respective coupling constants. The resonance centered at 174.20 ppm shows values of 139.4 and 30 Hz, while the resonance at 165.91 ppm shows values of 24.4 and 5.6 Hz. The value of 139.4 Hz for a coupling constant J_{P-C} indicates the mutual trans arrangement of the orthometalated carbon and the phosphine group[17] as depicted in Scheme 2 for structure **4b** (the major isomer), while the measured values for the resonance at 166 ppm indicate a cis arrangement (structure **4a**, minor isomer, Scheme 2). Moreover, the observation of resonances centered at 52.03 and 50.00 ppm with respective coupling constants $^1J_{P-C}$ of 108.8 and 109.6 Hz confirms the formation of the −C(H)=PPh_3 fragment by deprotonation of the phosphonium moiety.[13] The ^{31}P{^{1}H} NMR spectrum of **4** is in good agreement with the foregoing data and shows two sets of three resonances which can be easily analyzed in terms of the structures shown in Scheme 2.

The complex [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)Cl(PPh_3)](ClO_4) also reacts with (acac)$AuPPh_3$ (1:1 molar ratio, CH_2Cl_2, room temperature), resulting in the formation of the cationic derivative[Pd(C_6H_4-2-PPh_2C(H)COCH(AuPPh$_3$)PPh_3)Cl(PPh_3)](ClO_4) (**5**), as deduced from its elemental analysis as well as IR and NMR spectra. The IR spectrum of **5** shows the ylidic carbonyl stretch at 1605 cm^{-1}, suggesting, as described for **3**, that deprotonation of the phosphonium unit and formation of a new C_{ylide}−Au bond have taken place. The NMR data of **5** show the presence of only one diastereoisomer in solution (see Experimental Section) and are in good agreement with the structure depicted in Scheme 2. In this case the reaction proceeds with high stereoselectivity, since only one diastereoisomer is observed—as described for **1**—and, in addition, the reaction occurs with retention of configuration at the palladium atom since only one geometrical isomer is observed.

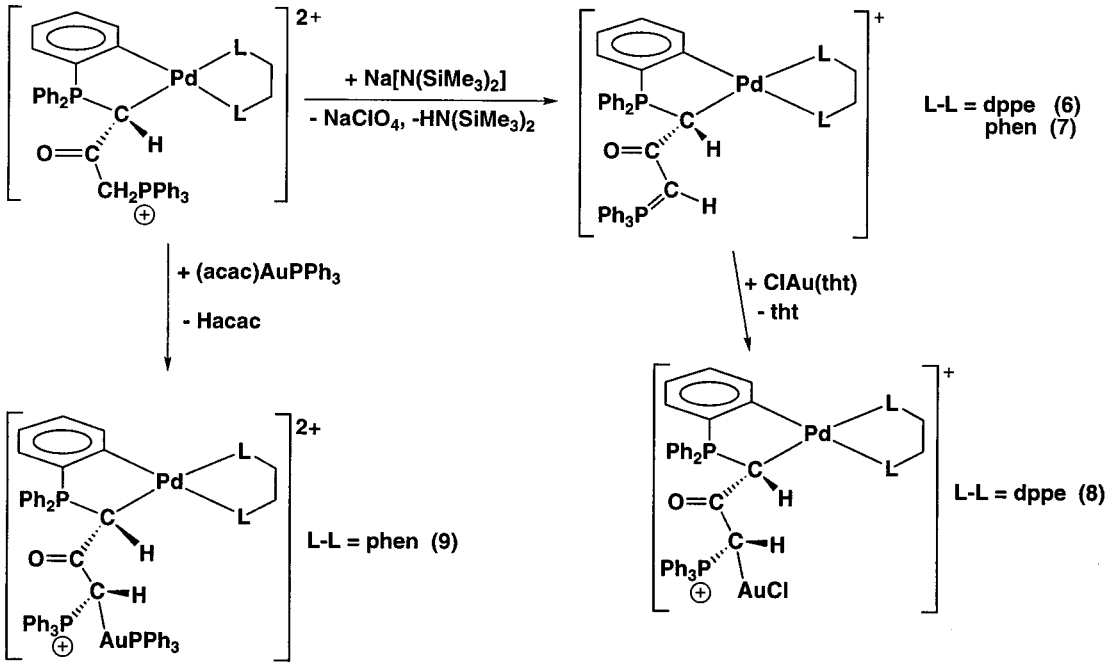
We are unaware of the reasons for the formation of geometrical isomers in **4**, considering that the *transphobic* behavior of the palladium atom makes the trans arrangement of the aryl and phosphine ligands unfavorable.[18] However, this "unfavourable" trans arrangement is not uncommon and in some cases constitutes the only isomer observed.[6] The observation of only one diastereoisomer in **5** is explained in the same terms as those described for **1**; that is, we assign to the ylidic carbons the absolute configurations of the corresponding enantiomers (R_{C-Pd}/S_{C-Au}) and (S_{C-Pd}/R_{C-Au}).

The influence of the ancillary ligands coordinated to the fragment [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)] seems to play also an important role in the stabilization of the resulting [Pd(C_6H_4-2-PPh_2C(H)-C(O)-C(H)=PPh_3)] moiety. Chelating ligands have been shown to be particularly useful in this stabilization. Thus, the deprotonation of the complexes [Pd(C_6H_4-2-PPh_2C(H)$COCH_2$-

(17) Avis, M. W.; Vrieze, K.; Ernsting, J. M.; Elsevier: C. J.; Veldman, N.; Spek, A. L.; Katti, K. V.; Barnes, C. L. *Organometallics* **1996**, *15*, 2376−2392.

(18) Vicente, J.; Arcas, A.; Bautista, D.; Jones, P. G. *Organometallics* **1997**, *16*, 2127−2138.

Scheme 3



PPh_3)(L−L)]$(ClO_4)_2$ (L−L = dppe (1,2-bis(diphenylphosphino)-ethane), phen(1,10-phenanthroline) with $Na[N(SiMe_3)_2]$ (1:1 molar ratio, THF, room temperature) gives good yields of the corresponding [Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)(L−L)]-(ClO_4) (L−L = dppe (**6**), phen (**7**) derivatives (see Scheme 3), as deduced from their elemental analyses and mass spectra. The characterization of complexes **6** and **7** is based on the observation of the same key features described for complexes **3′** and **5**. The IR spectra show the carbonyl absorption at 1521 (**6**) and 1517 (**7**) cm^{-1}; the ^1H NMR spectra show resonances at 3.07 ppm (**6**, d, $^2J_{P-H}$ = 24.6 Hz) and 3.54 ppm (**7**, d, $^2J_{P-H}$ = 24 Hz); the $^{31}P\{^1H\}$ NMR spectra show signals at 14.81 ppm (**6**) and 14.56 ppm (**7**); and the $^{13}C\{^1H\}$ NMR spectra show resonances at 53.54 ppm (**6**, dd, $^1J_{P-C}$ = 109 Hz) and 54.14 ppm (**7**, dd, $^1J_{P-C}$ = 108 Hz). All these data are in good agreement with the proposed structures for **6** and **7**, shown in Scheme 3.

Further reactivity of complex **6** has been attempted. Complex **6** reacts with 1 equiv of ClAu(tht) (tht = tetrahydrothiophene, SC_4H_8), resulting in the displacement of the tht ligand from the Au center and coordination of the "free" ylidic carbon, giving the dinuclear complex [Pd(C_6H_4-2-PPh_2C(H)CO*C*(H)(AuCl)-(PPh_3))(dppe)](ClO_4) (**8**) as deduced from its elemental analysis and mass spectrum. The IR spectrum of **8** shows the carbonyl absorption at 1621 cm^{-1}, shifted, as expected, to higher energy with respect to **7** (1517 cm^{-1}). The NMR data show the presence of only one diastereoisomer in solution (as the racemic mixture of the enantiomers) and also show the expected changes in the chemical shifts and coupling constants of the $-C(H)PPh_3$ unit after coordination to the gold(I) center (see Experimental Section). Following the same experimental method described for **3** and **5**, the complex [Pd(C_6H_4-2-PPh_2C(H)COCH_2PPh_3)-(phen)]$(ClO_4)_2$ reacts with 1 equivalent of (acac)$AuPPh_3$ (CH_2Cl_2, room temperature), affording the corresponding dinuclear derivative [Pd(C_6H_4-2-PPh_2C(H)CO*C*(H)($AuPPh_3$)(PPh_3))(phen)]-(ClO_4)$_2$ (**9**) as a single diastereoisomer. The spectroscopic characterization of **9** clearly shows the presence of the unit $-C(O)C(H)(AuPPh_3)(PPh_3)$, as inferred from the position of the carbonyl stretch (1622 cm^{-1}) in the IR spectrum and from the chemical shifts and *J* values of the nuclei in this unit. The methine proton $-C(H)(AuPPh_3)PPh_3$ appears as a doublet of doublets at 5.38 ppm in the ^1H NMR spectrum, the phosphorus nucleus $-C(H)(AuPPh_3)PPh_3$ appears at 26.87 ppm in the $^{31}P\{^1H\}$ NMR spectrum, and the ylidic carbon $-C(H)(AuPPh_3)(PPh_3)$ appears at 51.23 ppm as a doublet of doublets of doublets in the $^{13}C\{^1H\}$ NMR spectrum.

Conclusion

All deprotonating agents employed in the syntheses of **1**−**9** give a clear reactivity affording new complexes with the "free ylide" $-C(O)C(H)=PPh_3$ moiety or with a second metal center coordinated to the carbon atom of this newly generated ylidic fragment; this second process shows a high degree of stereoselectivity. This free ylide moiety closely resembles a genuine free ylide $Ph_3P=C(H)C(O)R$, and we have previously observed that this kind of ylide can behave as an ambidentate ligand, coordinating either through the ylidic carbon atom or through the carbonyl oxygen. However, in all of the complexes reported here, we have observed a selective coordination through the ylidic carbon. Further studies are now in progress aimed at obtaining new coordination modes and possible applications (e.g., Wittig reactions) of this kind of bidentate−tridentate ligands.

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 19.

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 and toluene over sodium. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Infrared spectra (200−4000 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from 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 $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker

(19) Wolsey, W. C. *J. Chem. Educ.* **1973**, *50*, A335−A337.

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%). Mass spectra (positive ion FAB) were recorded on a V. G. Autospec spectrometer from CH_2Cl_2 solutions. The starting complexes [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$-(ClO_4)$_2$, [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)Cl(PPh_3)](ClO_4), [Pd(C_6H_4-2-PPh_2C(H)CO−CH_2PPh_3)(L−L)](ClO_4)$_2$ (L−L = dppe, phen),[2a] [(acac)-$AuPPh_3$], and (NBu_4)[Au(acac)$_2$][5] were prepared according to published methods.

[Pd$_2$Hg(μ-Cl)$_2$(C_6H_4-2-PPh_2C(H)$CO C$(H)(PPh_3)-$\kappa C,C,C$)$_2$]-(ClO_4)$_2$ (1). To a solution of [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2$-PPh_3)]$_2$(ClO_4)$_2$ (0.400 g, 0.244 mmol) in CH_2Cl_2 (25 mL) was added $Hg(OOCCH_3)_2$ (0.078 g, 0.24 mmol). The resulting solution was stirred at room temperature for 1 h and then evaporated to dryness. The orange residue was stirred with MeOH (10 mL), giving **1** as a yellow solid which was filtered, washed with MeOH (5 mL) and Et_2O (20 mL), and air-dried. Obtained: 0.372 g (83% yield). IR (ν, cm^{-1}): 1619 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.08−7.76 (m, 29H, Ph + C_6H_4), 5.66 (dd, 1H, C(H)Hg, $^2J_{P-H}$ = 5.1 Hz, $^4J_{P-H}$ = 1.8 Hz), 4.82 (d, 1H, C(H)Pd, $^2J_{P-H}$ = 5.1 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.93 (d, C(H)PHg, $^2J_{Hg-P}$ = 87 Hz, $^4J_{P-P}$ = 11 Hz), 21.52 (d, C_6H_4-2-PPh_2). $^{13}C\{^1H\}$ NMR (CD_2-Cl_2): δ 194.83 (t, CO, $^2J_{P-C}$ = 4 Hz), 156.51 (d, C_1, C_6H_4, $^2J_{P-C}$ = 19 Hz), 119.80−136.61 (Ph + C_6H_4), 55.86 (dd, C(H)Hg, $^1J_{P-C}$ = 46 Hz, $^3J_{P-C}$ = 12 Hz), 43.16 (dd, C(H)Pd, $^1J_{P-C}$ = 63 Hz, $^3J_{P-C}$ = 11 Hz). Anal. Calcd for $C_{78}H_{62}Cl_4HgO_{10}P_4Pd_2$ (1838.35 g/mol): C, 50.96; H, 3.40. Found: C, 50.83; H, 3.32. Mass spectrum [*m*/*z*, %]: 1739 [(M_3 − ClO_4)$^+$, 70].

[Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(acac-*O,O′*)](ClO_4) (2). To a solution of [Pd(μ-Cl)(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)]$_2$(ClO_4)$_2$ (0.409 g, 0.249 mmol) in CH_2Cl_2 (25 mL) was added Tl(acac) (0.151 g, 0.498 mmol). The resulting suspension was stirred at room temperature for 1 h, filtered over Celite, and evaporated to dryness. The pale yellow residue was treated with Et_2O (30 mL), giving **2** as a pale yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.354 g (80% yield). IR (ν, cm^{-1}): 1642 (ν_{CO}(ylide)), 1580, 1516 (ν_{CO}(acac)). ^1H NMR (CD_2Cl_2): δ 7.44−7.83 (m, 26H, Ph + C_6H_4), 7.24 (m, 1H, C_6H_4), 7.14 (m, 2H, C_6H_4), 5.28 (ddd, 1H, CH_2P, $^2J_{H-H}$ = 17.1 Hz, $^2J_{P-H}$ = 10.8 Hz, $^4J_{P-H}$ = 2.1 Hz), 5.28 (s, 1H, CH− acac), 4.80 (dd, 1H, CH_2P, $^2J_{H-H}$ = 17.1 Hz, $^2J_{P-H}$ = 15 Hz), 4.38 (dd, 1H, C(H)Pd, $^2J_{P-H}$ = 5.7 Hz, $^4J_{P-H}$ = 2.7 Hz), 2.05 (s, 3H, Me− acac), 1.68 (s, 3H, Me−acac). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 23.02 (d, C_6H_4-2-PPh_2, $^4J_{P-P}$ = 7 Hz), 21.48 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2-Cl_2): δ 189.63 (dd, CO, $^2J_{P-C}$ = 6.5 Hz, $^2J_{P-C}$ = 2.7 Hz), 187.70, 186.93 (2s, CO, acac), 158.57 (d, C_1, C_6H_4, $^2J_{P-C}$ = 21 Hz), 128.32− 136.46 (Ph), 125.38 (d, C_6H_4, J_{P-C} = 12 Hz), 119.10 (d, C_{ipso}, Ph, $^1J_{P-C}$ = 88 Hz), 100.25 (d, CH, acac, $^5J_{P-C}$ = 5.6 Hz), 40.88 (dd, PC(H)Pd, $^1J_{P-C}$ = 63 Hz, $^3J_{P-C}$ = 30 Hz), 37.4−38.8 (m, CH_2P), 28.33 (d, CH_3, acac, $^5J_{P-C}$ = 12 Hz), 28.00 (d, CH_3, acac, $^5J_{P-C}$ = 6.5 Hz). Anal. Calcd for $C_{44}H_{39}ClO_7P_2Pd$ (883.59 g/mol): C, 59.81; H, 4.45. Found: C, 59.43; H, 4.14. Mass spectrum [*m*/*z*, %]: 783 [(M − ClO_4)$^+$, 15].

[Pd(C_6H_4-2-PPh_2C(H)COC(H)($AuPPh_3$)(PPh_3))(acac-*O,O′*)](C-lO_4) (3). To a solution of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(acac)]-(ClO_4) (0.125 g, 0.141 mmol) in CH_2Cl_2 (25 mL) was added (acac)$AuPPh_3$ (0.0787 g, 0.141 mmol). The resulting solution was stirred at room temperature for 30 min and evaporated to dryness. The pale yellow residue was treated with Et_2O (30 mL), giving **3** as a pale yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.136 g (72% yield). This product was spectroscopically characterized as a mixture of the two diastereoisomers (*RR*/*SS* and *RS*/*SR*) in molar ratio (major/minor = 2/1). IR (ν, cm^{-1}): 1614 (ν_{CO}(ylide)), 1580, 1515 (ν_{CO}(acac)). ^1H NMR ($CDCl_3$): δ 6.99−7.85 (m, Ph + C_6H_4), 5.26 (s, CH−acac, major), 5.09 (dt, CHAu, major, $^3J_{P-H}$ = 9.3 Hz, $^2J_{P-H} \cong {}^4J_{P-H}$ = 3.3 Hz), 4.62 (dt, CHAu, minor, $^3J_{P-H}$ = 9.3 Hz, $^2J_{P-H} \cong {}^4J_{P-H}$ = 1.8 Hz), 4.56 (s, CH−acac, minor), 4.41 (d, CHPd, minor, $^2J_{P-H}$ = 5.7 Hz), 4.22 (t, C(H)Pd, major, $^2J_{P-H} \cong {}^4J_{P-H}$ = 3.9 Hz), 2.10 (s, Me−acac, major), 1.75 (s, Me−acac, major + minor), 1.66 (s, Me−acac, minor). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.19 (d, $AuPPh_3$, major, $^3J_{P-P}$ = 11 Hz), 38.42 (d, $AuPPh_3$, minor, $^3J_{P-P}$ = 13 Hz), 25.75 (m, $CHPPh_3$, major + minor), 24.71 (d, C_6H_4-2-PPh_2, major, $^4J_{P-P}$ = 9 Hz), 20.70 (d, C_6H_4-2-PPh_2, minor, $^4J_{P-P}$ = 14 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 198.57 (dt, CO, minor, $^3J_{P-C}$ = 3.5 Hz, $^2J_{P-C}$ = 3 Hz), 195.75 (dt, CO, major, $^3J_{P-C}$ = 5.8 Hz, $^2J_{P-C}$ = 3.9 Hz), 187.89, 187.19 (2s, CO, acac, major), 187.01, 186.83 (2s, CO, acac, minor), 159.39 (d, C_1, C_6H_4, minor, $^2J_{P-C}$ = 22.5 Hz), 159.35 (d, C_1, C_6H_4, major, $^2J_{P-C}$ = 22.5 Hz), 123.48−139.05 (Ph + C_6H_4, both isomers), 100.13 (s, CH, acac, both isomers), 51.54 (dt, C(H)Au, minor, $^1J_{P-C}$ = 48 Hz, $^2J_{P-C} \cong {}^3J_{P-C}$ = 13 Hz), 50.73 (dt, C(H)Au, major, $^1J_{P-C}$ = 50 Hz, $^2J_{P-C} \cong {}^3J_{P-C}$ = 9 Hz), 39.09 (dt, C(H)Pd, minor, $^1J_{P-C}$ = 61 Hz, $^3J_{P-C} \cong {}^4J_{P-C}$ = 11 Hz), 38.94 (dt, C(H)Pd, major, $^1J_{P-C}$ = 61 Hz, $^3J_{P-C} \cong {}^4J_{P-C}$ = 10 Hz), 28.12, 26.95 (2s, 2 CH_3, acac, minor), 28.01, 26.83 (2s, 2 CH_3, acac, major). Anal. Calcd for $C_{62}H_{53}AuClO_7P_3Pd$ (1341.84 g/mol): C, 55.49; H, 3.98. Found: C, 55.60; H, 4.04. Mass spectrum [*m*/*z*, %]: 1241 [(M − ClO_4)$^+$, 40].

[Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)(acac-*O,O′*)] (3′). To a solution of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(acac-*O,O′*)](ClO_4) (**2**) (0.200 g, 0.226 mmol) in THF (25 mL) was added Na[$N(SiMe_3)_2$] (226 μL, 0.226 mmol). The resulting solution was stirred at room temperature for 4 h and then evaporated to dryness. The orange residue was extracted with CH_2Cl_2 (25 mL) and filtered over Celite. The resulting orange solution was evaporated to small volume (3 mL). Addition of Et_2O (10 mL) and stirring gave a yellow solid identified as impure **3′** (see text). Obtained: 0.140 g. IR (ν, cm^{-1}): 1583, 1515 (ν_{CO}(ylide) + ν_{CO}-(acac)). ^1H NMR ($CDCl_3$): δ 7.26−7.89 (m, 25H, Ph), 7.11 (m, 2H, C_6H_4), 6.98 (m, 2H, C_6H_4), 5.16 (s, 1H, CH−acac), 4.03 (d, 1H, C(H)-Pd, $^2J_{P-H}$ = 2 Hz), 3.77 (dd, 1H, C(H)=P, $^2J_{P-H}$ = 26 Hz, $^4J_{P-H}$ = 2 Hz), 1.97 (s, 3H, Me−acac), 1.64 (s, 3H, Me−acac). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 25.45 (d, C_6H_4-2-PPh_2, $^4J_{P-P}$ = 11 Hz), 15.19 (d, C(H)= PPh_3).

[Pd(C_6H_4-2-PPh_2C(H)COC(H)=PPh_3)Cl(PPh_3)] (4a, b). To a suspension of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)Cl(PPh_3)](ClO_4) (0.300 g, 0.277 mmol) in MeOH (25 mL) was added a solution of NBu_4OH in MeOH (1 M, 277 μL, 0.277 mmol). The resulting pale yellow solution was stirred at room temperature for 1 h and evaporated to dryness. The residue was extracted with $CHCl_3$ (10 mL), filtered through $MgSO_4$, and evaporated to dryness. This second residue was extracted with toluene (10 mL) and stirred for 30 min with $MgSO_4$. The suspension was filtered through Celite and the resulting solution evaporated to small volume. During the evaporation a pale yellow solid precipitated, which was filtered, washed with *n*-hexane (20 mL), air-dried, and identified spectroscopically as the mixture (**4a**, **4b**) in molar ratio (**4a**/**4b** = 1/1.6). Obtained: 0.132 g (49% yield). IR (ν, cm^{-1}): 1504 (ν_{CO}(ylide)), 278 (ν_{Pd-Cl}). ^1H NMR (CD_2Cl_2): δ 6.58−8.52 (m, Ph + C_6H_4, both isomers), 4.93 (dd, C(H)Pd, **4b**, $^2J_{P-H}$ = 9 Hz, $^4J_{P-H}$ = 2.4 Hz), 4.28 (dd, C(H)=P, **4b**, $^2J_{P-H}$ = 28 Hz, $^4J_{P-H}$ = 1 Hz), 3.50 (ddd, C(H)-Pd, **4a**, $^2J_{P-H}$ = 2.1 Hz, $^3J_{P-H}$ = 9.9 Hz, $^4J_{P-H}$ = 0.6 Hz), 3.33 (dd, C(H)=P, **4a**, $^2J_{P-H}$ = 27 Hz, $^4J_{P-H}$ = 1.2 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 31.36 (d, Pd−PPh_3, **4a**, $^3J_{P-P}$ = 23 Hz), 18.58 (dd, C_6H_4-2-PPh_2, **4a**, $^3J_{P-P}$ = 23 Hz, $^4J_{P-P}$ = 14 Hz), 14.85 (d, C(H)=PPh_3, **4a**, $^4J_{P-P}$ = 14 Hz), 23.87 (dd, C_6H_4-2-PPh_2, **4b**, $^3J_{P-P}$ = 34 Hz, $^4J_{P-P}$ = 9 Hz), 20.80 (d, Pd−PPh_3, **4b**, $^3J_{P-P}$ = 34 Hz), 15.14 (d, C(H)=PPh_3, **4b**, $^4J_{P-P}$ = 9 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 189.05 (broad s, CO, **4a**), 187.85 (dd, CO, **4b**, $^2J_{P-C}$ = 4.9 Hz, $^2J_{P-C}$ = 3.5 Hz), 174.20 (dd, C_1, C_6H_4, **4b**, $^2J_{P-C_{trans}}$ = 139.4 Hz, $^2J_{P-C}$ = 30 Hz), 165.91 (dd, C_1, C_6H_4, **4a**, $^2J_{P-C}$ = 24.4 Hz, $^2J_{P-C_{cis}}$ = 5.6 Hz), 123.05−139.69 (Ph + C_6H_4), 52.03 (dd, C(H)=P, **4b**, $^1J_{P-C}$ = 108.8 Hz, $^3J_{P-C}$ = 9.2 Hz), 50.00 (dd, C(H)=P, **4a**, $^1J_{P-C}$ = 109.6 Hz, $^3J_{P-C}$ = 13.2 Hz), 47.49 (ddd, C(H)Pd, **4a**, $^1J_{P-C}$ = 54.6 Hz, $^2J_{P_{trans}-C}$ = 71.8 Hz, $^3J_{P-C}$ = 18 Hz), 41.83 (ddd, C(H)Pd, **4b**, $^1J_{P-C}$ = 48 Hz, $^2J_{P_{cis}-C}$ = 4.5 Hz, $^3J_{P-C}$ = 17.1 Hz). Anal. Calcd for $C_{57}H_{46}ClOP_3Pd$ (981.77 g/mol): C, 69.73; H, 4.72. Found: C, 69.41; H, 4.77.

[Pd(C_6H_4-2-PPh_2C(H)COC(H)($AuPPh_3$)(PPh_3))Cl(PPh_3)](ClO_4) (5). To a solution of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)Cl(PPh_3)](ClO_4) (0.250 g, 0.231 mmol) in CH_2Cl_2 (25 mL) was added (acac)$AuPPh_3$ (0.129 g, 0.231 mmol). The resulting solution was stirred at room temperature for 30 min and evaporated to dryness. The pale yellow residue was treated with Et_2O (30 mL), giving **5** as a pale yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.318 g (89% yield). Anal. Calcd for $C_{75}H_{61}AuCl_2O_5P_4Pd$ (1540.48 g/mol): C, 58.48; H, 3.99. Found: C, 58.51; H, 3.96. IR (ν, cm^{-1}): 1605 (ν_{CO}(ylide)), 270 (ν_{Pd-Cl}). ^1H NMR ($CDCl_3$): δ 6.99− 7.83 (m, 56H, Ph + C_6H_4), 6.84 (m, 1H, C_6H_4), 6.62 (m, 1H, C_6H_4), 6.55 (m, 1H, C_6H_4), 5.99 (d, 1H, C(H)Au, $^2J_{P-H}$ = 7.8 Hz), 5.12 (quint,

1H, C(H)Pd, $^2J_{P-H} \cong {}^3J_{P-H} \cong {}^4J_{P-H} \cong {}^5J_{P-H} = 5.1$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.17 (d, $AuPPh_3$, $^3J_{P-P} = 9$ Hz), 29.89 (d, $PdPPh_3$, $^3J_{P-P} = 17$ Hz), 24.77 (broad s, C_6H_4-2-PPh_2), 18.42 (broad s, $CHPPh_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 196.07 (broad s, CO), 165.62 (dd, C_1, C_6H_4, $^2J_{P-C} = 22.2$ Hz, $^2J_{P-C} = 2.9$ Hz), 124.16−139.82 (Ph + C_6H_4), 51.03 (dt, 2C overlapped, C(H)Au + C(H)Pd, $^1J_{P-C} = 61$ Hz, $^2J_{P-C} \cong {}^3J_{P-C} = 10$ Hz).

[Pd(*C*$_6$H$_4$-2-PPh$_2$*C*(H)COC(H)=PPh$_3$)(dppe)](ClO$_4$) (6). To a suspension of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(dppe)]$(ClO_4)_2$ (0.169 g, 0.132 mmol) in THF (25 mL) was added Na[$N(SiMe_3)_2$] (132 μL, 0.132 mmol). The resulting pale yellow solution was stirred at room temperature for 1 h and then evaporated to dryness. The yellow residue was extracted with CH_2Cl_2 (25 mL) and filtered over Celite. The resulting solution was evaporated to small volume (3 mL). Addition of Et_2O (10 mL) and continuous stirring gave **6** as a pale yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.100 g (64% yield). Recrystallization of **6** from CH_2Cl_2/*n*-hexane gave yellow crystals of **6**·CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of solvent was determined by ^{1}H NMR integration. IR (ν, cm^{-1}): 1521 (ν_{CO}(ylide)). ^{1}H NMR ($CDCl_3$): δ 6.76−7.73 (m, 49H, Ph + C_6H_4), 3.96 (t, 1H, PC(H)Pd, $^2J_{P-H} \cong {}^3J_{P-H} = 7.2$ Hz), 3.07 (d, 1H, C(H)=P, $^2J_{P-H} = 24.6$ Hz), 1.78−2.57 (m, 4H, CH_2−dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.13 (t, PPh_2 trans to C-ylide, $^3J_{P-P} = 21$ Hz), 44.15 (dd, PPh_2 cis to C-ylide, $^3J_{P-P} = 31$ Hz, $^3J_{P-P} = 21$ Hz), 26.26 (ddd, C_6H_4-2-PPh_2, $^3J_{P-P} = 31$ Hz, $^3J_{P-P} = 21$ Hz, $^4J_{P-P} = 7$ Hz), 14.81 (d, C(H)=PPh_3, $^4J_{P-P} = 7$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 186.90 (t, CO, $^2J_{P-C} = 2$ Hz), 171.08 (dd, C_1, C_6H_4, $^2J_{P_{trans}-C} = 126$ Hz, $^2J_{P-C} = 5$ Hz), 139.27 (t, C_6H_4, $J_{P-C} = 12$ Hz), 128.89−135.31 (Ph + C_6H_4), 128.22 (d, C_{ipso}, C_6H_4, $^1J_{P-C} = 61$ Hz), 127.84 (d, C_{ipso}, Ph, $^1J_{P-C} = 90$ Hz), 125.48 (d, C_6H_4, $J_{P-C} = 13$ Hz), 53.54 (dd, C(H)=PPh_3, $^1J_{P-C} = 109$ Hz, $^3J_{P-C} = 10$ Hz), 45.68 (m, PC(H)Pd), 29.21 (dd, CH_2, dppe, $^1J_{P-C} = 30$ Hz, $^2J_{P-C} = 18$ Hz), 28.66 (dd, CH_2, dppe, $^1J_{P-C} = 28$ Hz, $^2J_{P-C} = 15$ Hz). Anal. Calcd for $C_{65}H_{55}ClO_5P_4Pd$·CH_2Cl_2 (1266.83 g/mol): C, 62.57; H, 4.53. Found: C, 62.66; H, 4.45. Mass spectrum [*m*/*z*, %]: 1080 [(M − H − ClO_4)$^+$, 55].

[Pd(*C*$_6$H$_4$-2-PPh$_2$*C*(H)COC(H)=PPh$_3$)(phen)](ClO$_4$) (7). To a suspension of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(phen)]$(ClO_4)_2$ (0.394 g, 0.370 mmol) in THF (25 mL) was added Na[$N(SiMe_3)_2$] (370 μL, 0.370 mmol). The initial suspension gradually dissolved, and the resulting solution was stirred at room temperature for 30 min and then evaporated to dryness. The yellow residue was subjected to the same experimental workup as that described for **6**, giving **7** as a yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.270 g (76% yield). Recrystallization of **7** from CH_2Cl_2/Et_2O gave pale yellow crystals of **7**·0.6CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of solvent was determined by ^{1}H NMR integration. IR (ν, cm^{-1}): 1517 (ν_{CO}(ylide)). ^{1}H NMR ($CDCl_3$): δ 9.42 (d, 1H, H_α, phen, $^3J_{\alpha\beta} = 4.5$ Hz), 9.08 (d, 1H, $H_{\alpha'}$, phen, $^3J_{\alpha'\beta'} = 4.8$ Hz), 8.61 (dd, 1H, $H_{\gamma'}$, phen, $^3J_{\gamma'\beta'} = 8.1$ Hz, $^4J_{\gamma'\alpha'} = 0.9$ Hz), 8.52 (dd, 1H, H_γ, phen, $^3J_{\gamma\beta} = 8.2$ Hz, $^4J_{\gamma\alpha} = 0.9$ Hz), 7.24−7.90 (m, 33H, Ph + C_6H_4 + phen), 3.90 (dd, 1H, C(H)P, $^2J_{P-H} = 6.9$ Hz, $^4J_{P-H} = 5.1$ Hz), 3.54 (d, 1H, CH=P, $^2J_{P-H} = 24$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.26 (s, C_6H_4-2-PPh_2), 14.56 (s, C(H)=P). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 187.48 (s, CO), 167.12 (d, C_1, C_6H_4, $^2J_{P-C} = 24$ Hz), 151.26, 150.99 (2s, C_1, $C_{1'}$, phen), 150.99 (s, C_6H_4), 146.05, 145.51 (2s, C_5, $C_{5'}$, phen), 139.13, 138.76 (2s, C_3, $C_{3'}$, phen), 138.66 (d, C_2, C_6H_4, $^1J_{P-C} = 114$ Hz), 136.15 (d, C_6H_4, $J_{P-C} = 16$ Hz), 133.92 (d, C_6H_4, $J_{P-C} = 10$ Hz), 132.63−133.07 (Ph), 130.14, 129.87 (2s, C_4, $C_{4'}$, phen), 129.40 (d, C_6H_4, $J_{P-C} = 12$ Hz), 128.41−129.11 (Ph), 127.59, 127.25 (2s, C_6, $C_{6'}$, phen), 126.54 (d, C_{ipso}, Ph, $^1J_{P-C} = 91$ Hz), 126.27 (d, C_{ipso}, Ph, $^1J_{P-C} = 91$ Hz), 125.81, 125.44 (2s, C_2, $C_{2'}$, phen), 54.14 (dd, C(H)=P, $^1J_{P-C} = 108$ Hz, $^3J_{P-C} = 4$ Hz), 39.18 (dd, C(H)-Pd, $^1J_{P-C} = 41$ Hz, $^3J_{P-C} = 16$ Hz). Anal. Calcd for $C_{51}H_{39}ClN_2O_5P_2Pd$·0.6$CH_2Cl_2$ (1014.64 g/mol): C, 61.08; H, 3.99; N, 2.76. Found: C, 61.29; H, 3.66; N, 2.86. Mass spectrum [*m*/*z*, %]: 862 [(M − ClO_4)$^+$, 65].

[Pd(*C*$_6$H$_4$-2-PPh$_2$*C*(H)CO*C*(H)(AuCl)(PPh$_3$))(dppe)](ClO$_4$) (8). To a solution of **6** (0.100 g, 0.085 mmol) in CH_2Cl_2 (25 mL) was added ClAu(tht) (0.028 g, 0.085 mmol). The resulting solution was stirred at room temperature for 30 min and then evaporated to dryness. The residue was stirred with Et_2O (10 mL), giving **8** as a pale yellow solid which was filtered, washed with Et_2O (10 mL), and air-dried. Obtained: 0.075 g (63% yield). Recrystallization of **8** from CH_2Cl_2/*n*-hexane gave pale yellow crystals of **8**·0.6CH_2Cl_2, which were used for analytical and spectroscopic measurements. The amount of solvent was determined by ^{1}H NMR integration. IR (ν, cm^{-1}): 1612 (ν_{CO}(ylide)), 325 (ν_{Au-Cl}). ^{1}H NMR ($CDCl_3$): δ 7.01−8.08 (m, 41H, Ph), 6.90 (m, 2H, C_6H_4), 6.69 (m, 4H, Ph), 6.55 (m, 2H, C_6H_4), 5.06 (dt, 1H, C(H)Au, $^2J_{P-H} = 4.5$ Hz, $^4J_{P-H} \cong {}^5J_{P-H} = 7.2$ Hz), 3.64 (m, 1H, C(H)Pd), 2.76, 2.61, 2.43, 2.26 (4m, 4H, CH_2−dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.97 (t, PPh_2 trans to C-ylide, $^3J_{P-P} = 20$ Hz), 41.56 (dd, PPh_2 cis to C-ylide, $^3J_{P-P} = 27$ Hz, $^3J_{P-P} = 20$ Hz), 26.34 (d, C(PPh_3)-AuCl, $^4J_{P-P} = 14$ Hz), 24.69 (ddd, C_6H_4-2-PPh_2, $^3J_{P-P} = 27$ Hz, $^3J_{P-P} = 20$ Hz, $^4J_{P-P} = 14$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 198.94 (t, CO, $^2J_{P-C} = 4.5$ Hz), (C_1 was not observed), 125.01−139.71 (Ph + C_6H_4), 123.63 (d, C_{ipso}, Ph, $^1J_{P-C} = 87$ Hz), 43.25 (dd, C(H)Pd, $^1J_{P-C} = 53.6$ Hz, $^2J_{P-C} = 15.4$ Hz), 38.15 (dd, C(H)Au, $^1J_{P-C} = 51.2$ Hz, $^3J_{P-C} = 12.1$ Hz), 28.20 (dd, CH_2, dppe, $^1J_{P-C} = 29$ Hz, $^2J_{P-C} = 14$ Hz), 27.34 (dd, CH_2, dppe, $^1J_{P-C} = 32$ Hz, $^2J_{P-C} = 19$ Hz). Anal. Calcd for $C_{65}H_{55}AuCl_2O_5P_4Pd$·0.6$CH_2Cl_2$ (1465.28 g/mol): C, 53.77; H, 3.86. Found: C, 53.49; H, 4.09. Mass spectrum [*m*/*z*, %]: 1313 [(M − ClO_4)$^+$, 100].

[Pd(*C*$_6$H$_4$-2-PPh$_2$*C*(H)CO*C*(H)(AuPPh$_3$)(PPh$_3$))(phen)](ClO$_4$) (9). To a suspension of [Pd(C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$)(phen)]$(ClO_4)_2$ (0.220 g, 0.206 mmol) in CH_2Cl_2 (25 mL) was added (acac)Au(PPh_3) (0.115 g, 0.206 mmol). The initial suspension gradually dissolved, and the resulting solution was stirred at room temperature for 1 h and then evaporated to dryness. The deep yellow residue was treated with Et_2O (20 mL), giving **9** as a deep yellow solid which was filtered, washed with Et_2O (20 mL), and air-dried. Obtained: 0.265 g (90% yield). IR (ν, cm^{-1}): 1622 (ν_{CO}(ylide)). ^{1}H NMR ($CDCl_3$): δ 10.06 (dd, 1H, H_α, phen, $^3J_{\alpha\beta} = 4.2$ Hz, $^4J_{\alpha\gamma} = 1.5$ Hz), 8.88 (d, 1H, $H_{\alpha'}$, phen, $^3J_{\alpha'\beta'} = 4.5$ Hz, $^4J_{\alpha'\gamma'} = 1.2$ Hz), 8.54 (dd, 1H, $H_{\gamma'}$, phen, $^3J_{\gamma'\beta'} = 7.5$ Hz), 8.51 (dd, 1H, H_γ, phen, $^3J_{\gamma\beta} = 7.5$ Hz), 8.17 (dd, 1H, H_β), 7.94 (dd, 1H, $H_{\beta'}$), 7.82 (d, 1H, H_δ, $^3J_{\delta\delta'} = 9$ Hz), 6.97−7.78 (m, 40H, Ph + C_6H_4 + phen), 6.77 (m, 1H, C_6H_4), 6.50 (m, 4H, Ph), 5.57 (s, 1H, C(H)-PPd), 5.38 (dd, 1H, C(H)PAu, $^2J_{P-H} = 2.7$ Hz, $^3J_{P-H} = 6.3$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.31 (d, $AuPPh_3$, $^3J_{P-P} = 12$ Hz), 26.87 (dd, C(H)PAu), 19.42 (d, C_6H_4-2-PPh_2, $^4J_{P-P} = 18$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 200.94 (pseudo-quartet, CO, $^2J_{P-C} \cong {}^3J_{P-C} = 4.5$ Hz), 164.88 (d, C_1, C_6H_4, $^2J_{P-C} = 21.6$ Hz), 152.92, 152.77 (2s, C_1, $C_{1'}$, phen), 151.36 (d, C_6H_4, $J_{P-C} = 11$ Hz), 146.37, 145.02 (2s, C_5, $C_{5'}$, phen), 139.88, 139.56 (2s, C_3, $C_{3'}$, phen), 137.86 (d, C_2, C_6H_4, $^1J_{P-C} = 114$ Hz), 123.28−135.41 (Ph + C_6H_4 + phen), 51.23 (ddd, C(H)AuP, $^1J_{P-C} = 61$ Hz, $^2J_{P-C} = 52$ Hz, $^3J_{P-C} = 14$ Hz), 42.72 (ddd, C(H)-Pd, $^1J_{P-C} = 57$ Hz, $^3J_{P-C} = 14$ Hz, $^4J_{P-C} = 11$ Hz). Anal. Calcd for $C_{69}H_{54}AuClN_2O_5P_3Pd$ (1422.95 g/mol): C, 58.24; H, 3.82; N, 1.97. Found: C, 57.95; H, 3.74; N, 1.84. Mass spectrum [*m*/*z*, %]: 1421 [M$^+$, 25].

Crystal Structure Determination of 1. A yellow crystal of **1** 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 (room temperature) on an automated four-circle Enraf-Nonius CAD4 diffractometer. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the $a-c$ and [1 1 1] axes to verify the Laue symmetry and cell dimensions. Accurate unit cell dimensions were determined from 25 centered reflections in the range $22.25 \le 2\theta \le 28.78°$. For intensity data collection, $\omega - (1/3)\theta$ scans were used with $\Delta\omega = 1.17 + 0.35 \tan\theta$. Three monitor reflections were measured after every 3 h of beam time, and the orientation of the crystal was checked after every 400 intensity measurements. Absorption corrections[20] were based on azimuthal scans of 15 reflections which had Eulerian angle χ spread between 90 and 30° when in their bisecting positions.

The structure was solved and developed by Patterson and Fourier methods.[21] All non-hydrogen atoms were assigned anisotropic displacement parameters. The hydrogen atoms of the aromatic moieties were

(20) Absorption corrections and molecular graphics were done using the following commercial package: *SHELXTL-PLUS*, Release 4.21/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

(21) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.

constrained to idealized geometries. The isotropic displacement parameter of each of these hydrogen atoms was set to a value of 1.2 times the equivalent isotropic displacement parameter of its parent carbon atom. The geometrical parameters of the ClO_4 moiety were idealized using similarity restraints. At the end of the refinement, there was only one difference Fourier peak with $\rho = 1.00$ e/Å^3, located near the ClO_4 anion. The data-to-parameter ratio in the final refinement was 14.4. The structure was refined to F_o^2, and all reflections were used in the least-squares calculation.[22] The residuals and other pertinent parameters are summarized in Table 1. Crystallographic calculations were done on a local area VAXCluster (VAX/VMS V5.5-2). Data reduction was done by the program XCAD4B.[23]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of **1** is available free of charge via the Internet at http://pubs.acs.org.

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(22) Sheldrick, G. M. *SHELXL-93: FORTRAN program for the refinement of crystal structures from diffraction data*; Göttingen University: Göttingen, Germany, 1993.

(23) Harms, K. Private communication, 1995.