Different Coordination Modes of the Polyfunctional Ylide Ph_3P=C(H)C(O)CH_2C(O)OEt: *C*- vs. *O*,*O*′-Bonding in Pd^{II}, Pt^{II} and Au^{I} Complexes

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Treatment of the polyfunctional ylide Ph_3P=C(H)C(O)CH_2-COOEt (**1**) with the solvated complexes [M(C^X)$(THF)_2$]ClO_4 gave the *O*,*O*′ derivatives [M(C^X)($Ph_3PCH_2C(O)$=C(H)–C(=*O*)OEt-κ-*O*,*O*′]ClO_4 [M(C^X) = Pd($C_6H_4CH_2NMe_2$) (**2**), Pd($CH_2C_9H_6N$) (**3**), Pd(NC_5H_4-2-C_6H_4) (**4**), Pd($NC_{13}H_8$) (**5**), Pd[(*S*)–$C_6H_4C(H)MeNMe_2$] (**6**), Pt[*o*-$CH_2C_6H_4P$(*o*-tol)$_2$] (**7**), Pd[*o*-$CH_2C_6H_4P$(*o*-tol)$_2$] (**8**), and Pd(C_6F_5)(SC_4H_8) (**9**)]. During the reaction, one proton of the methylene unit is transferred to the ylidic carbon, which is transformed into a phosphonium group generating the zwitterion [$Ph_3PCH_2C(O)$=C(H)–C(=*O*)OEt], which coordinates to the metal center as an *O*,*O*′-chelating ligand. Treatment of **1** with [AuCl(SC_4H_8)] or [Au(PPh_3)($OCMe_2$)]ClO_4 gave [AuCl{C(H)(PPh_3)C(O)-CH_2COOEt}] (**10**) or [Au{C(H)(PPh_3)C(O)CH_2COOEt}-(PPh_3)]ClO_4 (**11**), in which the ylide is *C*-bonded. The X-ray crystal structures of complexes **2a**, **9** and **10** have been determined.

Introduction

We have recently shown that the keto-stabilized ylides [Ph_3P=C(H)C(O)R] (R = Me, OMe, Ph) can behave as ambidentate ligands towards Pd^{II} complexes, since they can coordinate either through the soft ylidic C_α atom or through the hard carbonyl oxygen depending on the vacant coordination site at the palladium precursor. This coordination occurs with notable selectivity, which has been explained in terms of the anti-symbiotic effect and the nature of the donor atoms bonded to the Pd^{II} center.[1] In all cases studied, the ylide bonds to the metal center using only one donor atom. Further introduction of new functional groups at the molecular skeleton of the ylide should result in an expansion of its bonding abilities and in the transformation of the aforementioned ambidenticity to polydenticity. We are currently pursuing the study of the coordinating properties of polydentate ylides, and how the presence of new functionalities alters the bonding patterns observed in ambidentate ylides.

Here we describe the complete characterization of ethyl 3-oxo-4-(triphenylphosphoranylidene)butanoate [Ph_3P=C(H)C(O)CH_2COOEt] (**1**) and its reactivity towards complexes of Pd^{II}, Pt^{II} and Au^{I}, in order to determine its coordinating ability. The ylide **1** could behave, at first sight, as a C-donor ligand (through the C_α atom), as an O-donor ligand (through three different O atoms) or as a polydentate ligand (using combinations of the four possible donor atoms). The synthesis of **1** was reported four decades ago[2] but, with the exception of applications in purely synthetic organic processes,[3] its bonding properties have remained unexplored. We have found quite different patterns of reactivity of this ylide as a function of the metallic precursor: *C*-bonding in Au^{I} complexes (leaving the β-keto ester functionality unchanged) and *O*,*O*′-coordination in Pd^{II} and Pt^{II} derivatives (which generates a phosphonium functionality). This paper describes the results obtained, and synthetic possibilities are also discussed.

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Results and Discussion

1. Palladium(II) and Platinum(II) Complexes

The ylide **1** was prepared following the method described by Serratosa and Solé,[2b] and has been characterized through its analytical and spectroscopic data. Here we also report the ^1H and $^{13}C\{^1H\}$ NMR spectroscopic parameters, since they were not provided in the original[2] or subsequent works[3f] (see Exp. Sect.). In order to check the chelating ability of **1**, its reactivity towards the bis(solvated) derivatives [M(C^X)$(THF)_2$]ClO_4 was examined (see Scheme 1). These bis(solvate) complexes were prepared by treatment of the corresponding dinuclear μ-halide complexes [M(C^X)(μ-Cl)]$_2$ with $AgClO_4$ (1:2 molar ratio) in THF, followed by removal of AgCl by filtration. The freshly prepared solutions of [M(C^X)$(THF)_2$]ClO_4 were treated with the stoichiometric amount of **1**. After the initial dissolution of **1**, complexes **2**–**9** precipitated as yellow solids from the

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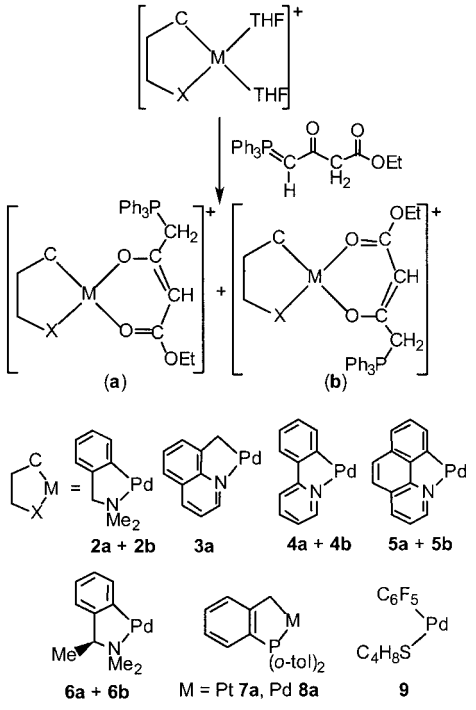
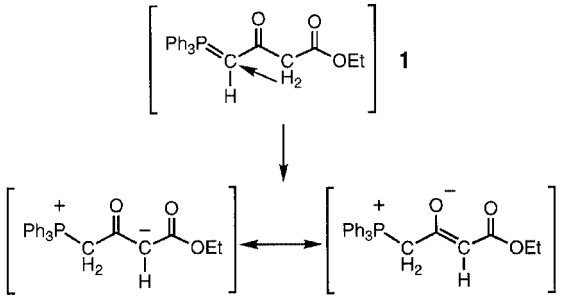
respective reaction solutions. The process is represented in Scheme 1.



Scheme 1

Complexes **2**−**9** gave elemental analyses in good agreement with the stoichiometries depicted in Scheme 1, and the mass spectra in all cases show the presence of the cationic molecular peak $[M - ClO_4]^+$ with the correct isotopic distribution. The IR spectra of **2**−**9** clearly show two strong absorptions in the 1500−1630 cm^{-1} region: one at approximately 1614−1628 cm^{-1} (attributed to the ν_{COO} stretch) and the other one at around 1502−1525 cm^{-1}, assigned to the ν_{CO} stretch of the carbonyl group adjacent to the ylide unit. A comparison of these values with those obtained for the free ylide **1** (1717 and 1546 cm^{-1}, respectively)[2b] shows that both absorptions have been shifted to lower energies. This fact strongly suggests that both carbonyl groups are bonded to the metal center, since it has been well established that *C*-coordination of the keto-stabilized ylides produces a high energy shift of the ν_{CO} stretch (with respect to the free ylide)[1] and, thus, a shift of the absorption at 1546 cm^{-1} to higher wavenumbers should be observed for *C*-bonding of **1**.

The NMR spectra of complex **2** provide valuable structural information. Firstly, all NMR spectra (^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$) display two identical sets of signals (ratio 4.5:1), showing the presence of two isomers (a) and (b) in solution. Due to the asymmetric nature of **1** and its *O*,*O*′-bonding mode, two geometric isomers can be envisaged. In addition, the ^1H NMR spectrum of **2** shows three notable features: (i) the signals due to the CH_2N and NMe_2 protons appear as singlets, indicating that the molecular plane is a symmetry plane; (ii) signals which could result from the methylene protons or the ylidic proton $P{=}C_\alpha(H)$ were not observed; (iii) instead, two singlets appear at δ = 4.5−5 ppm (δ = 4.81 ppm, major isomer; 4.86 ppm, minor isomer) and two doublets at about 4.15 ppm (δ = 4.13 ppm, J_{PH} = 13.8 Hz, major isomer, 4.16 ppm, J_{PH} = 13.8 Hz, minor isomer), with a relative intensity ratio singlet/doublet = 1:2. These observations strongly suggest that the methylene-ylide skeleton [$-CH_2-C(O)-C(H){=}P$] in **1** has been transformed into the phosphonium-enolate functionality [$-C(H){=}C(O)-CH_2P$] in **2**, by the transfer of one H atom from the methylene group to the ylidic carbon C_α (see Scheme 2). The signals in the range 4.5−5 ppm can then be attributed to the $=C(H)-$ proton (shifted slightly to high-field with respect to the usual position in β-diketonate ligands)[4] and the signals at about 4.15 ppm can be assigned to the CH_2P protons.[5] The resultant structure of the coordinated ligand in **2** is shown in Scheme 1.



Scheme 2. Proton transfer in **1** and resonance forms of the zwitterion [$Ph_3PCH_2-C(O){=}C(H)C(=O)OEt$]

The structures depicted in Scheme 1 also account for the observation, in the $^{31}P\{^1H\}$ NMR spectrum of **2**, of two resonances at approximately 22 ppm, typical for phosphonium groups.[5] In addition, the $^{13}C\{^1H\}$ NMR spectrum (acquired as APT) of **2** also shows signals characteristic of the generated phosphonium-enolate moiety: (i) two doublets at about 36 ppm ($^1J_{P,C} \approx 53$ Hz) with negative phase can be attributed to the CH_2P carbon atoms, and (ii) two doublets at about 90 ppm ($^3J_{P,C} \approx 7$ Hz) with positive phase can be assigned to the $=C(H)$ carbon atoms. Finally, the question of whether structure (a) or (b) in Scheme 1 corresponds to the major isomer must be addressed. The assignment of structure (a) to the major isomer can easily be inferred from the ^1H NMR spectrum in which the signals assigned to the protons of the metallated C_6H_4 group, for the major isomer, appear well spread in the range δ = 7.0−5.8 ppm, with the signal due to the H^6 proton (*ortho* to the metallated position) at δ = 5.89 ppm. This signal is clearly shifted to high field with respect to its position in the starting dinuclear derivative $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2)]_2$ (δ ≈ 7.0 ppm), and this high-field shift must be due to the anisotropic shielding[6] produced by a phenyl ring of the PPh_3 group. This fact implies a *cis* arrangement of the C_6H_4 fragment of the metallated ligand and the PPh_3 unit of the phosphonium-enolate ligand, which occurs in structure (a). Moreover, this anisotropic shielding should not be produced in the other isomer (which possesses an OEt group in a position remote from the H^6 proton) and, in fact, the

aromatic resonances of the metallated C_6H_4 ring in the minor isomer all appear around 7.0 ppm. We can thus conclude, on the basis of the NMR spectroscopic data, that the major isomer is that represented in Scheme 1 by structure (a) and the minor isomer by structure (b).

The IR data of complexes **2**−**9**, and their comparison with those for the free ylide **1** show that, in all cases, the bonding mode of the ylide to the metal center should be the same (*O*,*O*′-chelate), since the same shifts of the carbonyl absorptions were observed.

Moreover, the NMR spectroscopic data of complexes **2**−**9** show two relevant facts: (i) in all cases the coordinated ylide has undergone a proton transfer and, hence, the actual *O*,*O*′-bonded ligand is the zwitterionic tautomer of **1** [$Ph_3(P^+)-CH_2-C(O^-)=C(H)C(O)OEt$] (Scheme 2); (ii) complexes **3**, **7**, **8**, and **9** were obtained as single isomers, within the limit of detection of the technique, while complexes **2**, **4**, **5** and **6** were obtained as a mixture of the geometric isomers (a) and (b) depicted in Scheme 1.

For complexes **4**, **5**, and **6**, the assignment of structure (a) to the major isomers can be inferred, as for complex **2**, from their ^1H NMR spectra. In the case of **4**, the resonance assigned to the $H^{6'}$ proton (*ortho* to the metallated position) in the major isomer appears shifted to high field (δ = 6.07 ppm), and the same shift was observed in complex **5** (δ =6.05 ppm). In complex **6**, the signal due to the H^6 proton appears at δ = 5.88 ppm, virtually the same chemical shift as that observed for **2**. Thus, we can assign structure (a) for the major isomers of **4**, **5** and **6**.

The assignment of structure (a) to complex **3** rests on the similarity of the chemical shifts of the carbonyl C atoms in the $^{13}C\{^1H\}$ NMR spectrum with those in **2a** and **4a**−**6a**. These chemical shifts appear in a very narrow range of frequencies [δ_{CO} = 173.44 (**3**), 173.67 (**2a**), 173.89 (**4a**), 173.90 (**5a**), 173.78 (**6a**) ppm; δ_{COO} = 171.33 (**3**), 171.21 (**2a**), 171.57 (**4a**), 171.51 (**5a**), 171.21 (**6a**) ppm], suggesting quite similar chemical environments and a very similar structural arrangement. In comparison, the corresponding resonances of the minor isomers (b) appear, systematically, at lower field. Moreover, the resemblance of the ancillary *C*,*N*-cyclometallated ligands in **3** with those in **2**, **4**, **5** or **6** (they do not show notable structural differences and similar behavior should be expected) also supports this assignment. These extrapolations cannot be performed for complexes **7** and **8**. Here, changes in the donor atom (N replaced by P) induce a change in the electronic requirements at the *trans* position, and the substituents at the donor atom also change (the P atom contains two bulky *ortho*-tolyl groups) so that the steric requirements at the *cis* position are different. However, the assignment of structure (a) for **7** and **8** can be inferred from the $^{13}C\{^1H\}$ NMR spectra, since the signal of the methylene carbon CH_2P appears as a doublet of doublets through coupling with the adjacent phosphonium P atom and with the *trans* P atom of the cyclometallated ligand [$^4J_{P,C}$ = 5.9 Hz for **7** and $^4J_{P,C}$ = 5.1 Hz for **8**]. Moreover, the remote *trans* location of the two bulkiest fragments of the molecule, $-CH_2PPh_3$ and $P(o\text{-tol})_2$, should be energetically more stable, since it minimizes intramolecular steric repulsions.

In the case of complex **9** we have also observed the formation of a single isomer, although we do not have direct spectroscopic evidence in favor of a given structure for this complex. Throughout the description of the structures of **2**−**8** it is possible to detect a repetitive arrangement of the ligands, which places the carbonyl oxygen of the C(O)OEt unit *trans* to the metallated carbon atom, and the oxygen of the enolate group *trans* to the heteroatom. Since we also have a metallated carbon atom (C_6F_5 ligand) and a neutral heteroatom (the S atom of the SC_4H_8 ligand) in **9**, we propose a similar stereochemistry for **9** and, thus, the structure (a) as depicted in Scheme 1. This hypothesis has been corroborated through the determination of the X-ray structure (see below).

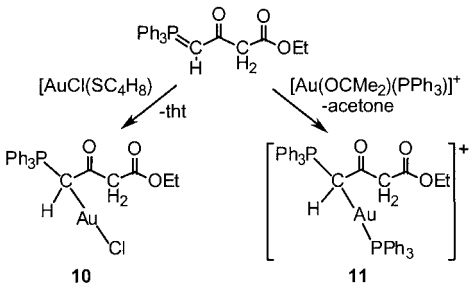
In summary, the interaction of the ylide **1** with Pd^{II} and Pt^{II} complexes promotes the generation of the phosphonium-enolate [$Ph_3(P^+)-CH_2-C(O^-)=C(H)C(O)OEt$] ligand in all cases. It is remarkable to observe the presence of a free phosphonium unit in a ligand strongly anchored to the metal center. This phosphonium moiety could be the clue for further functionalization of the ligand, since its deprotonation would generate a new ylide unit, which could be involved in a variety of new processes (e.g. synthesis of polynuclear complexes, Wittig reactions, etc.) which are not possible starting from the free ligand **1**.

2. Gold(I) Complexes

As we have seen in the preceding discussion, the reactivity of **1** towards cationic bis(solvate) complexes of Pd^{II} and Pt^{II} does not result in the expected *C*-coordination. In an attempt to involve the ylidic C_α atom in bonding to a transition metal, we have focused our attention to gold(I) compounds, taking into account the exceptional stability of Au^I complexes with *C*-bonded α-stabilized P-ylides,[7] and also that the *O*-coordination of keto-stabilized P-ylides to Au^I remains unknown.

Treatment of [$AuCl(SC_4H_8)$] with **1** (1:1 molar ratio) in CH_2Cl_2 at room temperature occurs with displacement of the labile ligand SC_4H_8 and *C*-bonding of the ylide, giving the neutral derivative [$AuCl\{C(H)(PPh_3)C(O)CH_2C(O)OEt\}$] (**10**). In addition, treatment of the solvated complex [$Au(OCMe_2)(PPh_3)]ClO_4$ (obtained by treatment of [$AuCl(PPh_3)$] with $AgClO_4$ in acetone, see details in Exp. Sect.) with **1** (1:1 molar ratio) results in the formation of [$Au\{C(H)(PPh_3)COCH_2COOEt\}(PPh_3)]ClO_4$ (**11**), which also contains the *C*-coordinated ylide. These two processes are presented in Scheme 3.

Both complexes gave elemental analyses and mass spectra in good agreement with the proposed structures. The C-bonding of the ylide **1** in compounds **10** and **11** can be inferred from the IR spectra, since the absorptions assigned to the C=O stretch appear at 1731 cm^{-1} (ν_{COO}) and 1666 cm^{-1} (ν_{CO}) in **10**, and at 1724 and 1657 cm^{-1} for the respective absorptions in **11**. A comparison of these values with those reported for the free ylide (1717 and 1546 cm^{-1})[2b] shows that the absorption of the carboxylate



Scheme 3

group undergoes very small shifts, suggesting that it does not interact with the metal center, whereas that due to the carbonyl adjacent to the ylide group appears shifted to high energy by up to 120 cm^{-1}. This latter shift implies a higher participation of the keto-form in the description of the bonded ylide, and it is a clear indicator of the presence of a *C*-coordinated ylide.[1]

Additional evidence for the *C*-coordination of the ylide, and for the concomitant hybridization change ($sp^2 \rightarrow sp^3$), comes from the analysis of the NMR spectroscopic data. Key features of the NMR spectra of **10** and **11** are: (i) the ylidic proton $PC_\alpha(H)$ appears at about 4.8 ppm as a singlet in **10** or as a doublet in **11**, with a small coupling constant $^2J_{PH}$ (9 Hz); (ii) the methylene protons appear diastereotopic, showing the absence of a symmetry plane; (iii) the P atom $PC_\alpha(H)$ appears in the $^{31}P\{^1H\}$ NMR spectrum as a singlet (**10**) or as a doublet (**11**), shifted to low field (24.84 ppm for **10**, 26.15 ppm for **11**) with respect to the free ylide (δ =15.50 ppm); (iv) the ylidic carbon atom $PC_\alpha(H)$ appears in the $^{13}C\{^1H\}$ NMR spectrum (acquired as APT) as a doublet with positive phase, with a $^1J_{P,C}$ coupling constant (55.7 Hz for **10**, 58.6 Hz for **11**) smaller than that observed in **1** (108.3 Hz), and shifted to high field with respect to the corresponding signal in **1**. All these changes are in good agreement with the presence of a *C*-bonded ylide.[1]

As expected, the chemical behavior in this case is quite different from that observed in Pd^{II} and Pt^{II} complexes. The *C*-bonding of the ylide **1** blocks further reactivity at the C_α atom, but leaves the β-keto ester moiety unchanged. It seems likely then, that any further reactivity of the gold complexes could be directed selectively to the methylene group. This is not possible in the free ligand **1**, in which most of its reactivity occurs at the C_α center after deprotonation of the CH_2 unit.

Crystal Structure of $[Pd(C_6H_4CH_2NMe_2)(Ph_3PCH_2C(O)=C(H)C(=O)OEt\text{-}\kappa\text{-}O,O')]ClO_4$ (2a)

A solution of a mixture of **2a**/**2b** in CH_2Cl_2 was slowly evaporated to dryness at room temperature. During this process very regular yellow crystals were formed, which should be a mixture of the complexes **2a** and **2b** in the same molar ratio as that of the crude complex, and from this mixture of crystals, a yellow block was selected. The structure corresponds to that of complex **2a**, already established by spectroscopic methods.

A drawing of the cationic organometallic fragment is shown in Figure 1. The parameters concerning the data collection and refinement are given in Table 1, and selected bond lengths and angles are collected in Table 2. The Pd atom is located in a slightly distorted square-planar environment, surrounded by the *ortho*-metallated carbon atom C(25), the aminic N atom N(1), and the two oxygen atoms, O(1) and O(2), of the phosphonium-enolate [$Ph_3PCH_2C(O)=CH-C(O)OEt$] ligand, which coordinates as an *O*,*O*′-chelate. The structural parameters of the *ortho*-

Table 1: Crystal data and structure refinement for complexes **2a**, **9** and **10**

	2a	**9**	**10**
Empirical formula	$C_{33}H_{35}ClNO_7PPd$	$C_{34}H_{31}ClF_5O_7PPdS$	$C_{24}H_{23}AuClO_3P$
Mol mass	730.44	851.47	622.81
Crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P21/n$
a (Å)	11.3130(6)	11.7925(8)	12.2186(11)
b (Å)	12.2269(6)	11.8733(8)	14.5885(13)
c (Å)	14.2943(7)	13.2719(9)	12.9320(12)
α (°)	94.123(1)	77.936(1)	
β (°)	112.790(1)	87.107(1)	96.1960(10)
γ (°)	116.409(1)	79.959(1)	
V (Å^3)	1559.61(14)	1789.2(2)	2291.7(4)
Z	2	2	4
$D_{calcd.}$ (Mg·m^{-3})	1.555	1.580	1.805
μ (mm^{-1})	0.782	0.769	6.628
Reflections collected	9964	9962	13973
Unique reflections	6729, R_{int} = 0.0103	6237, R_{int} = 0.0183	5157, R_{int} = 0.0264
Data/restraints/parameters	6729/0/400	6237/0/452	5157/0/272
*R*1 [$I > 2\sigma(I)$]	0.0220	0.0590	0.0248
*wR*2 [$I > 2\sigma(I)$]	0.0556	0.1450	0.0620
Goodness of fit	1.087	1.045	1.041
T/K	100(2)	291(2)	100(2)
λ(Mo-K_α)/Å	0.71073	0.71073	0.71073

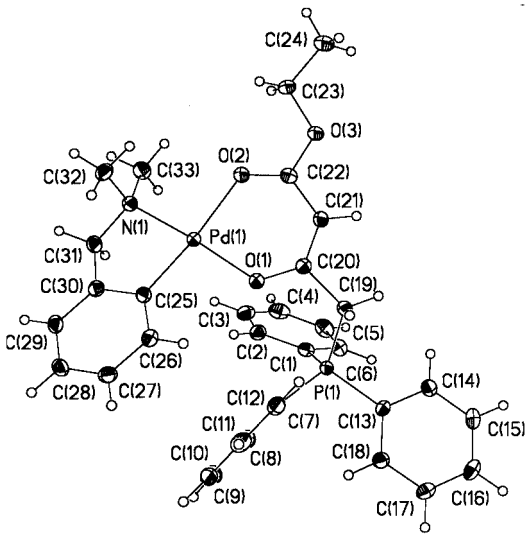


Figure 1. Thermal ellipsoid plot of the cationic fragment of **2a**. Non-hydrogen atoms are drawn at the 50% probability level

Table 2. Selected bond lengths (Å) and angles (°) for **2a**

Pd(1)−C(25)	1.9619(16)	Pd(1)−O(1)	2.0390(11)
Pd(1)−N(1)	2.0511(14)	Pd(1)−O(2)	2.1265(11)
P(1)−C(7)	1.7840(16)	P(1)−C(1)	1.7930(17)
P(1)−C(13)	1.7941(16)	P(1)−C(19)	1.8129(16)
C(19)−C(20)	1.521(2)	C(20)−O(1)	1.2876(19)
C(20)−C(21)	1.372(2)	C(21)−C(22)	1.426(2)
C(22)−O(2)	1.240(2)	C(22)−O(3)	1.3376(19)
O(3)−C(23)	1.4546(19)	C(23)−C(24)	1.504(2)
C(25)−C(26)	1.394(2)	C(25)−C(30)	1.398(2)
C(26)−C(27)	1.396(2)	C(27)−C(28)	1.385(3)
C(28)−C(29)	1.390(3)	C(30)−C(31)	1.498(2)
C(31)−N(1)	1.497(2)	N(1)−C(33)	1.481(2)
N(1)−C(32)	1.487(2)		
C(25)−Pd(1)−O(1)	93.73(6)	C(25)−Pd(1) −N(1)	82.39(6)
O(1)−Pd(1)−N(1)	175.490(5)	C(25)−Pd(1)−O(2)	174.25(6)
O(1)−Pd(1)−O(2)	90.91(4)	N(1)−Pd(1)−O(2)	93.11(5)
C(7)−P(1)−C(1)	111.86(8)	C(7)−P(1)−C(13)	105.77(7)
C(1)−P(1)−C(13)	112.50(8)	C(7)−P(1)−C(19)	112.28(8)
C(1)−P(1)−C(19)	107.54(7)	C(13)−P(1)−C(19)	106.85(7)
C(20)−C(19)−P(1)	111.41(11)	O(1)−C(20)−C(21)	129.57(15)
O(1)−C(20)−C(19)	113.40(13)	C(21)−C(20)−C(19)	117.02(14)
C(20)−C(21)−C(22)	124.69(15)	O(2)−C(22)−O(3)	127.33(15)
O(3)−C(22)−C(21)	112.75(14)		

metallated $C_6H_4CH_2NMe_2$ ligand are similar to those reported in related complexes and they do not show special features.[8] The two Pd−O bond lengths are different [Pd(1)−O(1) = 2.0390(11) Å; Pd(1)−O(2) = 2.1265(11) Å] probably due to two concurrent facts, namely (i) the different nature of the two oxygen atoms involved, since the C(22)−O(2) bond shows a higher double bond character [1.240(2) Å] than the C(20)−O(1) bond [1.2876(19) Å] (see Scheme 2), and (ii) the different *trans* influences of the C- and N-donor atoms of the $C_6H_4CH_2NMe_2$ ligand. A comparison of these distances with those of related complexes shows that the Pd(1)−O(1) bond length falls in the range usually reported for *O,O′*-acetylacetonate derivatives of Pd^{II} (range 2.007−2.073 Å),[9] while the Pd(1)−O(2) bond length is only slightly shorter than those found in other *O*-bonded α-stabilized keto-ylides [2.154(2) Å].[8b] These facts are in good agreement with a higher keto character for the C(22)−O(2) bond and a higher enolic character for the C(20)−O(1) bond. Moreover, the C−C bond lengths in the chelate ring are also quite different. The C(21)−C(22) bond length [1.426(2) Å] shows a small double bond component, since it is intermediate between a single σ(C−C) bond and a double C=C bond,[10] while the C(20)−C(21) bond length [1.372(2) Å] clearly shows double bond character. Outside the ring, the C(19)−C(20) bond length [1.521(2) Å] implies a single σ(C−C) bond, and all P−C bond lengths are also in the range found for single bonds.[10]

The geometry around the carbon atoms C(20) and C(22) is strictly planar [sum of the bond angles = 359.99(15)° in both cases] and the bond angle C(20)−C(21)−C(22) [124.69(15)°] also reflects its sp^2 character. The environments around the atoms C(19) and P(1) are tetrahedral. Furthermore, the intramolecular distance P(1)−O(1) [3.001(2) Å] is shorter than the sum of the van der Waals radii (3.32 Å),[11] suggesting an intramolecular interaction between the positively charged phosphonium atom P(1) and the formally anionic atom O(1). This type of 1,4-interaction has recently been described by us for keto-stabilized P-ylides.[12] However, this intramolecular interaction should be weaker than those described in P-ylides, as can be deduced from the value of the torsion angle P(1)−C(19)−C(20)−O(1) (51.2°), which is considerably different from the value obtained in the more stable *cisoid* forms of the ylides (nearly 0°).[12] Finally, the H atom H(26) [bonded to C(26)] points to the phenyl ring C(7)−C(12), the distance between H(26) and the best least-squares plane defined by the C atoms of the Ph ring being 2.74 Å. It is reasonable to assume that this short intramolecular distance could explain the strong anisotropic shielding exhibited by this proton in the ^1H NMR spectrum of **2a**.

Crystal Structure of [Pd(C_6F_5)(SC_4H_8)($Ph_3PCH_2C(O)$=C(H)C(=O)OEt-κ-*O,O′*)]ClO_4 (9)

A solution of **9** in CH_2Cl_2 was very slowly evaporated to dryness at room temperature. During this process yellow crystals were formed. A drawing of the cationic organometallic fragment is shown in Figure 2. The parameters concerning the data collection and refinement are summarized in Table 1, and selected bond lengths and angles are given in Table 3. The Pd atom is located in a distorted square-planar environment, surrounded by the *ipso* carbon atom C(1) of the C_6F_5 ligand, the S(1) atom of the tht ligand, and the two oxygen atoms, O(1) and O(2), of the phosphonium-enolate [$Ph_3PCH_2C(O)$=CH−C(O)OEt] ligand. The structural arrangement confirms that the enolate oxygen O(2) is *trans* to the sulfur atom S(1) and, hence, that the carbonylic oxygen O(1) is *trans* to the *ipso* carbon atom C(1) of the C_6F_5 group, as we proposed previously. The Pd(1)−C(1) bond length [1.987(5) Å] is typical for C_6F_5 groups *trans* to O-donor ligands,[4b] and the Pd(1)−S(1) bond length [2.2772(17) Å] also falls in the usual range of distances found in the literature for this type of bond.[9] The two

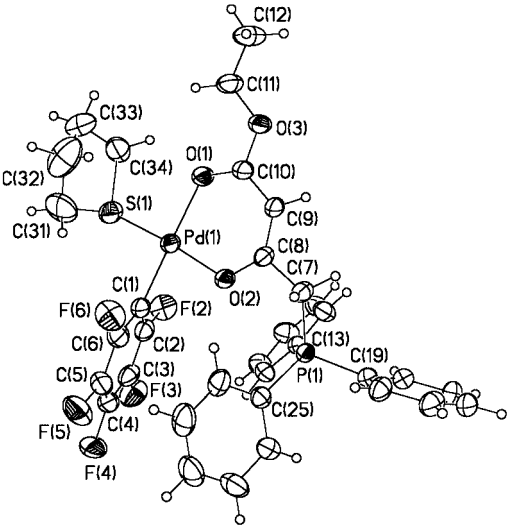


Figure 2. Thermal ellipsoid plot of the cationic fragment of **9**. Non-hydrogen atoms are drawn at the 50% probability level

Table 3. Selected bond lengths (Å) and angles (°) for **9**

Pd(1)−C(1)	1.987(5)	Pd(1)−O(1)	2.066(4)
Pd(1)−S(1)	2.2772(17)	Pd(1)−O(2)	2.028(3)
P(1)−C(25)	1.794(6)	P(1)−C(19)	1.797(5)
P(1)−C(13)	1.799(5)	P(1)−C(7)	1.804(5)
O(1)−C(10)	1.250(6)	O(2)−C(8)	1.283(6)
O(3)−C(10)	1.324(6)	O(3)−C(11)	1.453(7)
C(7)−C(8)	1.523(7)	C(8)−C(9)	1.351(7)
C(9)−C(10)	1.414(7)	C(11)−C(12)	1.473(9)
C(1)−Pd(1)−O(2)	86.94(18)	C(1)−Pd(1)−O(1)	178.47(18)
O(2)−Pd(1)−O(1)	91.57(14)	C(1)−Pd(1)−S(1)	87.76(15)
O(2)−Pd(1)−S(1)	173.97(11)	O(1)−Pd(1)−S(1)	93.74(11)
C(25)−P(1)−C(19)	107.1(3)	C(25)−P(1)−C(13)	111.2(2)
C(19)−P(1)−C(13)	110.9(3)	C(25)−P(1)−C(7)	111.9(3)
C(19)−P(1)−C(7)	105.0(2)	C(13)−P(1)−C(7)	110.5(3)
C(10)−O(1)−Pd(1)	123.7(3)	C(8)−O(2)−Pd(1)	122.9(3)
C(10)−O(3)−C(11)	118.4(4)	C(8)−C(7)−P(1)	114.6(4)
O(2)−C(8)−C(9)	129.2(5)	O(2)−C(8)−C(7)	113.6(4)
C(9)−C(8)−C(7)	117.1(5)	C(8)−C(9)−C(10)	125.3(5)
O(1)−C(10)−O(3)	118.9(5)	O(1)−C(10)−C(9)	127.1(5)
O(3)−C(10)−C(9)	114.0(5)	O(3)−C(11)−C(12)	108.0(5)

Pd−O bond lengths are different [Pd(1)−O(1) = 2.066(4) Å and Pd(1)−O(2) = 2.028(3) Å], as we have described for **2a**, reflecting the different *trans* influences of the *trans* donor atoms, although in **9** the differences between them are less pronounced than in **2a** [2.1265(11) Å and 2.0390(11) Å]. The internal bond lengths and angles of the phosphonium-enolate ligand are identical, within experimental error, to those described for complex **2a**, and thus the same structural conclusions can be derived here. Finally, the similarity between the structures of complexes **2a** and **9** is also reflected in the presence of short intramolecular P···O contacts[12] [P(1)−O(2) = 2.950(7) Å], although in this case the value of the torsion angle P(1)−C(7)−C(8)−O(2) (35.5°) is clearly narrower than that reported for **2a**.

Crystal Structure of [AuCl{C(H)(PPh_3)C(O)CH_2C(O)OEt}] (10)

Crystals of complex **10** were grown by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the crude complex at room temperature. A drawing of the molecular structure of **10** is shown in Figure 3. The parameters concerning the data collection and refinement are presented in Table 1, and selected bond lengths and angles are collected in Table 4. Complex **10** crystallizes in the monoclinic space group $P2_1/c$. Since this space group is centrosymmetric, and although the complex is chiral, the crystal as a whole is racemic. The structure shown in Figure 3 corresponds to an absolute configuration (*S*) for the ylidic carbon C_α, following the system of priorities of Cahn, Ingold and Prelog.[13] The gold atom lies in a nearly linear environment, since the bond angle C(19)−Au(1)−Cl(1) is 176.48(9)°. The bond lengths Au(1)−C(19) [2.079(3) Å] and Au(1)−Cl(1) [2.2928(9) Å] are similar to those found in the literature for related structural arrangements.[14] The bond lengths C(20)−O(1) [1.214(4) Å] and C(22)−O(3) [1.199(4) Å] are typical[8,9] for carbonyl groups which are not delocalized through adjacent functional groups (e.g. the ylide function), while the bond length C(19)−C(20) is identical (within ex-

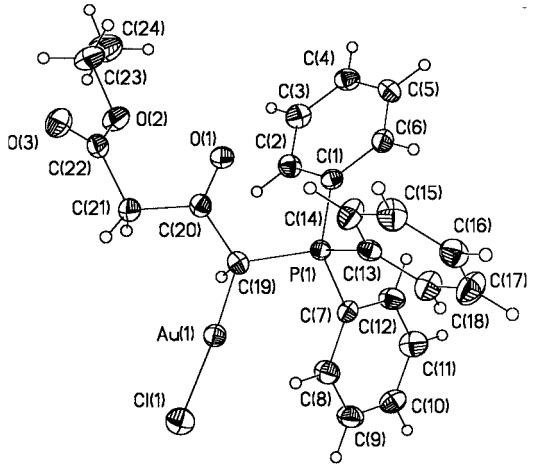


Figure 3. Thermal ellipsoid plot of **10**. Non-hydrogen atoms are drawn at the 50% probability level

Table 4. Selected bond lengths (Å) and angles (°) for **10**

Au(1)−C(19)	2.079(3)	Au(1)−C1(1)	2.2928(9)
P(1)−C(19)	1.780(3)	P(1)−C(7)	1.799(3)
P(1)−C(13)	1.800(3)	P(1)−C(1)	1.801(3)
C(19)−C(20)	1.487(5)	C(20)−O(1)	1.214(4)
C(20)−C(21)	1.529(4)	C(21)−C(22)	1.499(5)
C(22)−O(3)	1.199(4)	C(22)−O(2)	1.330(4)
C(23)−C(24)	1.501(6)		
C(19)−P(1)−C(13)	114.20(16)	C(7)−P(1)−C(13)	107.48(15)
C(19)−P(1)−C(1)	109.98(15)	C(7)−P(1)−C(1)	107.40(16)
C(13)−P(1)−C(1)	110.00(15)	C(20)−C(19)−P(1)	115.1(2)
C(20)−C(19)−Au(1)	104.9(2)	P(1)−C(19)−Au(1)	113.53(17)
O(1)−C(20)−C(19)	125.2(3)	O(1)−C(20)−C(21)	120.4(3)
C(19)−C(20)−C(21)	114.3(3)	C(3)−C(22)−O(2)	124.5(3)
O(3)−C(22)−C(21)	125.2(3)	C(19)−Au(1)−Cl(1)	176.48(9)
O(2)−C(22)−C(21)	110.2(3)	C(19)−P(1)−C(7)	107.50(16)

perimental error) to that found in other *C*-bonded keto-stabilized ylides.[8a] The P(1)−C(19) bond length [1.780(3) Å] is slightly shorter than the other P−C(Ph) bond lengths and, in turn, is similar to those found in other *C*-coordinated stabilized ylides.[8a] Typical single bond σ(C−C) distances are found for C(20)−C(21) [1.529(4) Å] and C(21)−C(22) [1.499(5) Å]. Finally, the environments around P(1) and C(19) are tetrahedral, while those around the carbonyl atoms C(20) and C(22) are strictly planar.

Conclusion

The polyfunctional ylide $[Ph_3P{=}C(H)C(O)CH_2C(O)OEt]$ (**1**) shows versatile reactivity towards different transition metals, giving very different structural motifs as a function of the metal center. Towards cationic Pd^{II} and Pt^{II} complexes with two available coordination sites, **1** undergoes a proton transfer giving the zwitterionic phosphonium-enolate $[Ph_3(P^+)CH_2C(O^-){=}CH{-}C(O)OEt]$ ligand, which coordinates as an *O,O′*-chelate. The presence of a phosphonium group, which can be easily deprotonated, could open new pathways of reactivity towards polynuclear complexes with a great variety of structural arrangements. On the other hand, the reactivity of **1** towards Au^I derivatives gives complexes with the ylide *C*-bonded, leaving the β-keto ester unit −C(O)CH$_2$C(O)OEt unchanged. This fact also opens new pathways of reactivity. This rich coordination chemistry is unprecedented for α-stabilized ylide ligands and the fine tuning of the reactivity allows us to suggest that new and more interesting results may await discovery.

Experimental Section

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and handled with great caution.[15]

General Methods: Solvents were dried and distilled under argon using standard procedures. Elemental analyses were carried out with a Perkin−Elmer 2400-B machine. Infrared spectra (4000−200 cm^{-1}) were recorded with a Perkin−Elmer 883 infrared spectrometer from nujol mulls between polyethylene sheets. Mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions with a V. G. Autospec spectrometer. ^{1}H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz), ^{19}F (282.40 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature with a Bruker ARX-300 spectrometer. The ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced using the residual solvent signal as the internal standard, whereas the $^{31}P\{^1H\}$ NMR spectra were referenced to external H_3PO_4 (85%). The ^{19}F NMR spectra were referenced to $CFCl_3$. The starting compounds were prepared following published methods: **1**,[2b] $[Pd(\mu\text{-}Cl)\{(C_6H_4CH_2NMe_2\text{-}(C^2,N)\}]_2$,[16] $[Pd(\mu\text{-}Cl)\{(S)\text{-}C_6H_4C(H)MeNMe_2(C^2,N)\}]_2$,[16] $[Pd(\mu\text{-}Cl)\{NC_{13}H_8(C^8,N)\}]_2$,[17] $[Pd(\mu\text{-}Cl)\{CH_2NC_9H_6(C^8,N)\}]_2$,[6,18] $[Pd(\mu\text{-}Cl)\{NC_5H_4\text{-}2\text{-}C_6H_4(C^2,N)\}]_2$,[19] $[Pd(\mu\text{-}Cl)(tht)(C_6F_5)]_2$,[20] $[M(\mu\text{-}Cl)\{o\text{-}CH_2C_6H_4P(o\text{-}tol_2)(C,P)\}]_2$ (M = Pd,[21] Pt[22]), [AuCl(tht)],[23] and $[AuCl(PPh_3)]$.[23]

$[Ph_3P{=}C(H){-}C(O){-}CH_2{-}COOEt]$ (1): The ylide **1** was prepared following the method reported by F. Serratosa and E. Solé.[2b] The analytical and IR data were in good agreement with those previously published. Here we present the MS and NMR spectroscopic data for **1**, which have not been reported previously. MS (FAB+): *m/z* (%) = 391 (100) [M$^+$]. ^{1}H NMR (CD_2Cl_2): δ = 1.26 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 3.29 (d, $^4J_{PH}$ = 1.5 Hz, 2 H, CH_2), 3.77 (d, $^2J_{PH}$ = 24.9 Hz, 1 H, P=CH), 4.16 (q, 2 H, OCH_2), 7.46−7.70 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.53 (CH_3), 48.63 (d, CH_2, $^3J_{P,C}$ = 15.5 Hz), 52.18 (d, $^1J_{P,C}$ = 108.3 Hz, P=C$_\alpha$), 60.81 (OCH_2), 127.13 (d, $^1J_{P,C}$ = 90.8 Hz, C$_{ipso}$, PPh_3), 129.28 (d, $^2J_{P,C}$ = 12.2 Hz, C$_{ortho}$, PPh_3), 132.66 (d, $^4J_{P,C}$ = 2.8 Hz, C$_{para}$, PPh_3), 133.50 (d, $^3J_{P,C}$ = 10.2 Hz, C$_{meta}$, PPh_3), 170.79 (s, COO), 184.22 (d, $^2J_{P,C}$ = 2.9 Hz, C=*O*) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 15.50 ppm.

Complex 2: To a suspension of $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2)]_2$ (0.0755 g, 0.137 mmol) in THF (20 mL) under argon, was added $AgClO_4$ (0.0567 g, 0.273 mmol). The resultant mixture was stirred at room temperature for 20 min with exclusion of light, then filtered through a Celite pad. The freshly prepared solution of the bis(solvate) was treated with **1** (0.107 g, 0.273 mmol) giving a yellow solution, which was stirred for an additional 30 min. During this time, **2** precipitated as a yellow solid, which was filtered, washed with Et_2O (10 mL) and air dried. Yield: 0.100 g (50%). Complex **2** was characterized by NMR spectroscopy as a mixture of the isomers **2a/2b** in molar ratio **2a/2b** = 4.5:1. $C_{33}H_{35}ClNO_7PPd$ (730.47): calcd. C 54.26, H 4.83, N 1.92; found C 54.26, H 4.83, N 1.93. MS (FAB+): *m/z* (%) = 630 (100) [M − ClO_4]$^+$. IR: $\tilde{\nu}$ = 1628 (ν_{COO}), 1525 (ν_{CO}) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 1.23 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **2a**), 1.27 (t, $^3J_{H,H}$ = 6.9 Hz, CH_3, **2b**), 2.24 (s, NMe_2, **2b**), 2.75 (s, NMe_2, **2a**), 3.76 (s, CH_2N, **2b**), 3.86 (s, CH_2N, **2a**), 4.06 (q, OCH_2, **2a**), 4.13 (d, $^2J_{PH}$ = 13.8 Hz, CH_2P, **2a**), 4.16 (d, $^2J_{PH}$ = 13.8 Hz, CH_2P, **2b**), 4.18 (q, OCH_2, **2b**), 4.81 (d, $^4J_{PH}$ = 0.6 Hz, = CH, **2a**), 4.86 (s, =CH, **2b**), 5.89 (dd, $^3J_{H^6H^5}$ = 8.1, $^4J_{H^6H^4}$ = 0.9 Hz, H^6, C_6H_4, **2a**), 6.43 (td, $^3J_{H^5H^6}$ = $^3J_{H^5H^4}$ = 8.1, $^4J_{H^5H^3}$ = 2.4 Hz, H^5, C_6H_4, **2a**), 6.83−7.01 [m, H^3 + H^4 (**2a**) + C_6H_4 (**2b**)], 7.66−7.87 (m, PPh_3, **2a** + **2b**) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.49 (Me, **2a** + **2b**), 36.36 (d, $^1J_{P,C}$ = 52.5 Hz, CH_2P, **2a**), 36.47 (d, $^1J_{P,C}$ = 54.2 Hz, CH_2P, **2b**), 52.36 (NMe_2, **2a** + **2b**), 61.26 (OCH_2, **2a**), 61.75 (OCH_2, **2b**), 73.20 (CH_2N, **2a**), 73.78 (CH_2N, **2b**), 88.91 (d, $^3J_{P,C}$ = 7.4 Hz, =CH, **2b**), 90.43 (d, $^3J_{P,C}$ = 7.0 Hz, =CH, **2a**), 118.50 (d, $^1J_{P,C}$ = 87.8 Hz, C$_{ipso}$, PPh_3, **2a**), 118.88 (d, C$_{ipso}$, PPh_3, **2b**, $^1J_{P,C}$ = 88.1 Hz), 121.67 (2 C), 124.74 (2 C), 143.33 (C^2), 147.53 (C^1) (C_6H_4, **2a**), 124.98 (2 C), 125.09 (2 C), 144.23 (C^2), 147.75 (C^1), (C_6H_4, **2b**), 130.72 (d, $^2J_{P,C}$ = 12.7 Hz, C$_{ortho}$, **2a** + **2b**), 134.11(C$_{para}$, **2b**), 134.34 (d, $^3J_{P,C}$ = 10.0 Hz, C$_{meta}$, **2a** + **2b**), 135.64 (C$_{para}$, **2a**, PPh_3), 171.21 (CO_2, **2a**), 172.48 (CO_2, **2b**), 173.67 (d, $^2J_{P,C}$ = 7.2 Hz, CO, **2a**), 175.18 (d, $^2J_{P,C}$ = 7.1 Hz, CO, **2b**) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.11 (**2b**), 22.71 (**2a**) ppm.

Complex 3: Complex **3** was prepared following a synthetic procedure similar to that reported for **2**. Thus, $[Pd(\mu\text{-}Cl)(CH_2C_9H_6N)]_2$ (0.192 g, 0.338 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.140 g, 0.676 mmol) and **1** (0.264 g, 0.676 mmol) to give **3** as a yellow solid. Yield: 0.344 g (69%). $C_{34}H_{31}ClNO_7PPd$ (738.45): calcd. C 55.30, H 4.23, N 1.89; found C 55.38, H 4.37, N 1.83. MS (FAB+): *m/z* (%) = 638 (100) [M − ClO_4]$^+$. IR: $\tilde{\nu}$ = 1624 (ν_{COO}), 1521 (ν_{CO}) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 1.31 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 3.02 (s, 2 H, CH_2Pd), 4.19 (d, $^2J_{PH}$ = 13.5 Hz, 2 H, CH_2P), 4.22 (q, 2 H, OCH_2), 4.92 (s, 1 H, =CH), 7.40−7.52 (m, 2 H, C_9H_6N), 7.62−7.76 (m, 15 H, PPh_3), 7.82−7.87 (m, 2 H, C_9H_6N), 8.31 (dd, $^3J_{H^4H^3}$ = 8.4, $^4J_{H^4H^2}$ = 1.5 Hz, 1 H, H^4, C_9H_6N),

8.58 (dd, $^3J_{H^2H^3}$ = 5.1, $^4J_{H^2H^4}$ = 1.5 Hz, 1 H, H^2, C_9H_6N) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.54 (CH_3), 22.48 (CH_2Pd), 37.08 (d, $^1J_{P,C}$ = 57.6 Hz, CH_2P), 61.15 (OCH_2), 89.32 (d, $^3J_{P,C}$ = 7.9 Hz, =CH), 119.34 (d, $^1J_{P,C}$ = 88.4 Hz, C_{ipso}, PPh_3), 121.93, 124.23, 128.65, 128.81, 129.47, 138.37, 147.85, 148.33, 153.61 (C_9H_6N), 130.52 (d, $^2J_{P,C}$ = 13 Hz, C_{ortho}), 134.25 (d, $^3J_{P,C}$ = 10.3 Hz, C_{meta}), 135.38 (d, $^4J_{P,C}$ = 3 Hz, C_{para}) (PPh_3), 171.33 (COO), 173.44 (d, $^2J_{P,C}$ = 7.2 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 23.15 ppm.

Complex 4: Complex **4** was prepared following a synthetic procedure similar to that reported for **2**. Thus, $[Pd(\mu\text{-}Cl)(NC_5H_4\text{-}2\text{-}C_6H_4)]_2$ (0.118 g, 0.20 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.083 g, 0.40 mmol) and **1** (0.156 g, 0.40 mmol) to give **4** as a yellow solid. Yield: 0.227 g (75.8%). Complex **4** was characterized by NMR as a mixture of the isomers **4a/4b** in molar ratio **4a/4b** = 3.2:1. $C_{35}H_{31}ClNO_7PPd$ (750.46): calcd. C 56.02, H 4.16, N 1.87; found C 55.69, H 4.49, N 1.67. MS (FAB+): *m/z* (%) = 650 (100) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1620 (ν_{COO}), 1515 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.28 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **4a**), 1.30 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **4b**), 4.16 (q, OCH_2, **4a**), 4.18 (d, $^2J_{PH}$ = 14 Hz, CH_2P, **4b**), 4.20 (d, $^2J_{PH}$ = 16 Hz, CH_2P, **4a**), 4.24 (q, OCH_2, **4b**), 4.87 (d, $^4J_{PH}$ = 1 Hz, =CH, **4a**), 4.90 (s, =CH, **4b**), 6.07 (dd, $^3J_{H,H}$ = 7.8, $^4J_{H,H}$ = 1.2 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 6.58 (td, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.2 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 6.68 (td, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 1.2 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4b**), 7.01 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 7.16 (m, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 7.33 (dd, $^3J_{H,H}$ = 7.9, $^4J_{H,H}$ = 1.2 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 7.88−7.57 (m, PPh_3 + $NC_5H_4\text{-}2\text{-}C_6H_4$), 8.35 (dd, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1 Hz, $NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**) ppm. The assignment of resonances for the $NC_5H_4\text{-}2\text{-}C_6H_4$ ligand could be performed unequivocally only for the major isomer **4a**, due to extensive overlapping of the signals of the minor isomer **4b** with those of the major isomer and with the PPh_3 group. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.43 (CH_3, **4a** + **4b**), 36.23 (d, $^1J_{P,C}$ = 52.1 Hz, CH_2P, **4a** + **4b**), 61.56 (OCH_2, **4a**), 62.03 (OCH_2, **4b**), 89.89 (d, $^3J_{P,C}$ = 7.3 Hz, =CH, **4b**), 91.07 (d, $^3J_{P,C}$ = 6.7 Hz, =CH, **4a**), 118.37 (d, $^1J_{P,C}$ = 87.7 Hz, C_{ipso}, PPh_3, **4a**), 118.58 (d, $^1J_{P,C}$ = 86.0 Hz, C_{ipso}, PPh_3, **4b**), 119.15, 122.79, 123.49, 125.18, 129.16, 131.30, 139.57, 145.24, 148.45, 151.47, 165.51 ($NC_5H_4\text{-}2\text{-}C_6H_4$, **4a**), 119.20, 122.58, 123.49, 125.48, 129.41, 131.31, 139.58, 145.32, 148.41, 152.67, 165.91 ($NC_5H_4\text{-}2\text{-}C_6H_4$, **4b**), 130.76 (d, $^2J_{P,C}$ = 12.4 Hz, C_{ortho}, PPh_3), 134.35 (d, $^3J_{P,C}$ = 9.1 Hz, C_{meta}, PPh_3), 135.69 (s, C_{para}, PPh_3, both isomers), 171.57 (COO, **4a**), 172.69 (COO, **4b**), 173.89 (d, $^2J_{P,C}$ = 7.3 Hz, CO, **4a**), 175.23 (d, $^2J_{P,C}$ = 6.6 Hz, CO, **4b**) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.57 (**4b**), 22.84 (**4a**) ppm.

Complex 5: Complex **5** was prepared following a synthetic procedure similar to that reported for **2**. Thus, $[Pd(\mu\text{-}Cl)(C_{13}H_8N)]_2$ (0.101 g, 0.158 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.065 g, 0.32 mmol) and **1** (0.123 g, 0.316 mmol) to give **5** as a yellow solid. Yield: 0.0622 g (25.5%). Complex **5** was characterized by NMR as a mixture of the isomers **5a/5b** in molar ratio **5a/5b** = 3.6:1. $C_{37}H_{31}ClNO_7PPd$ (774.48): calcd. C 57.38, H 4.03, N 1.81; found C 56.90, H 4.05, N 1.79. MS (FAB+): *m/z* (%) = 674 (100) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1616 (ν_{COO}), 1512 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.33 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **5a**), 1.35 (t, $^3J_{H,H}$ = 6.3 Hz, CH_3, **5b**), 4.21 (q, OCH_2, **5a**), 4.21 (d, $^2J_{PH}$ = 13.8 Hz, CH_2P, **5b**), 4.28 (d, $^2J_{PH}$ = 13.8 Hz, CH_2P, **5a**), 4.30 (q, OCH_2, **5b**), 4.93 (s, =CH, **5b**), 4.94 (s, =CH, **5a**), 6.05 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 0.6 Hz, $C_{13}H_8N$, **5a**), 6.94 (t, $^3J_{H,H}$ = 7.5 Hz, $C_{13}H_8N$, **5a**), 6.97 (dd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 5.1 Hz, $C_{13}H_8N$, **5b**), 7.18 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.2 Hz, $C_{13}H_8N$, **5b**), 7.30 (dd, $^3J_{H,H}$ = 8.1, $^3J_{H,H}$ = 5.1 Hz, $C_{13}H_8N$, **5a**), 7.30 (dd, $^3J_{H,H}$ = 6.0, $^4J_{H,H}$ = 0.9 Hz, $C_{13}H_8N$, **5b**), 7.39 (t, $^3J_{H,H}$ = 7.5 Hz, $C_{13}H_8N$, **5b**), 7.47 (d, $^3J_{H,H}$ = 7.5 Hz, $C_{13}H_8N$, **5a**), 7.51 (d, $^3J_{H,H}$ = 8.7 Hz, $C_{13}H_8N$, **5a**), 7.55 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 0.6 Hz, $C_{13}H_8N$, **5b**), 7.85−7.63 (m, PPh_3 + $C_{13}H_8N$, **5a** + **5b**), 8.16 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, $C_{13}H_8N$, **5a**), 8.20 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2 Hz, $C_{13}H_8N$, **5b**), 8.31 (dd, $^3J_{H,H}$ = 5.1, $^4J_{H,H}$ = 1.2 Hz, $C_{13}H_8N$, **5a**) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (signals due to **5b** in the low field region were not observed) = 14.50 (CH_3, **5a** + **5b**), 36.26 (d, $^1J_{P,C}$ = 52.3 Hz CH_2P, **5a** + **5b**), 61.63 (OCH_2, **5a**), 62.12 (OCH_2, **5b**), 88.92 (d, $^3J_{P,C}$ = 5.9 Hz, =CH, **5b**), 91.12 (d, $^3J_{P,C}$ = 6.7 Hz, =CH, **5a**), 118.47 (d, $^1J_{P,C}$ = 87.8 Hz, C_{ipso}, PPh_3, **5a**), 118.63 (d, $^1J_{P,C}$ = 87.8 Hz, C_{ipso}, PPh_3, **5b**), 121.66, 122.92, 123.65, 128.37, 128.74, 129.15, 133.44, 137.55, 141.03, 147.26, 148.43, 154.83 ($C_{13}H_8N$, **5a**, one of the quaternary carbon atoms was not observed), 130.76 (d, PPh_3, $^2J_{P,C}$ = 12.8 Hz, C_{ortho}), 134.40 (d, $^3J_{P,C}$ = 9.4 Hz, C_{meta}, PPh_3), 135.63 (C_{para}, PPh_3), 171.51 (COO, **5a**), 173.90 (d, $^2J_{P,C}$ = 6.9 Hz, CO, **5a**) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 23.08 (**5a**), 22.74 (**5b**) ppm.

Complex 6: Complex **6** was prepared following a synthetic procedure similar to that reported for **2**. Thus, $[Pd(\mu\text{-}Cl)\{(S)\text{-}C_6H_4C(H)MeNMe_2\}]_2$ (0.105 g, 0.181 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.075 g, 0.362 mmol) and **1** (0.142 g, 0.36 mmol) to give **6** as a yellow solid. Yield: 0.2627 g (97.5%). Complex **6** was characterized by NMR spectroscopy as a mixture of the isomers **6a/6b** in molar ratio **6a/6b** = 4.3:1. $C_{34}H_{37}ClNO_7PPd$ (744.50): calcd. C 54.85, H 5.01, N 1.88; found: C 55.19, H 4.73, N 1.89. MS (FAB+): *m/z* (%) = 644 (65) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1622 (ν_{COO}), 1505 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.23 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **6a**), 1.26 (t, $^3J_{H,H}$ = 7.2 Hz, CH_3, **6b**), 1.35 [d, $^3J_{H,H}$ = 6.9 Hz, CH(*Me*), **6b**], 1.48 [d, $^3J_{H,H}$ = 6.6 Hz, CH(*Me*), **6a**], 2.03 (s, NMe_2, **6b**), 2.31 (s, NMe_2, **6b**), 2.55 (s, NMe_2, **6a**), 2.81 (s, NMe_2, **6a**), 3.86 [q, C*H*(Me), **6a**], 4.06 (q, OCH_2, **6a**), 4.12−4.25 [m, OCH_2 (**6b**) + C*H*(Me) (**6b**) + CH_2P (**6a**) + CH_2P (**6b**)], 4.83 (s, =CH, **6a**), 4.88 (s, =CH, **6b**), 5.88 (dd, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.2 Hz, H^6, C_6H_4, **6a**), 6.42 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.5 Hz, H^5, C_6H_4, **6a**), 6.77 (d, $^3J_{H,H}$ = 7 Hz, C_6H_4, **6a**), 6.90 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.2 Hz, C_6H_4, **6a**), 6.92 (td, $^3J_{H,H}$ = 4.0, $^4J_{H,H}$ = 1.2 Hz, C_6H_4, **6b**), 6.97−7.02 (m, C_6H_4, **6b**), 7.65−7.84 (m, PPh_3, **6a** + **6b**) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.51 (CH_3, **6a**), 17.38 (CH_3, **6b**), 18.28 (CH*Me*), **6a**), 30.53 (CH*Me*), **6b**), 36.30 (d, $^1J_{P,C}$ = 52.8 Hz, CH_2P, **6a**), 36.51 (d, CH_2P, **6b**, $^1J_{P,C}$ = 54.2 Hz), 46.12 (NMe_2, **6b**), 46.34 (NMe_2, **6a**), 51.58 (NMe_2, **6b**), 51.87 (NMe_2, **6a**), 61.23 (OCH_2, **6a**), 61.67 (OCH_2, **6b**), 75.30 [*C*H(Me), **6a**], 75.72 [*C*H(Me), **6b**], 88.88 (d, $^3J_{P,C}$ = 6.6 Hz, =CH, **6b**), 90.30 (d, $^3J_{P,C}$ = 6.8 Hz, =CH, **6a**), 118.59 (d, $^1J_{P,C}$ = 87.8 Hz, C_{ipso}, PPh_3, **6a**), 118.94 (d, $^1J_{P,C}$ = 88.1 Hz, C_{ipso}, PPh_3, **6b**), 122.16 (2 C, C_6H_4, **6a**), 124.71 (2 C, C_6H_4, **6a**), 122.32, 124.98, 125.08, 125.21 (C_6H_4, **6b**), 130.69 (d, $^2J_{P,C}$ = 11.5 Hz, C_{ortho}, PPh_3, **6a** + **6b**), 134.35 (d, $^3J_{P,C}$ = 10.0 Hz, C_{meta}, PPh_3, **6a** + **6b**), 135.60 (C_{para}, PPh_3, **6a** + **6b**), 143.87 (C_6H_4, **6a**), 144.91 (C_6H_4, **6b**), 152.77 (C_6H_4, **6b**), 152.80 (C_6H_4, **6a**), 171.21 (COO, **6a**), 172.48 (COO, **6b**), 173.78 (d, CO, **6a**, $^2J_{P,C}$ = 7.2 Hz), 175.26 (d, $^2J_{P,C}$ = 6.9 Hz, CO, **6b**) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.74 (**6a**), 22.10 (**6b**) ppm.

Complex 7: Complex **7** was prepared following a synthetic procedure similar to that reported for **2**. Thus, $[Pt(\mu\text{-}Cl)\{o\text{-}CH_2C_6H_4P(o\text{-}tol)_2\}]_2$ (0.135 g, 0.126 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.052 g, 0.25 mmol) and **1** (0.103 g, 0.264 mmol) to give **7** as a pale yellow solid. Yield: 0.222 g (88.6%). $C_{45}H_{43}ClO_7P_2Pt$ (988.32): calcd. C 54.69, H 4.38; found C 54.52, H 4.08. MS (FAB+): *m/z* (%) = 888 (45) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1614 (ν_{COO}), 1520 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.18 (t,

$^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 2.40 (s, 3 H, Me tolyl), 2.64 (s, 3 H, Me tolyl), 2.98 (s broad, 2 H, CH_2Pt), 3.61 (q, 2 H, OCH_2), 4.27 (d, $^2J_{PH}$ = 13.5 Hz, 2 H, CH_2P), 5.08 (s, 1 H, =CH), 6.78−7.74 (m, 27 H, PPh_3 + C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 7.77 ($PtCH_2$), 13.98 (CH_3), 22.19 (CH_3 tolyl), 30.31 (CH_3 tolyl), 36.21 (dd, $^1J_{P,C}$ = 55.4, $^4J_{P,C}$ = 5.9 Hz, CH_2P), 60.97 (OCH_2), 90.41 (d, $^3J_{P,C}$ = 7.5 Hz, =CH), 118.86 (d, $^1J_{P,C}$ = 88.02 Hz, C_{ipso}, PPh_3), 125.66 (d, $J_{P,C}$ = 9.1 Hz, C_6H_4, tolyl), 127.09 (d, $J_{P,C}$ = 15.9 Hz, C_6H_4, tolyl), 130.07 (d, $^2J_{P,C}$ = 13.0 Hz, C_{ortho}, PPh_3), 130.40−132.62 (m, C_6H_4, tolyl), 133.90 (d, $^3J_{P,C}$ = 10.3 Hz, C_{meta}, PPh_3), 134.61 (C^1, C_6H_4, tolyl), 134.80 (d, $^4J_{P,C}$ = 2.5 Hz, C_{para}, PPh_3), 158.51 (d, $^2J_{P,C}$ = 24.7 Hz, C^2, C_6H_4, tolyl), 169.26 (s, COO), 172.22 (d, $^2J_{P,C}$ = 7.3 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 23.27 (s, PPh_3), 10.72 [s, $^1J_{Pt,P}$ = 4739 Hz, Pt(C^P)] ppm.

Complex 8: Complex **8** was prepared following a synthetic procedure similar to that reported for (**2**). Thus, [Pd(μ-Cl){*o*-$CH_2C_6H_4P(o\text{-tol})_2$}]$_2$ (0.129 g, 0.145 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.060 g, 0.29 mmol) and **1** (0.113 g, 0.290 mmol) to give **8** as a pale yellow solid. Yield: 0.190 g (72.8%). $C_{45}H_{43}ClO_7P_2Pd$ (899.63): calcd. C 60.08, H 4.82; found C 60.25, H 4.46. MS (FAB+): *m*/*z* (%) = 799 (100) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1619 (ν_{COO}), 1512 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.18 (t, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 2.40 (s, 3 H, CH_3 tolyl), 2.52 (d, $^2J_{H,H}$ = 11.0 Hz, 1 H, CH_2Pd), 2.63 (s, 3 H, CH_3 tolyl), 2.91 (d, 1 H, CH_2Pd), 3.56 (q, 2 H, OCH_2), 4.24 (d, $^2J_{PH}$ = 13.2 Hz, 2 H, CH_2P), 4.92 (s, 1 H, =CH), 6.67−7.74 (m, 27 H, C_6H_4 + PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.34 (CH_3), 22.73 (d, $^3J_{P,C}$ = 9.8 Hz, CH_3 tolyl), 28.72 ($PdCH_2$), 30.51 (CH_3 tolyl), 37.53 (dd, $^1J_{P,C}$ = 56, $^4J_{P,C}$ = 5.1 Hz, CH_2P), 60.72 (OCH_2), 88.68 (d, $^3J_{P,C}$ = 7.1 Hz, =CH), 119.45 (d, $^1J_{P,C}$ = 88.2 Hz, C_{ipso}, PPh_3), 125.83 (C_6H_4, tolyl), 126.58 (d, $J_{P,C}$ = 8.2 Hz, C_6H_4, tolyl), 127.51 (d, $J_{P,C}$ = 10.5 Hz, C_6H_4, tolyl), 127.88 (C_6H_4, tolyl), 130.47 (d, $^2J_{P,C}$ = 12.8 Hz, C_{ortho}, PPh_3), 131.43−133.66 (m, C_6H_4, tolyl), 134.28 (d, $^3J_{P,C}$ = 9.9 Hz, C_{meta}, PPh_3), 135.35 (s, C_{para}, PPh_3), 142.44 (d, $^2J_{P,C}$ = 13.0 Hz, C^2, C_6H_4, tolyl), 156.82 (d, $^1J_{P,C}$ = 29.1 Hz, C^1, C_6H_4, tolyl), 171.26 (s, COO), 173.78 (d, $^2J_{P,C}$ = 7.1 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 34.83 [s, Pd(C^P)], 23.43 (s, PPh_3) ppm.

Complex 9: Complex **9** was prepared following a synthetic procedure similar to that reported for **2**. Thus, [Pd(μ-Cl)(C_6F_5)(tht)]$_2$ (0.1164 g, 0.146 mmol) reacted, in THF (20 mL), with $AgClO_4$ (0.061 g, 0.29 mmol) and **1** (0.115 g, 0.292 mmol) to give **9** as a deep yellow solid. Yield: 0.189 g (75.7%). $C_{34}H_{31}ClF_5O_7PPdS$ (851.50): calcd. C 47.96, H 3.67; found C 47.89, H 3.36. MS (FAB+): *m*/*z* (%) = 752 (47) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1603 (ν_{COO}), 1502 (ν_{CO}), 1283 (tht), 959, 798 (C_6F_5) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.26 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 2.06 (s, 4 H, H_β, tht), 2.64 (s, 2 H, H_α, tht), 3.12 (s, 2 H, H_α, tht), 4.07 (q, $^3J_{H,H}$ = 7.2 Hz, 2 H, OCH_2), 4.23 (d, $^2J_{PH}$ = 13.5 Hz, 2 H, $-CH_2P$), 5.07 (s, 1 H, =CH), 7.43−7.81 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.40 (CH_3), 30.39 (C_β, SC_4H_8), 35.49 (d, $^1J_{P,C}$ = 57.2 Hz, CH_2P), 37.01 (C_α, SC_4H_8), 62.20 (OCH_2), 89.39 (d, $^3J_{P,C}$ = 8.1 Hz, =CH), 118.88 (d, $^1J_{P,C}$ = 88.7 Hz, C_{ipso}, PPh_3), 130.33 (d, $^2J_{P,C}$ = 12.7 Hz, C_{ortho}, PPh_3), 133.80 (d, $^3J_{P,C}$ = 10.0 Hz, C_{meta}, PPh_3), 135.21 (C_{para}, PPh_3), 137.13 (m, C_6F_5), 140.12 (m, C_6F_5), 146.29 (m, C_6F_5), 149.36 (m, C_6F_5), 171.84 (d, $^4J_{P,C}$ = 1.3 Hz, COO), 174.26 (d, $^2J_{P,C}$ = 7.1 Hz, CO) ppm. ^{19}F NMR (CD_2Cl_2): δ = −120.89 (d, $^3J_{F,F}$ = 22 Hz, 2 F, F_{ortho}), −159.33 (t, $^3J_{F,F}$ = 22 Hz, 1 F, F_{para}), −162.41 (t, 2 F, F_{meta}) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 22.61 ppm.

Complex 10: To a solution of **1** (0.110 g, 0.281 mmol) in CH_2Cl_2 (15 mL) was added [AuCl(tht)] (0.090 g, 0.28 mmol) at room temperature, and the resultant solution was stirred for 30 min. The solvent was then evaporated to dryness and the white residue treated with Et_2O (30 mL), giving **10** as a white solid, which was filtered, washed with additional Et_2O (10 mL) and air dried. Yield: 0.170 g (96.9%). $C_{24}H_{23}AuClO_3P$ (622.84): calcd. C 46.28, H 3.72; found C 46.21, H 3.71. MS (FAB+): *m*/*z* (%) = 623 (9) $[M + H]^+$, 587 (15) $[M - Cl]^+$. IR: $\tilde{\nu}$ = 1731 (ν_{COO}), 1666 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.24 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 3.48 (dd, $^2J_{H,H}$ = 15.3, $^4J_{PH}$ = 2.7 Hz, 1 H, CH_2), 3.93 (dd, $^2J_{H,H}$ = 15.3, $^4J_{PH}$ = 1.5 Hz, 1 H, CH_2), 4.15 (q, 2 H, OCH_2), 4.73 (s, 1 H, AuCHP), 7.53−7.83 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.34 (CH_3), 38.08 (d, $^1J_{P,C}$ = 55.7 Hz, AuCHP), 49.17 (d, $^3J_{P,C}$ = 10.3 Hz, CH_2), 61.82 (OCH_2), 123.89 (d, $^1J_{P,C}$ = 88.17 Hz, C_{ipso}, PPh_3), 129.84 (d, $^2J_{P,C}$ = 12.5 Hz, C_{ortho}, PPh_3), 134.07 (d, $^4J_{P,C}$ = 2.7 Hz, C_{para}), 134.24 (d, $^3J_{P,C}$ = 10 Hz, C_{meta}), 196.28 (d, $^2J_{P,C}$ = 4.5 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 24.84 ppm.

Complex 11: To a solution of [Au(Cl)PPh_3] (0.104 g, 0.210 mmol) in acetone (30 mL), was added $AgClO_4$ (0.0436 g, 0.210 mmol). The resultant suspension was stirred in the dark for 30 min at room temperature and then filtered through a Celite pad. To the freshly prepared solution of [Au($OCMe_2$)PPh_3]ClO_4 (0.210 mmol) was added the ylide **1** (0.0821 g, 0.210 mmol), and the resultant solution stirred for 15 min. The solvent was evaporated to dryness, and the oily residue treated with Et_2O (25 mL), giving complex **11** as a white solid. Yield: 0.131 g (65.6%). $C_{42}H_{38}AuClO_7P_2$ (949.13): calcd. C 53.15, H 4.04; found C 53.28, H 4.15. MS (FAB+): *m*/*z* (%) = 849 (15) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1724 (ν_{COO}), 1657 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.18 (t, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 3.65 (dd, $^2J_{H,H}$ = 15.3, $^4J_{PH}$ = 2.4 Hz, 1 H, CH_2), 3.93 (dd, $^2J_{H,H}$ = 15.3, $^4J_{PH}$ = 1.8 Hz, 1 H, CH_2), 4.10 (q, 2 H, OCH_2), 4.83 (d, $^2J_{PH}$ = 9 Hz, 1 H, AuCHP), 7.18−7.76 (m, 30 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 14.09 (CH_3), 49.33 (d, $^3J_{P,C}$ = 10.4 Hz, CH_2), 50.83 (dd, $^1J_{P,C}$ = 58.6, $^2J_{P,C}$ = 54.6 Hz, AuCHP), 61.35 (OCH_2), 123.02 (d, $^1J_{P,C}$ = 88.6 Hz, C_{ipso}, $CPPh_3$), 127.90 (d, $^1J_{P,C}$ = 58.6 Hz, C_{ipso}, $AuPPh_3$), 129.55 (d, $^2J_{P,C}$ = 11.8 Hz, C_{ortho}, $CPPh_3$), 129.78 (d, $^2J_{P,C}$ = 12.7 Hz, C_{ortho}, $AuPPh_3$), 132.27 (d, $^4J_{P,C}$ = 2.2 Hz, C_{para}, $AuPPh_3$), 133.64 (d, $^3J_{P,C}$ = 10.1 Hz, C_{meta}, $AuPPh_3$), 133.83 (d, $^3J_{P,C}$ = 9.6 Hz, C_{meta}, $CPPh_3$), 134.01 (C_{para}, $CPPh_3$), 167.94 (COO), 196.69 (t, $^2J_{P,C} \approx {}^3J_{P,C}$ = 4.9 Hz, CO) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 39.89 (d, $^3J_{P,P}$ = 11.2 Hz, $AuPPh_3$), 26.15 (d, $CHPPh_3$) ppm.

Crystallography

Data Collection: Crystals of complexes **2a** and **9** of adequate quality for X-ray purposes were obtained by slow evaporation of solutions of either the crude mixture of complexes **2a**/**2b**, or the crude complex **9** in CH_2Cl_2. In contrast, crystals of **10** were grown by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the crude complex at room temperature. A crystal of dimensions 0.36 × 0.34 × 0.22 mm (**2a**), 0.39 × 0.25 × 0.043 mm (**9**) or 0.49 × 0.30 × 0.19 mm (**10**) was mounted onto a quartz fiber in a random orientation and covered with epoxy. Data collection was performed at 100 K (**2a**, **10**) or at room temperature (**9**) with a Bruker Smart Apex CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). In all cases, a hemisphere of data was collected based on three ω-scan runs. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 10 s per frame. In all cases, the diffraction frames were integrated using the program SAINT[24] and the integrated intensities were corrected for systematic errors with SADABS.[25]

Structure Solution and Refinement: The structures were solved by Patterson and Fourier methods.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant − Fourier calculation and then refined as riding atoms with the torsion angles about the O−C(methyl) or N−C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[27]

The final difference Fourier map for **9** showed two peaks with densities of 1.88 and 1.16 e/Å^3, which delimit a vector roughly parallel to the Pd(1)−S(1) bond and displaced less than 1 Å from it, suggesting a possible minor disorder component for these two atoms. Detailed analysis of these peaks and their environment confirmed the possibility of an accompanying disorder of the tht moiety, and also indicated that such a disorder could exist without causing any important changes to the remainder of the structure. We refined a disordered model for Pd(1) and S(1), obtaining a population of 0.083(3) for the second component. However, no difference peaks appeared in the area of the tht, where the carbon atoms of a putative minor disorder component would be located. As a further diagnostic for the source of the difference peaks, we conducted a twin analysis using the program ROTAX.[28,29] No plausible twin model was obtained. We report here the results of the refinement without disorder. Results of a refinement including the minor congeners for Pd(1) and S(1), which did not involve observable changes in the geometric parameters of the principal component, are available from the authors.

CCDC-222324 (for **2a**), -222325 (for **9**), and -222326 (for **10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] R. Navarro, E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **1999**, 4111 and references given therein.
[2] [2a] H. Muxfeldt, G. Grethe, K. Uhlig, H. Zeugner, *Chem. Ber.* **1963**, *96*, 2943. [2b] F. Serratosa, E. Solé, *An. R. Soc., Esp. Fis. Quim. Ser. B* **1966**, *62*, 431.
[3] [3a] C. M. Moorhof, D. F. Schneider, D. Winkler, *J. Chem. Res. (S)* **1998**, 763. [3b] C. M. Moorhoff, *J. Chem. Soc., Perkin Trans. 1* **1997**, 1987 and references cited therein. [3c] S. G. Hegde, R. D. Bryant, *Synth. Commun.* **1993**, *23*, 2753. [3d] C. M. Moorhof, D. F. Schneider, *Tetrahedron Lett.* **1987**, *28*, 4721. [3e] K. M. Pietrusiewicz, J. Monkiewicz, *Tetrahedron Lett.* **1986**, *27*, 739. [3f] K. M. Pietrusiewicz, J. Monkiewicz, R. Bodalski, *J. Org. Chem.* **1983**, *48*, 788.
[4] [4a] J. Forniés, F. Martínez, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **1995**, *495*, 185. [4b] J. Forniés, R. Navarro, M. Tomás, E. P. Urriolabeitia, *Organometallics* **1993**, *12*, 940. [4c] J. Forniés, F. Martínez, R. Navarro, E. P. Urriolabeitia, *Organometallics* **1996**, *15*, 1813.
[5] [5a] L. R. Falvello, S. Fernández, R. Navarro, A. Rueda, E. P. Urriolabeitia, *Organometallics* **1998**, *17*, 5887. [5b] L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **1999**, *38*, 2445.
[6] A. J. Deeming, I. P. Rothwell, M. B. Hursthouse, L. New, *J. Chem. Soc., Dalton Trans.* **1978**, 1490.
[7] [7a] J. Vicente, M. T. Chicote, *Coord. Chem. Rev.* **1999**, 193−195, 1143 and references cited therein. [7b] J. Vicente, M. T. Chicote, M. C. Lagunas, *Helv. Chim. Acta* **1999**, *82*, 1202.
[8] [8a] L. R. Falvello, S. Fernández, R. Navarro, I. Pascual, E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **1997**, 763. [8b] L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **1996**, *35*, 3064.
[9] A. G. Orpen, L. Brammer, F. H. Allen, D. Kennard, D. G. Watson, R. Taylor, *J. Chem. Soc., Dalton Trans.* **1989**, S1−S83.
[10] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, 685−S1−S19).
[11] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[12] A. Lledós, J. J. Carbó, E. P. Urriolabeitia, *Inorg. Chem.* **2001**, *40*, 4913.
[13] R. S. Cahn, C. Ingold, V. Prelog, *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 385.
[14] [14a] J. P. Fackler, B. Trzcinska-Bancroft, *Organometallics* **1985**, *4*, 1891. [14b] L. C. Porter, H. Knachel, J. P. Fackler, *Acta Crystallogr., Sect. C* **1987**, *43*, 1833.
[15] W. C. Wolsey, *J. Chem. Educ.* **1973**, *50*, A335.
[16] A. C. Cope, E. C. Friedrich, *J. Am. Chem. Soc.* **1968**, *90*, 909.
[17] [17a] A. Kasara, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1272. [17b] B. N. Cockburn, D. V. Howe, T. Keating, B. F. G. Johnson, J. Lewis, *J. Chem. Soc., Dalton Trans.* **1973**, 404.
[18] G. E. Hartwell, R. V. Lawrence, M. J. Smas, *J. Chem. Soc., Chem. Commun.* **1970**, 912.
[19] M. A. Gutiérrez, G. R. Newkome, J. Selbin, *J. Organomet. Chem.* **1980**, *202*, 341.
[20] R. Usón, J. Forniés, P. Espinet, G. Alfranca, *Synth. Inorg. Metal-Org. Chem.* **1980**, *10*, 579.
[21] W. A. Herrmann, C. Brossman, K. Öfele, C. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844.
[22] J. Forniés, A. Martín, R. Navarro, V. Sicilia, P. Villarroya, *Organometallics* **1996**, *15*, 1826.
[23] R. Usón, A. Laguna, M. Laguna, *Inorg. Synth.* **1989**, *26*, 85.
[24] SAINT Version 5.0; Bruker Analytical X-ray Systems, Madison, WI, **1995**.
[25] G. M. Sheldrick, SADABS: Empirical absorption correction program; University Göttingen, **1996**.
[26] SHELXS-86, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.
[27] G. M. Sheldrick, SHELXL-97: FORTRAN program for the refinement of crystal structures from diffraction data; University of Göttingen, **1997**. Molecular graphics were done using the commercial package SHELXTL-PLUS, Release 5.05/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, **1996**.
[28] S. Parsons, R. O. Gould, ROTAX, a program to test for possible twin laws for merohedral and non-merohedral twins indexed on a single orientation matrix.
[29] R. I. Cooper, R. O. Gould, S. Parsons, D. J. Watkin, *J. Appl. Cryst.* **2002**, *35*, 168.

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