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Synthesis, Structure, and Reactivity of Pd Complexes with Mixed P,S-Bis(ylide), Ylide–Sulfide, and Ylide–Methanide Ligands

Elena Serrano,[a] Tatiana Soler,[b] and Esteban P. Urriolabeitia*[c]

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The coordination properties of the ylide–sulfonium salts $[Ph_3P{=}C(H)COCH_2S(R^1)R^2]X$ [R^1 = R^2 = Et, X = Br (**2**); R^1 = Me, R^2 = Ph, X = ClO_4 (**5**)], the phosphonium–sulfide salt $[Ph_3PCH_2COCH_2SEt]Br$ (**3**) and the neutral ylide–sulfide $[Ph_3P{=}C(H)COCH_2SPh]$ (**4**) towards Pd^{II} have been studied. Four different bonding modes have been characterized. The reactions of the ylide–sulfonium salts **2** and **5** with $PdCl_2(NCMe)_2$ and NEt_3 afford the chelating bis(ylide) complexes *cis*-$[PdCl_2\{Ph_3PC(H)COC(H)S(R^1)R^2$-κ*C*,*C*$\}]$ [R^1 = R^2 = Et (**6**); R^1 = Me, R^2 = Ph (**7**)], which are obtained selectively in the *meso* form (*RS*/*SR*). This bonding mode is characterized, including by X-ray crystallography, in the acetylacetonate (acac) complexes $[Pd(acac$-*O*,*O*′$)\{Ph_3PC(H)COC(H)S(R^1)R^2$-κ*C*,*C*$\}]ClO_4$ [R^1 = R^2 = Et (**8**); R^1 = Me, R^2 = Ph (**9**)], which were obtained by reaction of the respective precursor **6** or **7** with $AgClO_4$ and Tl(acac). On the other hand, the *C*,*S*-chelating bonding mode has been characterized in $[PdCl_2\{Ph_3PC(H)COCH_2SR$-κ*C*,*S*$\}]$ [R = Et (**10**); R = Ph (**11**)], obtained by reaction of the phosphonium–sulfide salt **3** with $PdCl_2(NCMe)_2$ and NEt_3 or by reaction of the ylide–sulfide **4** with $PdCl_2(NCMe)_2$, respectively. Furthermore, the tridentate bonding mode μ-*S*:κ*C*,*C*,*S* has been determined in the dinuclear derivative $[PdCl\{Ph_3PC(H)COC(H)SPh$-μ-*S*:κ*C*,*C*,S$\}]_2$ (**13**), synthesized by reaction of the ylide–sulfide **4** with $PdCl_2(NCMe)_2$ and NEt_3. Compound **13** reacts with PPh_3 to afford the κ*C*,*C*-chelate $[PdCl\{Ph_3PC(H)COC(H)SPh$-κ*C*,C$\}PPh_3]$ (**14**) after cleavage of the sulfide bridge. Compound **14** was obtained as a single diastereoisomer, which was characterized as the D,L form (*RR*/*SS*).

Introduction

The reactivity of stabilized ylides as ligands for transition metals has undergone an impressive development during recent years, and they display diverse chemical behaviors. The most studied topic, as evidenced by the number of reviews in the recent literature on this subject,[1,2] has been their versatility as ligands and their ability to act in different bonding modes.[3–8] When the ylide behaves as a monodentate ligand, its coordination mode can be tuned as a function of the metal, the bonding position, and the *trans* atom.[3,4] Ylides can also behave as polydentate ligands, either by using the ylide carbon atom and one heteroatom[5] or by using two carbon atoms.[1,6–8]

Bis(ylides) are a specific class of polydentate ylides, in which the two carbon atoms bonded to the metal atom are ylide carbon atoms (Figure 1). These species have been studied in depth in our group owing to their unique properties.[7c,9] In particular, we have been interested in the diastereoselective coordination of stabilized bis(ylides), because – in spite of the presence of two prochiral centers in the free ylide – their bonding always affords a single dia-

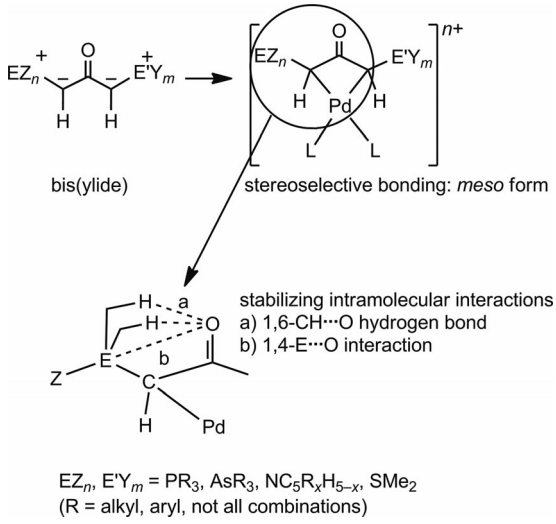

Figure 1. Selective coordination of bis(ylides) and phenomena responsible for this selectivity.

[a] Centro Universitario de la Defensa, Academia General Militar, 50090 Zaragoza, Spain
[b] Servicios Técnicos de Investigación, Facultad de Ciencias Fase II, 03690 San Vicente de Raspeig, Alicante, Spain
[c] Instituto de Síntesis Química y Catálisis Homogénea, CSIC-Universidad de Zaragoza, 50009 Zaragoza, Spain
Fax: +34-976-761187
E-mail: esteban@unizar.es
Homepage: www.unizar.es/icma/depart/quicorga/grupos/grupo2_chapo/g2_chapo.htm

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stereoisomer in the *meso* form. This type of bonding occurs regardless of the heteroatom involved (P, As, N, or S from the respective phosphonium, arsonium, pyridinium, or sulfonium units) and the type of substituents at the heteroatom (alkyl or aryl groups).[7,9]

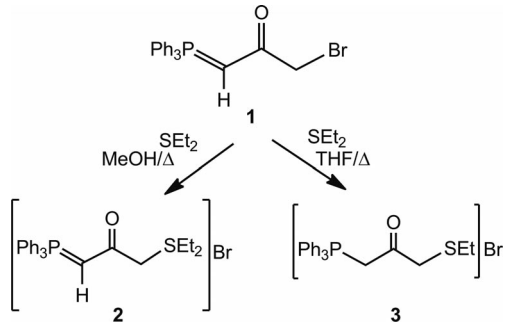
A closer inspection of this specific bonding mode with molecular modeling (DFT methods) revealed the existence of strong conformational preferences on the free ylides, which are the true reason for the stereoselective coordination. However, the ultimate origin of the conformational preferences lies in two different phenomena. In the case of P- or As-ylides, 1,4-E···O intramolecular interactions (Figure 1) can be established,[9c,9e,9f] whereas for N-ylides, 1,6-CH···O intramolecular hydrogen bonds have been characterized.[9c,9d] The case of the sulfur ylides is more complicated, and the DFT studies have shown that both phenomena can be operating at the same time.[9a,9b] Furthermore, we have pointed out that the conformational preferences can display a cooperative behavior, which means that they are not mutually exclusive.[9a,9c]

The studies of sulfur-containing bis(ylides) carried out up to now involved only SMe_2 derivatives, and this fact limits the prospects of available systems. The change of the substituents at the sulfur atom, for instance by introducing ethyl or aryl groups, changes in turn the availability of protons to establish hydrogen bonds and also the electron density around the sulfur atom. Therefore, it is clear that both facts could be reflected in the different intramolecular interactions that stabilize the *meso* form, namely, the hydrogen bonds and the electrostatic interactions. To determine in detail the effect of the change of the substituents on the establishment of intramolecular interactions, we have prepared new mixed bis(ylides) of sulfur and phosphorus [$Ph_3PC(H)COC(H)SEt_2$] and [$Ph_3PC(H)COC(H)SMePh$]. In this contribution, we describe their bonding properties towards Pd complexes, as well as those of the ylide–sulfides [$Ph_3P{=}C(H)COCH_2SR$] (R = Et, Ph), which, in spite of their similarity with the mixed bis(ylides), show a different chemical reactivity.

Results and Discussion

Synthesis of the Precursors

The reaction of the ylide $Ph_3P{=}C(H)COCH_2Br$ (**1**)[10] with an excess of SEt_2 (1:40 molar ratio) gives one of two different products depending on the reaction conditions (Scheme 1). When the reaction is carried out in refluxing methanol, the hygroscopic ylide–sulfonium salt [$Ph_3P{=}C(H)COCH_2SEt_2$]Br (**2**) is obtained in good yield as a white solid. However, when the reaction of **1** with SEt_2 (1:40 molar ratio) is carried out in tetrahydrofuran (THF), the phosphonium–sulfide salt [$Ph_3PCH_2COCH_2SEt$]Br (**3**) was obtained. In addition to the expected dealkylation process, well known in sulfonium salts,[11] we also observe the protonation of the ylide moiety with concomitant formation of the phosphonium–sulfide salt **3**. The presence of adventitious water could be responsible for this behavior. It is sensible to assume that the reaction gave the hypothetical ylide–sulfide [$Ph_3PC(H)COCH_2SEt$] and ethyl bromide, which could react with water to give EtOH and HBr, and the latter would be responsible for the protonation of the ylide moiety.

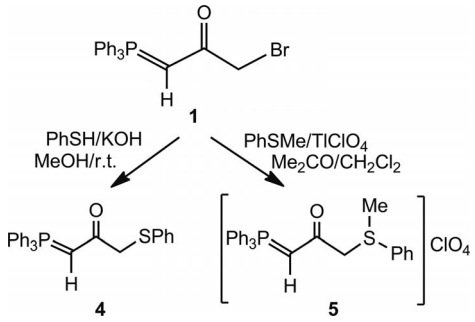


Scheme 1. Synthesis of precursors containing the SEt_2 and SEt units.

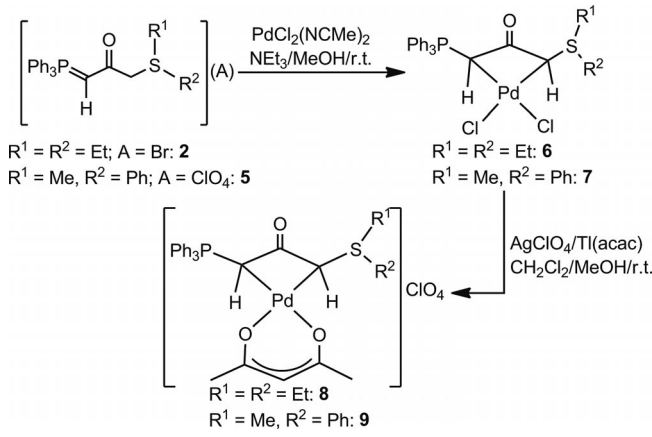
The mass spectra and elemental analyses of **2** and **3** are in agreement with the structures shown in Scheme 1. The IR spectrum of **2** shows an intense band at 1555 cm^{-1}, which is attributed to the resonance-stabilized carbonyl group,[3,4] whereas that of **3** shows the absorption due to the CO stretch at 1709 cm^{-1}; it is shifted to higher energy as it corresponds to a phosphonium group. The NMR spectra of **2** are in keeping with the presence of an ylide moiety, as can be inferred from the value of the $^2J_{P,H}$ coupling constant in the ^1H NMR spectrum (21.8 Hz), the ^{31}P chemical shift (δ = 15.10 ppm) in the ^{31}P NMR spectrum, and the value of the $^1J_{P,C}$ coupling constant in the ^{13}C NMR spectrum (107.4 Hz). All the values are diagnostic for the presence of a stabilized P-ylide in **2**. Moreover, the presence of the CH_2SEt_2 moiety is easily deduced from the corresponding resonances. On the other hand, inspection of the NMR spectroscopic data of **3** suggest that a phosphonium group is present, as the values of the $^2J_{P,H}$ and $^1J_{P,C}$ coupling constants decrease (11.4 and 62.46 Hz, respectively) and the ^{31}P chemical shift (δ = 20.61 ppm) indicates that the P nucleus is deshielded with respect to that of **2**.

The synthesis of sulfonium salts by the reaction of alkyl halides with sulfides and quaternization of the sulfur atom fails when aryl sulfides are used as reagents, probably because of the delocalization of the sulfur lone pairs on the aryl functional groups. Thus, the reaction of **1** with SPh_2 or with thioanisol (PhSMe) does not afford the expected ylide–sulfonium salts, and **1** is recovered in both cases. Therefore, alternative methods have been used. The synthesis of the ylide–sulfide **4** was carried out by the method reported by Alcázar et al.,[12] by the reaction of **1** with thiophenol and KOH (1:1:1 molar ratio) in MeOH (Scheme 2).

On the other hand, the removal of the bromide anion in **1** with a halide scavenger such as $TlClO_4$ in a CH_2Cl_2/Me_2CO mixture seems to produce an electrophilic methylene group that is reactive enough to react with thioanisol and to afford the ylide–sulfonium salt **5** (Scheme 2). The use of other classical reagents for the elimination of halides, such as $AgClO_4$, was not so efficient, and $TlClO_4$ proved



Scheme 2. Synthesis of precursors containing the SPh or the SPhMe units.



Scheme 3. Reactivity of the ylide–sulfonium salts **2** and **5** to give bis(ylide) derivatives **6**–**9**.

to be the best option. We then explored the possibility to prepare ylide–sulfonium salts from SPh_2 by using this method. However, despite many attempts, no derivatives could be obtained.

The characterization of the keto-stabilized P-ylide moieties in **4** and **5** was performed by applying the same key features as those described for **2** and **3**, that is, the position of the CO stretch in the IR spectra (1547 and 1548 cm^{-1}, respectively), the value of the $^2J_{P,H}$ and $^1J_{P,C}$ coupling constants (see Experimental Section, ^1H and ^{13}C NMR spectra), and the chemical shift of the P atom (δ = 15.96 and 15.02 ppm, respectively). It is also remarkable that the methylene CH_2S protons appear as a singlet signal in **4** but as diastereotopic signals in **5**, which reflects the asymmetry imposed by the sulfur atom.

Reactivity of the Ylide–Sulfonium Salts [$Ph_3PC(H)COCH_2SR^1R^2$]Br [$R^1 = R^2 = Et$ (2); $R^1 = Me$, $R^2 = Ph$ (5)]

The reaction of the mixed ylide–sulfonium salts [$Ph_3P{=}C(H)COCH_2SEt_2$]Br (**2**) or [$Ph_3P{=}C(H)COCH_2SMePh$]ClO_4 (**5**) with $PdCl_2(NCMe)_2$ in the presence of equimolar amounts (1:1:1 molar ratio) of a weak base (NEt_3) affords the corresponding mononuclear derivatives *cis*-[$PdCl_2${$Ph_3PC(H)COC(H)SR^1R^2$-κ*C*,*C*}] [$R^1 = R^2 = Et$ (**6**); $R^1 = Me$, $R^2 = Ph$ (**7**); Scheme 3). Although the analytical and IR data of **6** and **7** are in good agreement with the bis(ylide) structures proposed in Scheme 3, no reliable NMR parameters could be gathered owing to their low solubility in common NMR solvents. Therefore, complexes **6** and **7** were transformed into the more soluble acetylacetonate (acac) complexes [Pd(acac){$Ph_3PC(H)COC(H)SR^1R^2$-κ*C*,*C*}]ClO_4 [$R^1 = R^2 = Et$ (**8**); $R^1 = Me$, $R^2 = Ph$ (**9**)] by their one-pot reaction with $AgClO_4$ and Tl(acac) in a 1:1:1 molar ratio, as shown in Scheme 3.

The NMR spectroscopic data of **8** shows the presence of a single set of signals, which suggests that **8** is obtained as a single isomer. The *C*,*C*-coordination of the bis(ylide) is easily inferred from the observation of a doublet signal in the ^1H NMR spectrum at δ = 3.68 ppm with a small $^2J_{P,H}$ coupling constant (5.1 Hz), assigned to the C*H*P proton, and from the inequivalence of the two ethyl groups of the SEt_2 moiety. Additional NMR observations that support this are the presence of a peak at δ = 24.87 ppm in the ^{31}P NMR spectrum, downfield shifted with respect to that of **2**, or the presence of a doublet peak in the ^{13}C NMR spectrum at δ = 27.10 ppm with a $^1J_{P,C}$ coupling constant of 49.5 Hz. All these data are in good agreement with data reported in the literature for *C*,*C*-coordinated bis(ylides).[7,9] The characterization of the *meso* form as that adopted by the obtained diastereoisomer comes from the detection of a strong NOE on the peak at δ = 4.30 ppm (C*H*S) when the signal due to the C*H*P proton (δ =3.68 ppm) is irradiated. A parallel analysis of the NMR spectroscopic data of **9** can be performed, except that in this case two sets of signals (10:1 molar ratio) are observed in all spectra, owing to the presence of the sulfur atom as an additional stereogenic center. This is responsible for the formation of two diastereomeric species and the splitting of the NMR spectroscopic data, as the *C*,*C*-bonding of the bis(ylide) keeps the *meso* configuration.

The X-ray crystal structures of **8** and **9** have been determined and provide additional structural information. The molecular diagrams of the cationic parts are shown in Figures 2 and 3, respectively, together with selected bond lengths and angles. In both cases the Pd atom is located in a distorted square-planar environment, surrounded by the two oxygen atoms of the acac ligand and the two α-carbon atoms of the bis(ylide) ligand. As expected, the bis(ylide) is *C*,*C*-bonded and forms a strained four-membered ring. The sum of the angles around the Pd atom is virtually 360°, although individual values deviate notably in some cases from the theoretical value of 90°. For example, the bite angles subtended by the bis(ylide) ligands C(6)–Pd(1)–C(8) or C(21)–Pd(1)–C(19) in **8** and **9** are 69.59(8) and 69.07(9)°, respectively. The Pd–C_α bond lengths in **8** [2.066(5) and 2.063(5) Å] are identical and are also identical, within experimental error, to those found in the structurally related mononuclear [Pd(Cl)(PPh_3){η^2-[$Ph_3PC(H)C(O)C(H)NC_5H_5$]}]ClO_4 [2.080(3) Å][9c] or dinuclear [Pd(μ-Cl)($Ph_3PC(H)C(O)C(H)PPh_3$)]$_2(ClO_4)_2$ [range 2.053(11)–2.078(11) Å][7c] derivatives. However, the respective Pd–C_α

bond lengths in **9** are different [2.084(2) and 2.052(2) Å], although both of them fall in the usual range of bond lengths found in the literature for this type of bond.

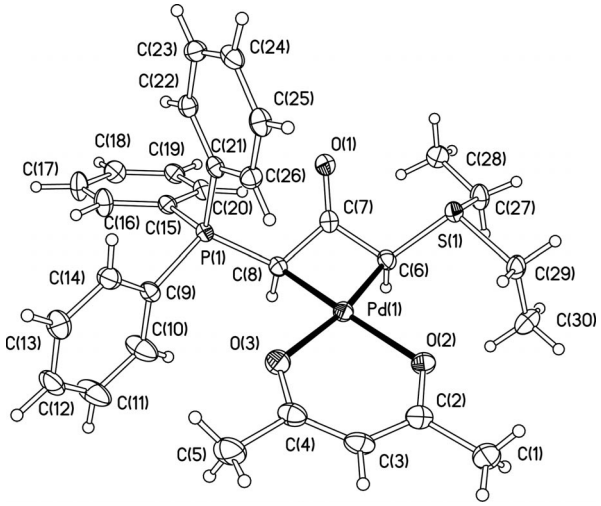


Figure 2. Molecular drawing of the cationic part of **8**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Pd1–O3 2.0588(18), Pd1–C6 2.061(2), Pd1–C8 2.065(2), Pd1–O2 2.0691(17), S1–C6 1.779(2), P1–C8 1.782(2), C6–C7 1.494(3), C7–O1 1.227(3), C7–C8 1.496(3); O3–Pd1–C6 167.64(8), O3–Pd1–C8 98.24(8), C6–Pd1–C8 69.54(9), O3–Pd1–O2 91.07(7), C6–Pd1–O2 100.73(8), C8–Pd1–O2 167.30(8), C7–C6–S1 110.77(16), C7–C6–Pd1 86.36(14), S1–C6–Pd1 121.78(13), O1–C7–C8 126.6(2), O1–C7–C6 127.6(2), C8–C7–C6 103.81(19), C7–C8–P1 115.86(16), C7–C8–Pd1 86.15(13), P1–C8–Pd1 124.53(13).

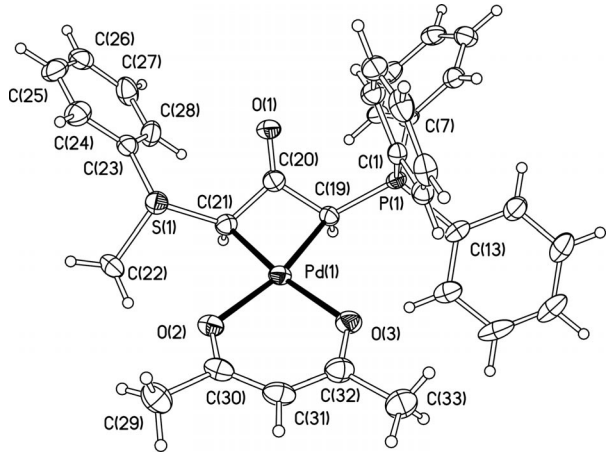


Figure 3. Molecular drawing of the cationic part of **9**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Pd1–O2 2.0415(19), Pd1–O3 2.0477(15), Pd1–C21 2.051(2), Pd1–C19 2.086(2), P1–C19 1.774(2), C19–C20 1.484(3), C20–O1 1.230(3), C20–C21 1.474(3), C21–S1 1.764(2); O2–Pd1–O3 91.75(7), O2–Pd1–C21 97.28(8), O3–Pd1–C21 170.93(8), O2–Pd1–C19 166.21(9), O3–Pd1–C19 102.00(8), C21–Pd1–C19 68.97(9), C20–C19–P1 115.80(18), C20–C19–Pd1 80.51(13), P1–C19–Pd1 123.18(14), O1–C20–C21 125.8(2), O1–C20–C19 127.2(2), C21–C20–C19 104.71(19), C20–C21–S1 113.86(16), C20–C21–Pd1 81.95(13), S1–C21–Pd1 113.47(12), C21–S1–C23 108.88(11), C21–S1–C22 99.75(12), C23–S1–C22 101.89(12).

The two structures also reveal a noteworthy fact, that the *cisoid–cisoid* conformation is adopted by the two *C*,*C*-chelating ylide fragments. Thus, the small values found for the dihedral angles O(1)–C(7)–C(8)–P(1) [–5.57(7)°] and O(1)–C(7)–C(6)–S(1) [9.57(8)°] for **8**, and O(1)–C(20)–C(19)–P(1) [–1.33(6)°] and O(1)–C(20)–C(21)–S(1) [–8.74(7)°] for **9** are similar to those found in structurally related *cisoid* arrangements.[9] In the same way, the short intramolecular distances between the phosphorus atom and the carbonyl oxygen atom [3.071(2) for **8** and 3.062(2) Å for **9**] are similar to values found in other bis(ylide) complexes,[9] and both of them are shorter than the sum of the van der Waals radii (3.35 Å),[13] which strongly suggests the existence of P···O interactions. The same facts are observed when the intramolecular sulfur–oxygen distances are examined, as both of them [2.976(2) for **8** and 2.979(2) Å for **9**] are shorter than the sum of the van der Waals radii (3.37 Å) and fall in the range observed in bis(ylide) complexes,[9] which indicates the presence of an S···O interaction.

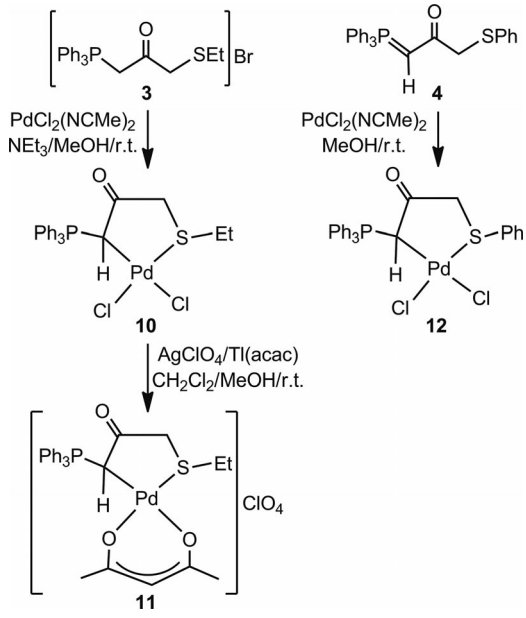
The arrangement of the ethyl groups of the SEt_2 fragment in **8**, or that of the methyl and phenyl units of the PhSMe moiety in **9**, with respect to the O atom, has been produced in such a way that one of the C–S vectors is pointing towards the oxygen atom. This is reflected in the angles C29–S1···O1 [154.87(3) Å] in **8** and C22–S1···O1 [153.35(3) Å] in **9**; these values are similar to those found in the literature for related environments.[9b,14] Moreover, this structural arrangement correlates well with the presence of short S···O intramolecular distances and suggests an incipient nucleophilic attack of the oxygen atom to the sulfonium atom.[15]

Therefore, a close analogy has been found in the reactivity of the ylide–sulfides **2** and **5**, studied in this work, and previous results obtained in our group with related species.[9a] The deprotonation occurs in all cases under smooth reaction conditions, and the bonding of the resulting bis(ylide) takes place with full diastereoselectivity, which allows for the selective synthesis of the *meso* form (*RS*/*SR*). These results suggest that the conformational preferences on the bis(ylide) skeleton are still established even when different substituents are present. This is not unexpected for the phosphorus atom, as in this part of the molecule the P···O interaction is mainly responsible for the conformation adopted (Figure 1). However, it is more remarkable at the sulfur atom, because here, in addition to the S···O interaction, intramolecular C–H···O hydrogen-bonding interactions are established, which should be sensitive to the presence of different substituents (methyl vs. ethyl vs. phenyl), as shown in Figure 1. Therefore, this is a noteworthy result, as it shows the generality of the scope of intramolecular interactions as a source of conformational preferences.

Reactivity of the Sulfide Salts $[Ph_3PCH_2COCH_2SEt]Br$ (3) and $[Ph_3PC(H)COCH_2SPh]$ (4)

In addition to the κ*C*,*C*-bonding mode observed for P,S-bis(ylides) in **6**–**9**, other coordination modes have been

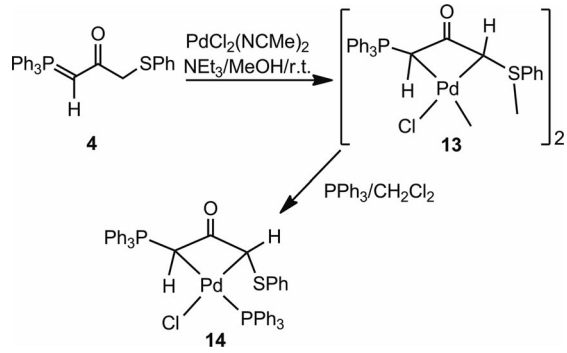
characterized. The reaction of the phosphonium–sulfide salt $[Ph_3PCH_2COCH_2SEt]Br$ (**3**) with $PdCl_2(NCMe)_2$ in the presence of a weak base such as NEt_3 (1:1:1 molar ratio) occurs with proton abstraction at the methylene group adjacent to the phosphonium unit, formation of the ylide–sulfide $[Ph_3P{=}C(H)COCH_2SEt]$, and *C*,*S*-coordination of the latter to give the chelate complex $PdCl_2\{Ph_3PC(H)COCH_2SEt\text{-}\kappa C,S\}$ (**10**; Scheme 4). The ylide–sulfide intermediate was not detected in the reaction of **1** with SEt_2, but it is reasonable to postulate its formation in the light of its coordinating behavior. According to the same pattern of reactivity, the ylide–sulfide $[Ph_3PC(H)COCH_2SPh]$ (**4**) reacts with $PdCl_2(NCMe)_2$ in MeOH (1:1 molar ratio) to give the *C*,*S*-chelate $PdCl_2\{Ph_3PC(H)COCH_2SPh\text{-}\kappa C,S\}$ (**12**; Scheme 4). Complex **12** has been characterized in solution, but no NMR spectroscopic data could be obtained for **10** because of its insolubility. Therefore, **10** was transformed into the more soluble acac derivative **11** by its reaction with $AgClO_4$ and Tl(acac) in a 1:1:1 molar ratio, and **11** was properly characterized.



Scheme 4. Reactivity of the ylide–sulfides **3** and **4** to give κ*C*,*S* chelates.

The C-bonding of the ylide fragment is inferred from the shift to high energy of the carbonyl stretch in the solid-state IR spectra of **10**–**12**, which appears in the range 1650–1670 cm^{-1}, typical of this bonding mode.[7,9] Additional evidence for the *C*-coordination in **11** and **12** come from the observation of an almost negligible $^2J_{P,H}$ coupling constant for the C*H*P signal in the ^1H NMR spectra, the downfield shift of the ^{31}P peak due to the CH*P* nucleus with respect to the ylide precursor, and the presence of a doublet peak in the ^{13}C NMR spectra attributed to the ylide *C*HP carbon atom with a $^1J_{P,C}$ coupling constant of ca. 55–57 Hz. Additionally, the *S*-coordination of the sulfide group is clearly reflected in the fact that the NMR spectra of **11** and **12** show two sets of signals each, which are attributed to the formation of the corresponding diastereoisomers (R_CR_S/S_CS_S and R_CS_S/S_CR_S) in 1:1 (**11**) and 6.7:1 (**12**) molar ratios. The different steric requirements of the SEt and SPh units are probably responsible for the observed differences.

The C,C-bis(ylide) and C(ylide)–S(sulfide) bonding modes described in the preceding sections can be further expanded by combining the coordinating abilities of all potential donor atoms in this type of system. The deprotonation of the methylene unit of the ylide–sulfide $[Ph_3PC(H)COCH_2SPh]$ (**4**) would generate the anion $[Ph_3PC(H)COC(H)SPh]^-$, which in principle displays three donor atoms: the ylide C, the methanide C, and the sulfide S atoms. We have constated that this deprotonation takes place under very mild reaction conditions. Therefore, the reaction of **4** with NEt_3 in MeOH at room temperature, followed by the addition of $PdCl_2(NCMe)_2$ (1:1:1 molar ratio), affords the dinuclear derivative **13** shown in Scheme 5. The sulfur bridge present in **13** can be broken by the addition of neutral ligands, as shown by the reaction of **13** with PPh_3 (1:2 molar ratio), which affords mononuclear **14** in good yield.



Scheme 5. Reactivity of the ylide–sulfide **4** to give ylide–methanide complexes.

The elemental analysis of **13** is in keeping with the stoichiometry shown in Scheme 5 and confirms the presence of one anionic ylide–methanide unit and a chlorido ligand per palladium atom. The dimeric nature of **13** is inferred from its mass spectrum, in which there is a peak at m/z = 1099.2 with the correct isotopic distribution for the cationic species $[Pd_2(Ph_3PCHCOCHSPh)_2Cl]^+$. The *C*-coordination of the ylide is clear from the position of the carbonyl stretch in the IR spectrum (1595 cm^{-1}) of **13**, which is shifted to high energy with respect to the stretch of the free ylide **4**. This position also suggest that a four-membered *C*,*C*-chelate has been formed, as it falls in the same wavenumber range as those previously observed in **6**–**9** (range 1550–1610 cm^{-1}) or in related complexes,[7] and it is quite different than that found for five-membered *C*,*X*-chelates; for instance, **10**–**12** show the C=O stretch in the range 1650–1680 cm^{-1}. The *C*,*C*-chelation of the ligand can also be inferred from the NMR spectra of **13**, by following the change with respect to **4** of the same key parameters previously analyzed; that is, δ(C*H*P) and $^2J_{P,H}$ in the ^1H NMR spectrum, δ(CH*P*) in the ^{31}P NMR spectrum, and δ(*C*HP) and $^1J_{P,C}$ in the ^{13}C

NMR spectrum. In addition, the coordination of the SPh moiety can be deduced from the deshielding experienced by the protons of the aromatic ring on **13** compared with those of **4**. This change is more relevant in the H_{ortho} nuclei (from δ = 7.35 ppm in **4** to δ = 7.70 ppm in **13**), but it is also noticeable in the H_{meta} and H_{para} protons (from δ = 7.06–7.17 ppm in **4** to δ = 7.20–7.26 ppm in **13**). All experimental data suggest that the anion $[Ph_3PC(H)COC(H)SPh]^-$ is coordinated to the Pd center as a *C*,*C*,*S*-tridentate ligand. We have previously shown that the anion $[Ph_3PC(H)COC(H)SMe]^-$ behaves as a *C*,*C*-chelate and *S*-bridging ligand.[9a] Given that the spectral changes seen for $[Ph_3PC(H)COC(H)SPh]^-$ follow the same tendencies as those reported for $[Ph_3PC(H)COC(H)SMe]^-$ and assuming a similar reactivity owing to close relationship of the two anions, we suggest the same bonding behavior for both of them. Therefore, we propose for **13** the structure shown in Scheme 5. It is remarkable that the proposed dinuclear structure for **13** displays up to six stereogenic centers, whereas their NMR spectra show a single set of signals in each case. We have previously shown that the four-membered *C*,*C*-ring is formed with full diastereoselectivity and that, once formed, this ring is very stable and does not undergo conformational changes.[9a] Therefore, the most reactive point of the molecule seems to be the *S*-bridge, and a rapid Pd–S bond-forming and -breaking mechanism could explain the equilibration of the different diastereoisomers. The measurement of the NMR spectra at low temperature (CD_2Cl_2, 188 K) points to a fast dynamic process as it shows a broadening of the signals, although not their complete splitting.

The reactivity of **13** to give **14** (Scheme 5) also suggests the weakness of the Pd–S bonds and the bridging system. The incorporation of a PPh_3 ligand is evident from the presence of two peaks in the ^{31}P NMR spectrum of **14**, whereas the PPh_3 ligand *trans* to the C-ylide arrangement is inferred from the appearance of the ylide *C*HP carbon atom as a doublet of doublets with a $^2J_{P,C}$ coupling constant value (58.6 Hz) in the range found in structurally related situations.[7,9] The nonbonded SPh unit is easily characterized by the shielding observed in the ^1H NMR spectrum for all peaks assigned to the Ph ring on going from **13** to **14**. Finally, the *anti* disposition of the methanide C*H*S and ylide C*H*P protons is proposed by analogy with related structurally characterized complexes.[9a] As previously explained, NOESY experiments are not informative in this case, because the absence of an NOE between the C*H*P and C*H*S nuclei is not a proof of their relative *transoid* disposition.[16]

Conclusions

Four different coordination modes have been characterized for bis(ylide) $[Ph_3PC(H)COC(H)SR^1R^2]$ (R^1 = R^2 = Et; R^1 = Me, R^2 = Ph), ylide–sulfide $[Ph_3PC(H)COCH_2SR]$ (R = Et, Ph), and ylide–methanide $[Ph_3PC(H)COC(H)SPh]^-$ species when bonded to a Pd^{II} center. The bis(ylides) $[Ph_3PC(H)COC(H)SR_2]$ coordinate as κ^2C,C-chelates and show full diastereoselectivity (*meso* form), whereas the ylide–sulfides $[Ph_3PC(H)COCH_2SR]$ act as *C*,*S*-chelates. The ylide–methanide $[Ph_3PC(H)COC(H)SPh]^-$ bonds as a μ-*S*:κ^2C,C (*C*,*C*-chelate and *S*-bridge) or κ^2C,C-chelate, and the latter also shows total diastereoselectivity, although it forms the D,L pair. The bonding behavior of bis(ylides) $[Ph_3PC(H)COC(H)SR_2]$ is the same as that observed for the bis(ylide) $[Ph_3PC(H)COC(H)SMe_2]$ and is due to the presence of conformational preferences based on the establishment of 1,4-P···O, 1,4-S···O, and 1,6-C–H···O intramolecular contacts. This work shows that these contacts, and therefore the concomitant conformational preferences, take place irrespective of the nature of the substituents at the S atom (alkyl or aryl); this expands the number of available substrates with which they can be operative. This wide scope is important for the design of complexes with a given configuration.

Experimental Section

Safety Note: ***Caution!*** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution.

General Methods: Solvents were dried and distilled before use by using standard procedures. Elemental analyses (CHNS) were carried out with a Perkin–Elmer 2400-B microanalyzer. Infrared spectra (4000–380 cm^{-1}) were recorded with a Perkin–Elmer Spectrum One IR spectrophotometer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded with Bruker AV300 and AV400 spectrometers (δ in ppm, *J* in Hz) at ^1H operating frequencies of 300.13 and 400.13 MHz, respectively. ^1H and ^{13}C NMR spectra were referenced to the solvent signal as an internal standard, and ^{31}P NMR spectra were referenced to H_3PO_4 (85%). ESI^+ mass spectra were recorded with an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonic GmbH) equipped with a standard ESI/atmospheric pressure chemical ionization (APCI) source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. The mass spectra (MALDI+) were recorded from $CHCl_3$ solutions with a MALDI-TOF Microflex (Bruker) spectrometer {*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as matrix}. The starting stabilized ylide $Ph_3P{=}C(H)COCH_2Br$ (**1**) was synthesized according to published methods.[10]

$[Ph_3PC(H)COCH_2SEt_2]Br$ (2): To a solution of $Ph_3PC(H)COCH_2Br$ (**1**) (0.201 g, 0.506 mmol) in MeOH, SEt_2 (2.18 mL, 20.24 mmol) was added, and the mixture was heated to reflux under Ar for 24 h. After this time, the solvent was evaporated to dryness, and the brown residue was extracted with CH_2Cl_2 (2 × 30 mL). The combined extracts were dried with anhydrous $MgSO_4$ (15 min stirring at room temp.) and filtered. The clear solution was concentrated to dryness, and the white residue was treated with Et_2O (20 mL) and stirred. Compound **2** was obtained as a white solid, which was collected by filtration, washed with additional Et_2O, and dried in vacuo. Yield: 0.186 g (75.3%). IR: $\tilde{\nu}$ = 1555 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.37 (br., 6 H, CH_3, Et), 3.64–3.75 (2 m, 4 H, CH_2, Et), 4.22 (d, $^2J_{P,H}$ = 21.8 Hz, 1 H, CHP), 4.77 (s, 2 H, CH_2S), 7.43 (m, 6 H, H_m, Ph_3P), 7.50–7.58 (m, 9 H, H_p, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 15.10 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.96 (s, CH_3, SEt_2), 33.94 (s, CH_2, SEt_2), 48.71

(d, $^3J_{P,C}$ = 20.7 Hz, CH_2S), 56.89 (d, $^1J_{P,C}$ = 107.4 Hz, CHP), 125.0 (d, $^1J_{P,C}$ = 91.5 Hz, C_i), 120.20 (d, $^3J_{P,C}$ = 12.5 Hz, C_m, Ph_3P), 132.85 (d, $^4J_{P,C}$ = 2.3 Hz, C_p, Ph_3P), 133.01 (d, $^2J_{P,C}$ = 10.4 Hz, C_o, Ph_3P), 176.71 (br. s, CO) ppm. MS (FAB+): *m/z* (%) = 407 (100) $[M - Br]^+$. $C_{25}H_{28}BrOPS$ (487.46): calcd. C 61.60, H 6.09, S 6.92; found C 61.39, H 5.89, S 6.91.

[$Ph_3PCH_2COCH_2SEt$]Br (3): Compound **3** was obtained according to the same experimental procedure as that described for **2**. Therefore, $Ph_3PC(H)COCH_2Br$ (0.502 g, 1.26 mmol) reacted with SEt_2 (5.50 mL, 50.5 mmol) in THF (15 mL) at reflux to give **3** as a brown solid. Yield: 0.38 g (66.2%). IR: $\tilde{\nu}$ = 1709 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.99 (t, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3, SEt), 2.07 (q, 2 H, CH_2, SEt), 3.69 (d, $^4J_{P,H}$ = 2.5 Hz, 2 H, CH_2S), 6.04 (d, $^2J_{P,H}$ = 11.4 Hz, 2 H, CH_2P), 7.58 (m, 6 H, H_m, Ph_3P), 7.69 (t, $^3J_{H,H}$ = 8.0 Hz, 3 H, H_p, Ph_3P), 7.79 (m, 6 H, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.61 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.95 (s, CH_3, SEt), 25.94 (s, CH_2, SEt), 37.84 (d, $^1J_{P,C}$ = 62.46 Hz, CH_2P), 44.83 (d, $^3J_{P,C}$ = 7.7 Hz, CH_2S), 118.65 (d, $^1J_{P,C}$ = 93.6 Hz, C_i), 130.17 (d, $^3J_{P,C}$ = 13.7 Hz, C_m, Ph_3P), 133.86 (d, $^2J_{P,C}$ = 10.7 Hz, C_o, Ph_3P), 134.82 (s, C_p, Ph_3P), 196.34 (d, $^2J_{P,C}$ = 7.4 Hz, CO) ppm. MS (FAB+): *m/z* (%) = 379 (100) $[M - Br]^+$. $C_{23}H_{24}BrOPS$ (459.41): calcd. C 60.14, H 5.26, S 6.98; found C 60.38, H 4.94, S 6.91.

[$Ph_3PC(H)COCH_2SPh$] (4): The synthesis of **4** was carried out according to previously reported procedures.[12] To a solution of PhSH (0.130 mL, 1.26 mmol) in MeOH (10 mL), KOH (0.070 g, 1.26 mmol) was added, and the resulting solution was stirred at 25 °C for 1 h. To this solution the ylide $Ph_3PC(H)COCH_2Br$ (**1**) (0.502 g, 1.26 mmol) was added, and stirring was maintained for 15 h. After this time, the solvent was evaporated to dryness, and the residue was extracted with CH_2Cl_2 (2 × 15 mL). The combined extracts were dried with anhydrous $MgSO_4$ and filtered, and the resulting solution was concentrated to a small volume (ca. 2 mL). After the addition of Et_2O (30 mL) and stirring, compound **4** was obtained as a white solid, which was collected by filtration, washed with Et_2O (30 mL), and dried in vacuo. Yield: 0.453 g (84.4%). IR: $\tilde{\nu}$ = 1547 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.62 (s, 2 H, CH_2S), 4.15 (d, $^2J_{P,H}$ = 23.3 Hz, 1 H, CHP), 7.06 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, H_p, PhS), 7.17 (t, $^3J_{H,H}$ = 7.5 Hz, 2 H, H_m, PhS), 7.31–7.38 (m, 8 H, H_m, Ph_3P, H_o, PhS), 7.45–7.53 (m, 9 H, H_o, H_p, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 15.96 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 41.78 (d, $^3J_{P,C}$ = 15.9 Hz, CH_2S), 51.74 CHP ($^1J_{P,C}$ = 107.8 Hz, CHP), 125.10 (s, C_p, SPh), 126.53 (d, $^1J_{P,C}$ = 92.9 Hz, C_i, Ph_3P), 128.00 (s, C_m, SPh), 128.65 (s, C_o, SPh), 128.88 (d, $^3J_{P,C}$ = 12.3 Hz, C_m, Ph_3P), 132.18 (d, $^4J_{P,C}$ = 1.2 Hz, C_p, Ph_3P), 133.13 (d, $^2J_{P,C}$ = 10.3 Hz, C_o, Ph_3P), 187.23 (s, CO) ppm; the signal due to C_i–SPh was not observed. MS (MALDI+): *m/z* (%) = 426.8 (100) $[M]^+$. $C_{27}H_{23}OPS$ (426.54): calcd. C 76.03, H 5.43, S 7.52; found C 76.09, H 5.07, S 7.56.

[$Ph_3PC(H)COCH_2SMePh$]ClO_4 (5): To a solution of $Ph_3PC(H)COCH_2Br$ (**1**) (0.150 g, 0.378 mmol) in Me_2CO/CH_2Cl_2 (1:1, 40 mL), thioanisol (PhSMe, 1.80 mL, 15.1 mmol) and $TlClO_4$ (0.114 g, 0.378 mmol) were added, and the resulting suspension was stirred at room temp. for 24 h. After this time, the precipitated TlCl was removed by filtration through Celite, and the resulting clear solution was concentrated to dryness. To the oily residue Et_2O (40 mL) was added. Further stirring gave **5** as a pale brown solid, which was filtered, washed with additional Et_2O (2 × 15 mL), and dried in vacuo. Yield: 0.151 g (74%). IR: $\tilde{\nu}$ = 1546 (ν_{CO}), 1080, 622 (ν_{ClO4}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.16 (s, 3 H, MeS), 4.21 (d, $^2J_{P,H}$ = 21.1 Hz, 1 H, CHP), 4.71 (d, $^2J_{H,H}$ = 14.3 Hz, 1 H, CH_2S), 4.95 (d, 1 H, CH_2S), 7.39 (td, $^3J_{H,H}$ = 7.5, $^4J_{P,H}$ = 3.1 Hz, 6 H, H_m, Ph_3P), 7.47 (dd, $^3J_{P,H}$ = 12.4 Hz, 6 H, H_o, Ph_3P), 7.52 (t, 3 H, H_p, Ph_3P), 7.48 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, H_m, PhS), 7.64 (t, 1 H, H_p, PhS), 7.98 (d, 2 H, H_o, PhS) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 15.02 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 26.71 (s, CH_3S), 56.66 (d, $^3J_{P,C}$ = 20.6 Hz, CH_2), 56.76 (d, $^1J_{P,C}$ = 107.1 Hz, CHP), 124.00 (s, C_i, PhS), 124.77 (d, $^1J_{P,C}$ = 91.5 Hz, C_i, Ph_3P), 129.21 (d, $^3J_{P,C}$ = 12.5 Hz, C_m, Ph_3P), 130.87 (s, C_m, PhS), 130.97 (s, C_o, PhS), 132.83 (d, $^4J_{P,C}$ = 2.7 Hz, C_p, Ph_3P), 132.97 (d, $^2J_{P,C}$ = 10.5 Hz, C_o, Ph_3P), 134.25 (s, C_p, PhS), 175.54 (s, CO) ppm. $C_{28}H_{26}ClO_5PS$ (541.002): calcd. C 62.16, H 4.84, S 5.93; found C 61.83, H 5.00, S 5.96.

[$PdCl_2${$Ph_3PC(H)COC(H)SEt_2$-κ*C*,*C*}] (6): To a solution of [$Ph_3PCHC(O)CH_2SEt_2$]Br (**2**) (0.115 g, 0.239 mmol) in MeOH (15 mL), NEt_3 (33.0 μL, 0.239 mmol) was added. No apparent change was observed. To this solution $PdCl_2(NCMe)_2$ (0.062 g, 0.239 mmol) was added, which dissolved in a few seconds. Almost instantaneously after the formation of this initial solution, an orange solid precipitated. After a few minutes of stirring at room temp., the solid was collected by filtration, washed with MeOH (10 mL) and Et_2O (25 mL), air-dried, and identified as **6**. Yield: 0.100 g (72.6%). IR: $\tilde{\nu}$ = 1583 (ν_{CO}) cm^{-1}. Complex **6** is insoluble in the usual NMR solvents, which precluded its characterization by this technique. MS (MALDI+): *m/z* (%) = 548.8 (10) $[M - Cl]^+$. $C_{25}H_{27}Cl_2OPPdS$ (583.87): calcd. C 51.43, H 4.66, S 5.50; found C 51.28, H 4.40, S 5.28.

[$PdCl_2${$Ph_3PC(H)COC(H)SMePh$-κ*C*,*C*}] (7): Complex **7** was prepared according to a synthetic method identical to that described for **6**. Thus, [$Ph_3PC(H)COCH_2SMePh$]ClO_4 (**5**) (0.120 g, 0.221 mmol) was treated with NEt_3 (31.0 μL, 0.221 mmol) and $PdCl_2(NCMe)_2$ (0.057 g, 0.221 mmol) in MeOH (20 mL) to give **7** as a yellow solid. Yield: 0.092 g (67%). IR: $\tilde{\nu}$ = 1546 (ν_{CO}) cm^{-1}. NMR: Complex **7** was insoluble in the usual NMR solvents, which precluded its characterization by this technique. $C_{28}H_{25}Cl_2OPPdS$ (617.86): calcd. C 54.43, H 4.57, S 5.19; found C 54.64, H 4.39, S 5.14. MS (MALDI+): *m/z* (%) = 583.0 (85.3) $[M - Cl]^+$.

[Pd(acac-*O*,*O*′){$Ph_3PC(H)COC(H)SEt_2$-κ*C*,*C*}]ClO_4 (8): To a suspension of **6** (0.047 g, 0.081 mmol) in a CH_2Cl_2/Me_2CO (9:1, 20 mL) mixture, $AgClO_4$ (0.017 g, 0.081 mmol) was added, and the resulting grey suspension was stirred in the dark for 30 min. After this time, Tl(acac) (0.025 g, 0.081 mmol) was added, and stirring was continued for an additional 30 min. The grey suspension was carefully filtered through a Celite pad, and the resulting pale yellow solution was concentrated to dryness. The oily residue was treated with Et_2O (20 mL) to give **8** as a yellow solid. Yield: 0.020 g (35%). IR: $\tilde{\nu}$ = 1611 (ν_{CO}), 1563, 1518 ($\nu_{CO\text{-}acac}$), 1085, 622 (ν_{ClO4}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.38 (t, $^3J_{H,H}$ = 7.8 Hz, 3 H, CH_3, SEt_2), 1.40 (t, $^3J_{H,H}$ = 7.4 Hz, 3 H, CH_3, SEt_2), 1.41 (s, 3 H, CH_3, acac), 1.80 (s, 3 H, CH_3, acac), 3.23–3.56 (m, 4 H, CH_2, SEt_2), 3.68 (d, $^2J_{P,H}$ = 5.1 Hz, 1 H, CHP), 4.30 (s, 1 H, CHS), 5.11 (s, 1 H, CH, acac), 7.49 (td, $^3J_{H,H}$ = 7.8, $^4J_{P,H}$ = 3.2 Hz, 6 H, H_m, Ph_3P), 7.47 (td, $^5J_{P,H}$ = 1.6 Hz, 3 H, H_p, Ph_3P), 7.70 (dd, $^3J_{P,H}$ = 13.0 Hz, 6 H, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 24.87 ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 9.47 (s, CH_3, SEt_2), 9.75 (s, CH_3, SEt_2), 26.03 (s, CH_3, acac), 26.69 (s, CH_3, acac), 27.10 (d, $^1J_{P,C}$ = 49.5 Hz, PCH), 32.91 (s, CH_2, SEt_2), 35.37 (s, CH_2, SEt_2), 39.42 (d, $^3J_{P,C}$ = 15.2 Hz, CHS), 99.59 (s, CH, acac), 121.58 (d, $^1J_{P,C}$ = 90 Hz, C_i, Ph_3P), 129.32 (d, $^3J_{P,C}$ = 13 Hz, C_m, Ph_3P), 132.66 (d, $^4J_{P,C}$ = 3 Hz, C_p, Ph_3P), 132.90 (d, $^2J_{P,C}$ = 11 Hz, C_o, Ph_3P), 173.91 (d, $^2J_{P,C}$ = 2 Hz, C=O), 185.78 (s, CO, acac), 186.07 (s, CO, acac) ppm. MS (MALDI+): *m/z* (%) = 612.0 (100) $[M - ClO_4]^+$. $C_{30}H_{34}ClO_7PPdS$ (711.53): calcd. C 50.64, H 4.82, S 4.50; found C 50.50, H 4.64, S 4.37.

[Pd(acac-*O*,*O*′){$Ph_3PC(H)COC(H)SMePh$-κ*C*,*C*}]ClO_4 (9): Compound **9** was obtained according to the same procedure as that

described for **8**. Therefore, **7** (0.08 g, 0.129 mmol) was treated with $AgClO_4$ (0.027 g, 0.129 mmol) and Tl(acac) (0.039 g, 0.129 mmol) in CH_2Cl_2/Me_2CO (9:1, 20 mL) to give **9** as a yellow solid. Complex **9** was characterized by NMR spectroscopy as a mixture of two diastereomers in a 10:1 molar ratio. Yield: 0.068 g (68.0%). IR: $\tilde{\nu}$ = 1616 (ν_{CO}), 1574, 1514 ($\nu_{CO\text{-}acac}$), 1082, 621 (ν_{ClO4}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 1.40 (s, CH_3, acac, minor), 1.43 (s, CH_3, acac, major), 1.60 (s, CH_3, acac, minor), 1.83 (s, CH_3, acac, major), 3.17 (s, CH_3, MeS, minor), 3.19 (s, CH_3, MeS, major), 3.58 (dd, $^2J_{P,H}$ = 4.8, $^4J_{H,H}$ = 0.9 Hz, CHP, minor), 3.60 (dd, $^2J_{P,H}$ = 4.7, $^4J_{H,H}$ = 0.9 Hz, CHP, major), 4.34 (s, CHS, minor), 4.42 (s, CHS, major), 5.09 (s, CH, acac, minor), 5.19 (s, CH, acac, major), 7.48 (m, H_m, Ph_3P, major, minor), 7.51–7.55 (m, H_m, PhS, major, minor), 7.58–7.67 (m, H_o, H_p Ph_3P, major, minor, H_p, PhS, major, minor), 7.86 (d, $^3J_{H,H}$ = 8.1 Hz, H_o, PhS, major), 7.92 (d, $^3J_{H,H}$ = 8.1 Hz, H_o, PhS, minor) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 24.61 (minor), 24.80 (major) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 25.41 (d, $^1J_{P,C}$ = 62.7 Hz, CHP, minor), 25.72 (s, CH_3, acac, major), 25.81 (s, CH_3, acac, minor), 26.14 (d, $^1J_{P,C}$ = 57.7 Hz, CHP, major), 26.59 (s, MeS, CH_3, acac, major), 26.78 (s, MeS, CH_3, acac, minor), 42.14 (d, $^3J_{P,C}$ = 15.7 Hz, CHS, minor), 44.02 (d, $^3J_{P,C}$ = 14.9 Hz, CHS, major), 98.69 (s, CH, acac, minor), 98.86 (s, CH, acac, major), 120.66 (d, $^1J_{P,C}$ = 89.4 Hz, C_i, Ph_3P), 127.28 (s, C_i, PhS), 128.56 (d, $^3J_{P,C}$ = 12.8 Hz, C_m, Ph_3P, major, minor), 128.70 (s, C_o, Ph, major), 129.55 (s, C_m, Ph, minor), 129.92 (s, C_m, Ph, major), 130.22 (s, C_o, Ph, minor), 132.80 (s, C_p, Ph, major), 132.89 (s, C_p, Ph, minor), 133.05–133.14 (m, C_p, C_o, Ph_3P, major, minor), 172.68 (s, broad, CO, ylide, major), 185.34 (s, CO, acac, major), 185.40 (s, CO, acac, minor), 185.80 (s, CO, acac, major), 185.87 (s, CO, acac, minor) ppm; the signals of C_i and C=O for the minor isomer were not observed owing to their low intensity. MS (MALDI+): *m/z* = 645.1 $[M - ClO_4]^+$. $C_{33}H_{32}ClO_7PPdS$ (745.55): calcd. C 53.16, H 4.19, S 4.17; found C 52.96, H 4.47, S 4.02.

[PdCl$_2${Ph$_3$PC(H)COCH$_2$SEt-κ*C*,*S*}] (10): To a solution of the phosphonium–sulfide salt [$Ph_3PCH_2C(O)CH_2SEt$]Br (**3**) (0.101 g, 0.218 mmol) in MeOH (10 mL), NEt_3 (30.4 μL, 0.218 mmol) and then $PdCl_2(NCMe)_2$ (0.056 g, 0.218 mmol) were added. A deep yellow solid precipitated after a few seconds. This suspension was stirred at room temp. for 20 min, and then the solid **10** was collected by filtration, washed with cold MeOH (15 mL) and Et_2O (2 × 10 mL), and dried in vacuo. Yield: 0.082 g (68%). IR: $\tilde{\nu}$ = 1650 (ν_{CO}) cm^{-1}. Complex **10** was insoluble in the usual NMR solvents, which precluded its characterization by this technique. MS (ESI+): *m/z* (%) = 520.8 (44) $[M - Cl]^+$. $C_{23}H_{23}Cl_2OPPdS$ (555.81): calcd. C 49.70, H 4.17, S 5.77; found C 49.84, H 4.04, S 5.62.

[Pd(acac-*O*,*O*′){Ph$_3$PC(H)COCH$_2$SEt-κ*C*,*S*}]ClO$_4$ (11): Compound **11** was obtained according to the same procedure as that described for **8**. Therefore, **10** (0.06 g, 0.108 mmol) was treated with $AgClO_4$ (0.022 g, 0.108 mmol) and Tl(acac) (0.033 g, 0.11 mmol) in CH_2Cl_2/Me_2CO (9:1, 20 mL) to give **11** as a deep yellow solid. Compound **11** was characterized as a mixture of two diastereomers in a 1:1 molar ratio. Yield: 0.045 g (61%). IR: $\tilde{\nu}$ = 1673 (ν_{CO}), 1557, 1514 ($\nu_{CO\text{-}acac}$), 1082, 622 (ν_{ClO4}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.97 (s, CH_3, acac), 0.98 (s, CH_3′, acac), 1.41 (t, $^3J_{H,H}$ = 7.4 Hz, CH_3, Et), 1.42 (t, $^3J_{H,H}$ = 7.4 Hz, CH_3′, Et), 1.86 (s, CH_3, acac), 1.87 (s, CH_3′, acac), 2.54 (dd, $^2J_{H,H}$ = 13.9, $^4J_{P,H}$ = 6.9 Hz, CH_2S), 2.74–2.86 (m, CH_2-Et, CH_2S′), 3.20 (dd, $^2J_{H,H}$ = 13.2, $^4J_{P,H}$ = 7.4 Hz, CH_2-Et), 3.48 (dd, $^2J_{H,H}$ = 13.1, $^4J_{P,H}$ = 7.2 Hz, CH_2-Et′), 4.17 (d, $^2J_{H,H}$ = 12.9 Hz, CH_2S′), 4.33 (d, CH_2S), 5.06 (s, CH, acac), 5.08 (s, CH′, acac), 5.62 (d, $^2J_{P,H}$ = 2.0 Hz, CHP), 5.88 (d, $^2J_{P,H}$ = 2.6 Hz, CHP′), 7.53 (m, H_m, Ph_3P), 7.63 (m, H_p, Ph_3P), 7.76 (dd, $^3J_{P,H}$ = 12.6, $^3J_{H,H}$ = 7.8 Hz, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 25.88 (Ph_3PCH), 26.17 ($Ph_3P'CH$) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 13.04 (s, CH_3-Et), 13.14 (s, CH_3-Et′), 25.32 (s, 2 CH_3, acac), 26.99 (s, 2 CH_3, acac′), 31.25 (s, CH_2-Et), 33.90 (d, $CHPPh_3$, $^1J_{P,C}$ = 55.1), 34.57 (d, $CHPPh_3$, $^1J_{P,C}$ = 54.9), 35.04 (s, CH_2-Et′), 36.83 (d, $^3J_{P,C}$ = 9.8 Hz, SCH_2), 37.82 (d, $^3J_{P,C}$ = 9.1 Hz, SCH_2), 99.62 (s, CH, acac), 100.03 (s, CH, acac′), 129.12 (d, $^3J_{P,C}$ = 12.8 Hz, C_m, Ph_3P), 129.16 (d, $^3J_{P,C}$ = 12.7 Hz, C_m, Ph_3P′), 133.39 (d, $^4J_{P,C}$ = 2.9 Hz, C_p, Ph_3P), 133.25 (d, $^4J_{P,C}$ = 2.9 Hz, C_p, Ph_3P′), 133.82 (d, $^2J_{P,C}$ = 10.0 Hz, C_o, Ph_3P), 133.86 (d, $^2J_{P,C}$ = 10.1 Hz, C_o, Ph_3P′), 183.36 (s, CO, acac), 183.61 (s, CO, acac′), 193.99 (d, $^2J_{P,C}$ = 2.1 Hz, C=O), 194.90 (d, $^2J_{P,C}$ = 2.1 Hz, C=O′) ppm; the signals of C_i were not observed. MS (MALDI+): *m/z* (%) = 583.0 (100) $[M - ClO_4]^+$. $C_{28}H_{30}ClO_7PPdS$ (683.48): calcd. C 49.20, H 4.42, S 4.69; found C 49.45, H 4.26, S 4.51.

[PdCl$_2${Ph$_3$PC(H)COCH$_2$SPh-κ*C*,*S*}] (12): Complex **12** was prepared according to a synthetic method identical to that described for **10**. Therefore, [$Ph_3PC(H)COCH_2SPh$] (**4**) (0.100 g, 0.234 mmol) was treated with $PdCl_2(NCMe)_2$ (0.061 g, 0.148 mmol) in MeOH (20 mL) to give **12** as a yellow-orange solid. Complex **12** was characterized by NMR spectroscopy as a mixture of two diastereomers in a 6.7:1 molar ratio. Yield: 0.102 g (72.0%). IR: $\tilde{\nu}$ = 1660 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 2.75 (dd, $^2J_{H,H}$ = 12.8, $^4J_{P,H}$ = 7.0 Hz, CH_2S, major), 3.04 (dd, $^2J_{H,H}$ = 13.2, $^4J_{P,H}$ = 5.0 Hz, CH_2S, minor), 4.32 (d, CH_2S, minor), 4.38 (d, CH_2S, major), 5.46 (br. s, CHP, minor), 5.87 (br. s, CHP, major), 7.36 (t, H_m, Ph, major, minor), 7.3–7.44 (m, H_m, Ph_3P, major, minor), 7.50–7.56 (m, H_p, Ph_3P, major, H_p, Ph, major, minor), 7.61 (t, H_p, Ph_3P, minor), 7.81 (dd, $^3J_{P,H}$ = 12.5, $^3J_{H,H}$ = 8.0 Hz, H_o, Ph_3P, major, minor), 8.05 (d, $^3J_{HH}$ = 7.2 Hz, H_o, Ph, major, minor) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 24.90 (minor), 27.31 (major) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 34.59 (d, $^1J_{P,C}$ = 54.8 Hz, CHP, minor), 34.67 (d, $^1J_{P,C}$ = 57.2 Hz, CHP, major), 42.97 (d, $^3J_{P,C}$ = 13.0 Hz CH_2S, minor), 43.53 (d, $^3J_{P,C}$ = 10.0 Hz, CH_2S, major), 129.13 (d, $^3J_{P,C}$ = 12.7 Hz, C_m, Ph_3P, major), 129.53 (d, $^3J_{P,C}$ = 12.4 Hz, C_m, Ph_3P, minor), 129.99 (s, C_m, PhS, major), 130.31(s, C_m, PhS, minor), 130.99 (s, C_p, PhS, major), 132.71 (s, C_p, Ph_3P, minor), 133.20 (d, $^4J_{P,C}$ = 2.4 Hz, C_p, Ph_3P, major), 133.78 (s, C_p, PhS, major), 133.97 (s, C_p, PhS, minor), 134.44 (d, $^2J_{P,C}$ = 9.8 Hz, C_o, Ph_3P, major), 134.63 (d, $^2J_{P,C}$ = 9.9 Hz, C_o, Ph_3P, minor) ppm; the signals of C_i and C=O were not observed. MS (MALDI+): *m/z* (%) = 533.1 (35.4) $[M - 2\,Cl + H]^+$. $C_{27}H_{23}Cl_2OPPdS$ (603.86): calcd. C 53.70, H 3.84, S 5.31; found C 53.63, H 3.62, S 5.00.

[PdCl{Ph$_3$PC(H)COC(H)Ph-μ-*S*:κ*C*,*C*,*S*}]$_2$ (13): To a solution of $Ph_3PCHCOCH_2SPh$ (**4**) (0.101 g, 0.234 mmol) in MeOH (15 mL), NEt_3 (32.7 μL, 0.234 mmol) was added. To this solution $PdCl_2(NCMe)_2$ (0.061 g, 0.234 mmol) was added, and in a few seconds a yellow solution formed. This solution was stirred at room temp. for 3 h. During this time, complex **13** precipitated as a yellow solid. After this time, **13** was collected by filtration, washed with cold MeOH (5 mL) and Et_2O (20 mL), and dried in vacuo. Yield: 0.078 g (58.2%). IR: $\tilde{\nu}$ = 1595 (ν_{CO}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 4.09 (d, $^4J_{P,H}$ = 5.2 Hz, 1 H, CHS), 4.45 (d, $^2J_{P,H}$ = 5.8 Hz, 1 H, CHP), 7.20–7.26 (m, 3 H, H_p, H_m, PhS), 7.49 (td, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 2.8 Hz, 6 H, H_m, Ph_3P), 7.61 (t, $^3J_{H,H}$ = 7.5 Hz, 3 H, H_p, Ph_3P), 7.70 (d, 2 H, H_o, PhS), 7.82 (dd, $^3J_{P,H}$ = 11.5 Hz, 6 H, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 25.64 ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 35.24 (d, $^1J_{P,C}$ = 69.0 Hz, CHP), 54.00 (d, $^3J_{P,C}$ = 10.1 Hz, CHS), 128.30 (s, C_p, Ph), 129.27 (s, C_m, Ph), 129.48 (d, $^3J_{P,C}$ = 12.7 Hz, C_m, Ph_3P), 129.50 (s, C_o, Ph), 133.78 (d, $^4J_{P,C}$ = 2.4 Hz, C_p, Ph_3P), 134.55 (d, $^2J_{P,C}$ = 10.2 Hz, C_o, Ph_3P), 138.90 (s, C_i, Ph), 178.98 (s, CO) ppm; the signal of C_i–Ph_3P was not observed. MS (MALDI+): *m/z* (%) = 1099.20 (18) $[M - Cl]^+$. $C_{54}H_{44}Cl_2O_2P_2Pd_2S_2$ (1134.8): calcd. C 57.15, H 3.91, S 5.65; found C 57.47, H 3.75, S 5.51.

[PdCl{$Ph_3PC(H)COC(H)SPh$-κ*C*,*C*}PPh_3] (14): To a suspension of **13** (0.061 g, 0.053 mmol) in CH_2Cl_2 (25 mL), PPh_3 (0.028 g, 0.108 mmol) was added. The initial yellow suspension was stirred at room temp., and the solid gradually dissolved; a clear solution was obtained after 10 min. Stirring was maintained for an additional 5 h. After this time, the solution was concentrated to dryness, and the residue was treated with Et_2O (15 mL) to give **14** as a yellow solid. Yield: 0.071 g (78.1%). IR: $\tilde{\nu}$ = 1605 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.32 (t, $^3J_{P,H}$ and $^4J_{P,H}$ = 6.8 Hz, 1 H, CHS), 4.80 (t, $^2J_{P,H}$ and $^3J_{P,H}$ = 9.6 Hz, 1 H, CHP), 7.06 (m, 1 H, H_p, PhS), 7.18 (m, 4 H, H_o, H_m, PhS), 7.28–7.40 (m, 9 H, H_p, H_m, Ph_3P), 7.52 (td, $^3J_{H,H}$ = 7.6, $^4J_{P,H}$ = 2.8 Hz, 6 H, H_m, Ph_3P), 7.63 (t, H_p, Ph_3P), 7.70 (dd, $^3J_{P,H}$ = 11.2, $^3J_{H,H}$ = 7.2 Hz, 6 H, H_o, Ph_3P), 7.89 (dd, $^3J_{P,H}$ = 12.8 Hz, 6 H, H_o, Ph_3P) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 24.69 (s, 1 P, Ph_3PCH), 26.32 (s, 1 P, Ph_3PPd) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 41.41 (dd, $^1J_{P,C}$ = 75.8, $^2J_{P,C}$ = 58.6 Hz, PCH), 51.80 (d, $^3J_{P,C}$ = 11.1 Hz, SCH), 123.72 (d, $^1J_{P,C}$ = 89.5 Hz, C_i, Ph_3P), 124.49 (s, C_p, PhS), 126.37 (s, C_m, PhS), 128.15 (d, $^3J_{P,C}$ = 10.1 Hz, C_m, Ph_3P), 128.54 (s, C_o, PhS), 128.92 (d, $^3J_{P,C}$ = 13.1 Hz, C_m, Ph_3P), 130.20 (d, $^4J_{P,C}$ = 3.0 Hz, C_p, Ph_3P), 131.78 (d, $^1J_{P,C}$ = 45.5 Hz, C_i, Ph_3P), 132.79 (d, $^4J_{P,C}$ = 3.0 Hz, C_p, Ph_3P), 134.21 (d, $^2J_{P,C}$ = 10.1 Hz, C_o, Ph_3P), 134.64 (d, $^2J_{P,C}$ = 12.1 Hz, C_o, Ph_3P), 142.15 (d, $^4J_{P,C}$ = 4.0 Hz, C_i, PhS), 178.79 (d, $^2J_{P,C}$ = 4.0 Hz, C=O) ppm. MS (MALDI+): *m*/*z* (%) = 794.0 (44.8) [M – Cl]$^+$. $C_{45}H_{37}ClOP_2PdS$ (829.72): calcd. C 62.14, H 4.59, S 3.86; found C 61.83, H 4.40, S 3.86.

X-ray Crystallography: Crystals of **8** and **9** of suitable quality for X-ray diffraction measurements were grown by vapor diffusion of Et_2O into CH_2Cl_2 solutions of the crude products at 25 °C. In each case, a single crystal was mounted at the end of a quartz fiber in a random orientation, covered with perfluorinated oil, and placed under a cold stream of N_2 gas. The data collections were performed with Bruker Smart Apex CCD or Oxford Diffraction Xcalibur2 diffractometers with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). In all cases, a hemisphere of data was collected based on ω- and ϕ-scan runs. The diffraction frames were integrated by using the programs SAINT[17] or CrysAlis RED,[18] and the integrated intensities were corrected for absorption with SADABS.[19] The structures were solved and developed by Fourier methods.[20] All non-hydrogen atoms were refined with anisotropic displacement parameters. The H atoms were placed at idealized positions and treated as riding atoms. Each H 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.[21] CCDC-913538 (for **8**) and -913539 (for **9**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): NMR spectra of organometallic compounds **8**–**14**.

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[1] E. P. Urriolabeitia, *Top. Organomet. Chem.* **2010**, *30*, 15.
[2] Selected recent reviews: a) E. P. Urriolabeitia, *Dalton Trans.* **2008**, 5673; b) T. Cantat, N. Mézailles, A. Auffrant, P. Le Floch, *Dalton Trans.* **2008**, 1957; c) P. Kuhn, D. Sémeril, D. Matt, M. J. Chetcuti, P. Lutz, *Dalton Trans.* **2007**, 515; d) M. Taillefer, H. J. Cristau, *Top. Curr. Chem.* **2003**, *229*, 41; e) R. Bertani, M. Casarin, L. Pandolfo, *Coord. Chem. Rev.* **2003**, *236*, 15; f) R. Chauvin, *Eur. J. Inorg. Chem.* **2000**, 577; g) J. Vicente, M. T. Chicote, *Coord. Chem. Rev.* **1999**, *193–195*, 1143; h) R. Navarro, E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **1999**, 4111; i) U. Belluco, R. A. Michelin, M. Mozzon, R. Bertani, G. Facchin, L. Zanotto, L. Pandolfo, *J. Organomet. Chem.* **1998**, *557*, 37. General books: j) O. I. Kolodiazhnyi in *Phosphorus Ylides*, Wiley-VCH, Weinheim, **1999**; k) A. W. Johnson in *Ylides and Imines of Phosphorus*, John Wiley & Sons, New York, **1993**.
[3] Selected examples of complexes with *C*-bonded ylides: a) M. Carbó, L. R. Falvello, R. Navarro, T. Soler, E. P. Urriolabeitia, *Eur. J. Inorg. Chem.* **2004**, 2338; b) L. R. Falvello, R. Llusar, M. E. Margalejo, R. Navarro, E. P. Urriolabeitia, *Organometallics* **2003**, *22*, 1132; c) I. C. Barco, L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **1998**, 1699; d) S. Fernández, M. M. García, R. Navarro, E. P. Urriolabeitia, *J. Organomet. Chem.* **1998**, *561*, 67; e) L. Pandolfo, G. Paiaro, L. K. Dragani, C. Maccato, R. Bertani, G. Facchin, L. Zanotto, P. Ganis, G. Valle, *Organometallics* **1996**, *15*, 3250; f) J. Vicente, M. T. Chicote, R. Guerrero, P. G. Jones, *J. Am. Chem. Soc.* **1996**, *118*, 699; g) J. Vicente, M. T. Chicote, M. D. Abrisqueta, P. González-Herrero, R. Guerrero, *Gold Bull.* **1998**, *31*, 126; h) G. Facchin, R. Bertani, M. Calligaris, G. Nardin, M. Mari, *J. Chem. Soc., Dalton Trans.* **1987**, 1381.
[4] Selected examples of complexes with *O*- or *N*-bonded ylides: a) L. R. Falvello, J. C. Ginés, J. J. Carbó, A. Lledós, R. Navarro, T. Soler, E. P. Urriolabeitia, *Inorg. Chem.* **2006**, *45*, 6803; b) L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **1997**, *36*, 1136; c) D. Soulivong, C. Wieser, M. Marcellin, D. Matt, A. Harriman, L. Toupet, *J. Chem. Soc., Dalton Trans.* **1997**, 2257; d) L. R. Falvello, S. Fernández, R. Navarro, I. Pascual, E. P. Urriolabeitia, *J. Chem. Soc., Dalton Trans.* **1997**, 763; e) U. Belluco, R. A. Michelin, R. Bertani, G. Facchin, G. Pace, L. Zanotto, M. Mozzon, M. Furlan, E. Zangrando, *Inorg. Chim. Acta* **1996**, *252*, 355; f) L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **1996**, *35*, 3064.
[5] *C*,*X*-Chelating ylides: a) R. Zurawinski, C. Lepetit, Y. Canac, M. Mikolajczyk, R. Chauvin, *Inorg. Chem.* **2009**, *48*, 2147; b) Y. Canac, C. Lepetit, M. Abdalilah, C. Duhayon, R. Chauvin, *J. Am. Chem. Soc.* **2008**, *130*, 8406; c) J. Vignolle, H. Gornitzka, L. Maron, W. W. Schoeller, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2007**, *129*, 978; d) J. Vignolle, B. Donnadieu, D. Bourissou, M. Soleilhavoup, G. Bertrand, *J. Am. Chem. Soc.* **2006**, *128*, 14810; e) L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *New J. Chem.* **1997**, *21*, 909; f) J. Vicente, M. T. Chicote, M. C. Lagunas, *Inorg. Chem.* **1993**, *32*, 3748. Chiral *C*,*X*-chelating ylides: g) R. Zurawinski, B. Donnadieu, M. Mikolajczyk, R. Chauvin, *Organometallics* **2003**, *22*, 4810; h) L. Viau, C. Lepetit, G. Commenges, R. Chauvin, *Organometallics* **2001**, *20*, 808.
[6] Orthometallated ylides: a) D. Aguilar, M. A. Aragüés, R. Bielsa, E. Serrano, R. Navarro, E. P. Urriolabeitia, *Organometallics* **2007**, *26*, 3541; b) W. Petz, C. Kutschera, B. Neumüller, *Organometallics* **2005**, *24*, 5038; c) L. R. Falvello, S. Fernández, C. Larraz, R. Llusar, R. Navarro, E. P. Urriolabeitia, *Organometallics* **2001**, *20*, 1424; d) C. Larraz, R. Navarro, E. P. Urriolabeitia, *New J. Chem.* **2000**, *24*, 623; e) L. R. Falvello, S. Fernández, R. Navarro, E. P. Urriolabeitia, *Inorg. Chem.* **1999**, *38*, 2455; f) L. R. Falvello, S. Fernández, R. Navarro, A. Rueda, E. P. Urriolabeitia, *Organometallics* **1998**, *18*, 5887; g) J. Vicente, M. T. Chicote, M. C. Lagunas, P. G. Jones, E. Bembenek, *Organometallics* **1994**, *13*, 1243; h) J. Vicente, M. T. Chicote, J. Fernández-Baeza, *J. Organomet. Chem.* **1989**, *364*, 407; i) M. L. Illingsworth, J. A. Teagle, J. L. Burmeister, W. C. Fultz, A. L. Rheingold, *Organometallics* **1983**, *2*, 1364.

[7] *C,C*-Chelating ylides and bis(ylides): a) Y. Canac, C. Duhayon, R. Chauvin, *Angew. Chem.* **2007**, *119*, 6429; *Angew. Chem. Int. Ed.* **2007**, *46*, 6313; b) L. R. Falvello, M. E. Margalejo, R. Navarro, E. P. Urriolabeitia, *Inorg. Chim. Acta* **2003**, *347*, 75; c) L. R. Falvello, S. Fernández, R. Navarro, A. Rueda, E. P. Urriolabeitia, *Inorg. Chem.* **1998**, *37*, 6007; d) I. J. B. Lin, H. C. Shy, C. W. Liu, L.-K. Liu, S.-K. Yeh, *J. Chem. Soc., Dalton Trans.* **1990**, 2509; e) J. Vicente, M. T. Chicote, I. Saura-Llamas, M. J. López-Muñoz, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1990**, 3683; f) J. Vicente, M. T. Chicote, I. Saura-Llamas, P. G. Jones, K. Meyer-Bäse, C. F. Erdbrügger, *Organometallics* **1988**, *7*, 997; g) H. Schmidbaur, T. Costa, B. Milewski-Mahrla, F. H. Köhler, Y.-H. Tsay, C. Krüger, J. Abart, F. E. Wagner, *Organometallics* **1982**, *1*, 1266.

[8] *C,C*-Bridging ylides and bis(ylides): a) L. A. Méndez, J. Jiménez, E. Cerrada, F. Mohr, M. Laguna, *J. Am. Chem. Soc.* **2004**, *127*, 852; b) R. Usón, A. Laguna, M. Laguna, J. Jiménez, P. G. Jones, *Angew. Chem.* **1991**, *103*, 190; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 198; c) R. G. Raptis, L. C. Porter, R. J. Emrich, H. H. Murray, J. P. Fackler Jr., *Inorg. Chem.* **1990**, *29*, 4408; d) J. Vicente, M. T. Chicote, I. Saura-Llamas, P. G. Jones, *Organometallics* **1989**, *8*, 767; e) C. King, D. D. Heinrich, J. C. Wang, J. P. Fackler Jr., G. Garzon, *J. Am. Chem. Soc.* **1989**, *111*, 2300; f) J. P. Fackler Jr., B. Trczinska-Bancroft, *Organometallics* **1985**, *4*, 1891; g) P. Jandik, U. Schubert, H. Schmidbaur, *Angew. Chem.* **1982**, *94*, 74; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 73; h) H. Schmidbaur, R. Franke, *Angew. Chem.* **1973**, *12*, 449; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 416; i) H. Schmidbaur, J. Adlkofer, W. Buchner, *Angew. Chem.* **1973**, *85*, 448; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 415.

[9] Structural and DFT studies of conformational preferences on ylides: a) E. Serrano, R. Navarro, T. Soler, J. J. Carbó, A. Lledós, E. P. Urriolabeitia, *Inorg. Chem.* **2009**, *48*, 6823; b) E. Serrano, T. Soler, R. Navarro, E. P. Urriolabeitia, *J. Mol. Struct.* **2008**, *890*, 57; c) E. Serrano, C. Vallés, J. J. Carbó, A. Lledós, T. Soler, R. Navarro, E. P. Urriolabeitia, *Organometallics* **2006**, *25*, 4653; d) A. Lledós, J. J. Carbó, R. Navarro, E. Serrano, E. P. Urriolabeitia, *Inorg. Chem.* **2004**, *43*, 7622; e) A. Lledós, J. J. Carbó, R. Navarro, E. P. Urriolabeitia, *Inorg. Chim. Acta* **2004**, *357*, 1444; f) A. Lledós, J. J. Carbó, E. P. Urriolabeitia, *Inorg. Chem.* **2001**, *40*, 4913; g) R. A. Aitken, N. Karodia, P. Lightfoot, *J. Chem. Soc. Perkin Trans. 2* **2000**, 333.

[10] a) R. F. Hudson, P. A. Chopard, *J. Org. Chem.* **1963**, *28*, 2446; b) A. Hercouet, M. Le Corre, *Tetrahedron* **1977**, *33*, 33.

[11] J. S. Clark in *Nitrogen, Oxygen and Sulfur Ylide Chemistry*, Oxford University Press, New York, **2002**.

[12] V. Alcázar, I. Tapia, M. Crego, J. R. Morán, *An. Quim.* **1991**, *87*, 113.

[13] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[14] a) D. S. Yufit, Y. T. Struchkov, S. I. Kozhushkov, P. S. Zefirov, *Bull. Acad. Sci. USSR Div. Chem. Sci. (Engl. Transl.)* **1991**, *40*, 68; b) J. Galloy, W. H. Watson, D. Craig, C. Guidry, M. Morgan, R. McKellar, A. L. Ternary Jr., G. Martin, *J. Heterocycl. Chem.* **1983**, *20*, 399.

[15] D. Britton, J. D. Dunitz, *Helv. Chim. Acta* **1980**, *63*, 1068.

[16] T. D. W. Claridge, *High Resolution NMR Techniques in Organic Chemistry*, 2nd ed., Elsevier, Oxford, **2009**.

[17] *SAINT*, *version 5.0*, Bruker Analytical X-ray Systems, Madison, WI.

[18] *CrysAlis RED*, *version 1.171.27p8*, Oxford Diffraction Ltd., Oxford, **2005**.

[19] G. M. Sheldrick, *SADABS, Program for absorption and other corrections*, Göttingen University, **1996**.

[20] SHELXS-86: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[21] SHELXL-97: G. M. Sheldrick, *Acta Crystallogr., Sect. A* **2008**, *64*, 112.

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