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α-Stabilized phosphoylides as versatile multifunctional ligands

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The coordination properties of α-stabilized phosphorus ylides show that these compounds can behave as ambidentate ligands towards palladium(II) complexes. Bonding through the carbon atom or through the heteroatom (O, N) and the coordination site can be conditioned by adequate choice of the organometallic precursor. On the other hand, the bis-ylide $Ph_3P{=}C(H){-}C(O){-}C(H){=}PPh_3$ coordinates as a C,C-chelating ligand towards Pd(II) complexes and it can undergo an intramolecular orthometallation in different ways, leading to substrates that are adequate for the synthesis of polynuclear derivatives with or without a metal–metal bond.

Introduction

Multifunctional ligands are organic entities that possess more than one functional group and the interest of chemists in these ligands lies in the wide field of applications that can be found, based on their multifunctionality. This general definition comprises almost all kinds of possible di- or poly-dentate ligands but in this paper our intention is to center our point of view on the coordination chemistry of the phosphorus ylides. The "Wittig reaction" is always associated with a "phosphorus ylide" and this process, which allows a C–C double bond to be created at a specific point in a given molecule, is, in fact, the most striking utility of phosphorus ylides.[1]

In addition to their merely "organic" properties and applications, the charge distribution on phosphoylides makes them potential ligands towards transition metals. The charge density centered on the ylidic carbon constitutes a powerful nucleophilic center and, in accordance with this, carbon–metal linked complexes (organometallic complexes) with practically no back-bonding can be prepared. A huge number of complexes are known, in a wide variety of coordination modes. Several reviews have appeared over the years concerning either transition metal complexes,[2–10] the synthesis of the ylides themselves,[11–14] and their synthetic applications,[15] in addition to specific paragraphs in comprehensive collections.[16]

One of the last reviews was almost entirely devoted to a special class among the phosphoylides, that formed by the so-called "stabilized" ylides.[8] They are known by this name because there is a functional group, usually a keto, cyano or isocyano group, which is able to delocalize the charge density otherwise centered on the ylidic carbon atom. The results of this delocalization can be observed at several levels. Firstly, there is a notable increase in stability since the products can usually be isolated, are air stable and can be stored. Secondly, the carbon atom has a low nucleophilic capacity. Thirdly, the presence of electron density at the heteroatom (nitrogen, oxygen, or other) confers on it the possibility of also behaving as donor atom and, because of this, we can call them "ambidentate" ligands. These facts are clear in Fig. 1 in which we show the canonical forms of a keto-stabilized ylide (forms **a**–**c**) and those of a cyano-stabilized one (forms **d**–**f**).

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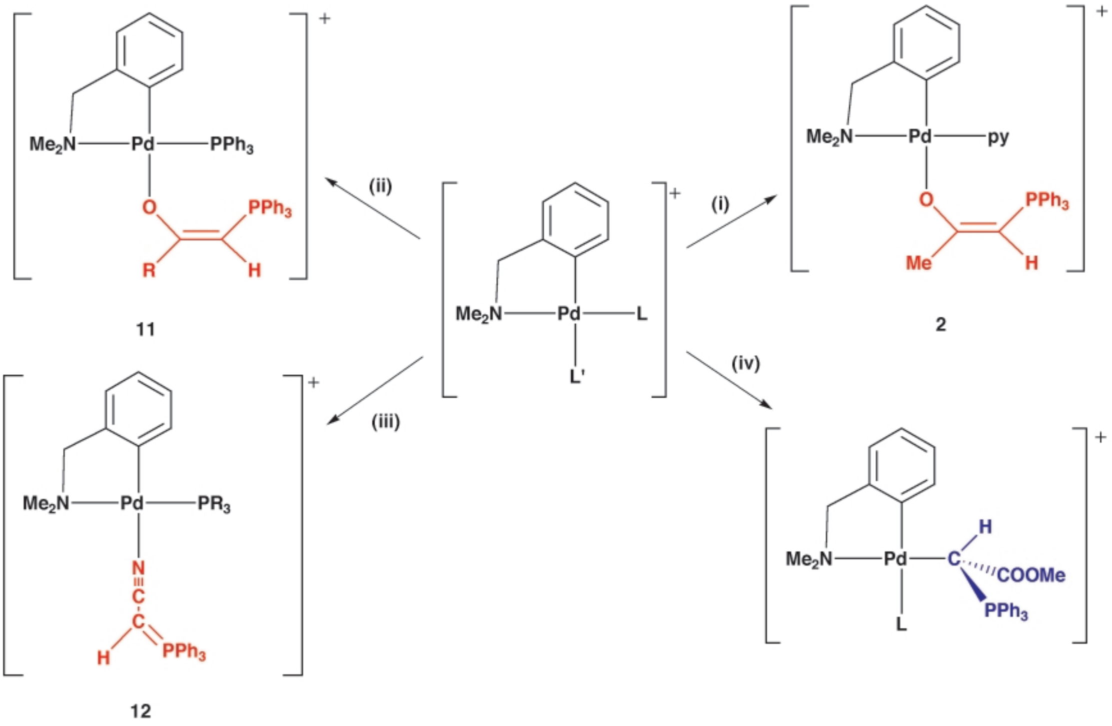


Scheme 1 (i) L = py; L′ = THF; +APPY; (ii) L = PPh$_3$; L′ = THF; +APPY, BPPY, CMPPY; (iii) L = PR$_3$; L′ = THF; +CPPY; (iv) L = L′ = NCMe; +CMPPY **7**; L = py; L′ = THF; +CMPPY **10**.

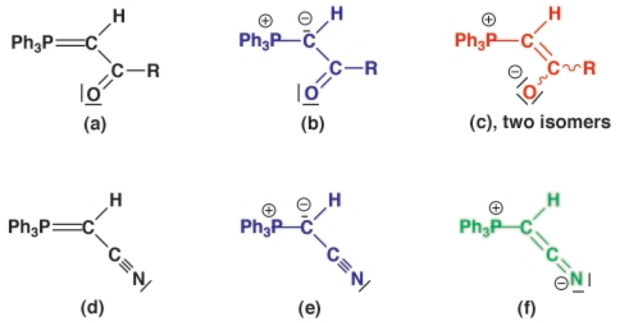


Fig. 1

Given these possibilities (carbon *versus* heteroatom-coordination) certain questions arise: (i) is there any preference for a certain coordination mode in the case of an ylide and a substrate?; (ii) is there any preference for a certain coordination site in the case of an ylide and a substrate with various vacant sites?; (iii) is there any preference for a certain coordination mode, given several ylides, as a function of the α-substituent? The answer to all these questions would seem to be yes and, although our analysis is restricted to Pd(II) and Pt(II) complexes, our aim is to show which factors must be taken into account to obtain a reasonable explanation for the behaviour of the ylides. In some cases, we will refer to other related ligands, such as stabilized iminophosphoranes, since their behaviour is similar.

We will also describe the behaviour of the bis-ylide [Ph$_3$P=CH]$_2$CO, (Section 2) since it reveals certain noteworthy facts when interacting with a metal, in this case palladium. For instance, the observed stereoselectivity in the C,C-chelating four-membered ring Pd[C(H)PPh$_3$]$_2$CO (only one of the *meso* forms was obtained), the ease with which this metallacycle is transformed into a five-membered orthometallated ring $Pd[\mathit{C}_6H_4\text{-2-}PPh_2\mathit{C}(H)COCH_2PPh_3]$ in a variety of ways, the possibility of obtaining a “free ylide” by deprotonation of the methylene group and, once again, the stereoselectivity observed in the metallation of this “free ylide” to give a C,C,C-terdentate ylide ligand.

1.1. Keto and cyano stabilized phosphoylides: ambidenticity

The coordination chemistry of α-stabilized ylides began with the pioneering work of Itoh and co-workers in 1975.[17a] Since then, several reports concerning C-bonded, α-stabilized, ylides have appeared[7,8,16] but it was not until 1985 that the first report of an O-bonded phosphoylide to a soft palladium center was given by Usón *et al.*, by reaction of [Pd(C$_6$F$_5$)L$_2$(OClO$_3$)] with Ph$_3$P=C(H)COMe (L = PPh$_3$, P^{n}Bu$_3$) **1** (see Chart 1).[17b] Previous to this report there have been very few descriptions of complexes with O-coordinated ylides, only those bonded to Sn(IV),[18] Pb(IV)[18] and W(0).[19] The O-coordination of the ylide in these compounds, instead of the more classical C-coordination, seems to be logical considering the oxophilic character of the tin and lead centres in a formal oxidation state (+4), but it is more intriguing in the case of the metallic center of tungsten(0). Following these reports, and almost until the present time, the only contributions to this field have been the work of Burmeister *et al.* on Ti, Zr and Hf(IV) complexes[20] (really oxophilics) and a related work of Facchin *et al.* on arsonium ylides.[21] However, over the last few years, we have witnessed the reappearance of stabilized phosphoylides as ligands and several groups are currently devoted to this research.

In 1996 our group reported the first structural characterization of a soft transition metal complex containing an O-bonded ylide.[22] The reaction of [Pd(dmba)(THF)(py)][ClO$_4$] with APPY [dmba = C$_6$H$_4$CH$_2$NMe$_2$-2; APPY = Ph$_3$P=C(H)C(O)Me] gives the cationic [Pd(dmba)(py)(O-APPY)][ClO$_4$] **2** (see Scheme 1) whose structure shows, without any doubt, the presence of the O-bonded ylide *trans* to the arylic carbon of the dmba ligand. In a contemporary contribution, Facchin *et al.*[23] reported the reactivity of several Pt(II) complexes with other P and As carbonyl stabilized ylides [APPY; BPPY = Ph$_3$P=C(H)C(O)Ph; CMPPY = Ph$_3$P=C(H)C(O)OMe; APAsY = Ph$_3$As=C(H)C(O)Me; BPAsY = Ph$_3$As=C(H)C(O)Ph; CMPAsY = Ph$_3$As=C(H)C(O)OMe]. They proposed that the steric repulsion between the coordinated ligands, including the ylide, is the only factor responsible for the bonding mode adopted;

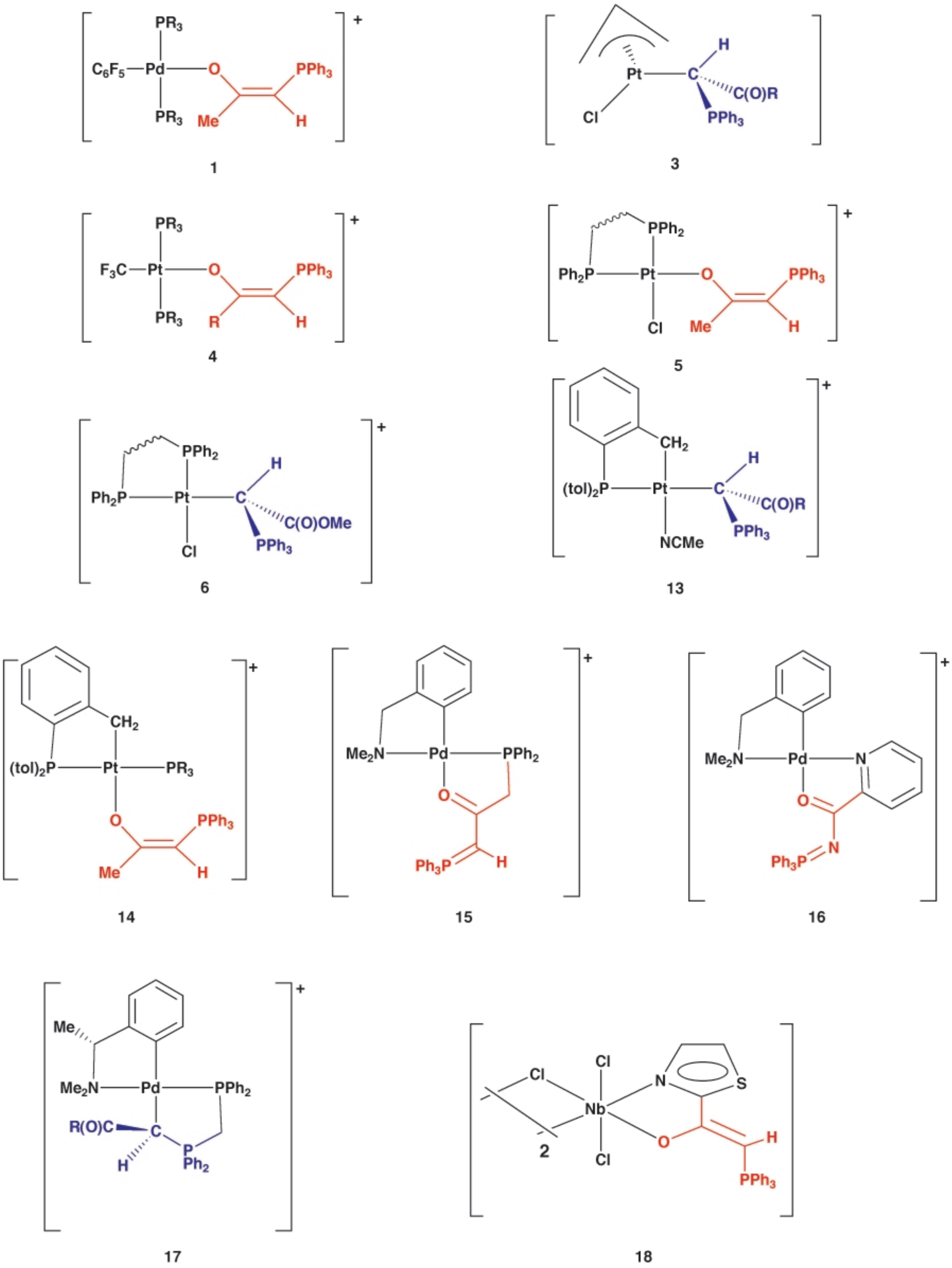
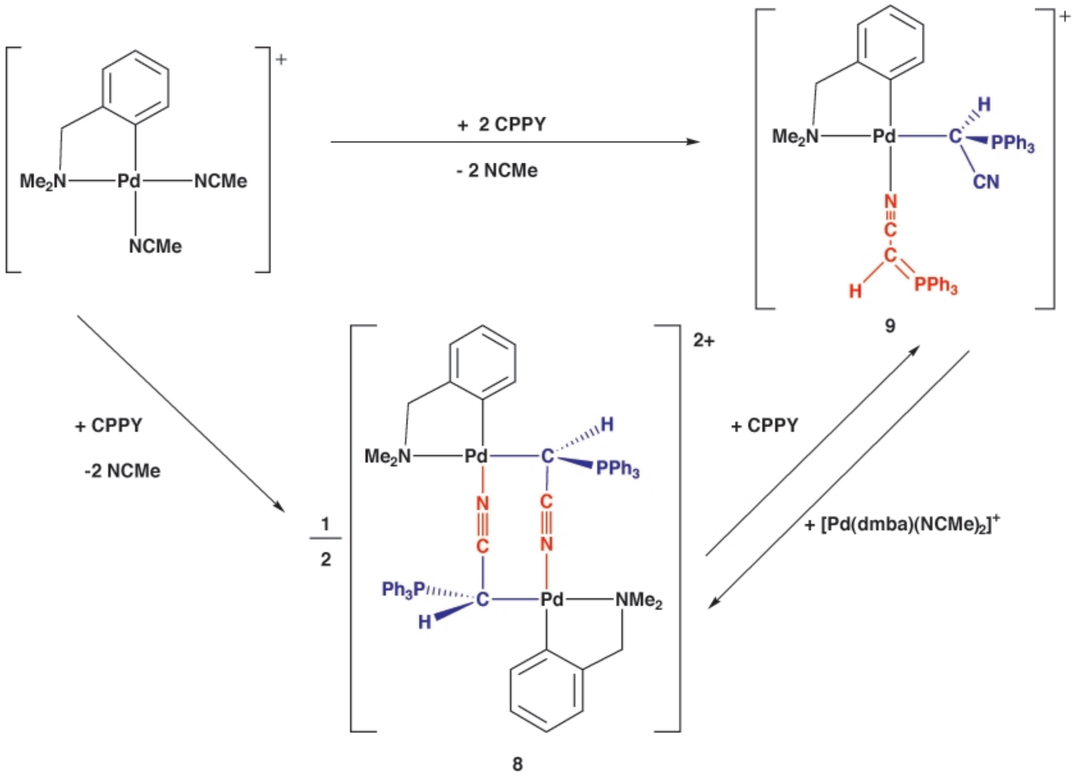


Chart 1

however, with the low sterically demanding group η^3-allyl ligand **3** and with the bulky C,P-orthometallated $(Bu^t)_2PC(Me)_2CH_2$ group, selective C-coordination was observed, while selective O-bonding was found with *trans*-$Pt(CF_3)(PPh_3)_2$ **4**. The fine tuning of the steric hindrance provided by diphosphines such as $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH{=}CHPPh_2$ seems to leave the final decision of the bonding mode to the nucleophilicity of the donor atoms of the ylide: APPY and BPPY act as O-donors **5** while the most nucleophilic CMPPY acts as a C-donor **6**. The complex *trans*-$[Pt(PPh_3)_2(CF_3)($*O*-CMPPY$)][BF_4]\cdot 0.5CH_2Cl_2$ was characterized crystallographically.[23]

These results prompted us to explore the reactivity of stabilized phosphoylides such as APPY, BPPY, CMPPY, DMPPY and CPPY [DMPPY = $Ph_3P{=}C(H)C(O)NMe_2$; CPPY = $Ph_3P{=}C(H)CN$] towards different C,N- and C,P-cyclometallated systems of Pd(II) and Pt(II). Our choice of cyclometallated systems was determined by the possiblity of changing one of the donor atoms (N *versus* P), maintaining a C-donor atom, as this would allow us to change the electronic properties of the starting compound, mainly in the *trans* position, and their steric requirements, by changing the substituents at P and at N. The coordination modes found for the aforementioned ylides, in their reactions towards solvated



Scheme 2

substrates [Pd(dmba)(L)(L′)][ClO$_4$], seems to be strongly dependent on the nature of the ligands L and L′ and on the nucleophilicity of the ylidic carbon atom.[24–26]

When L = L′ = NCMe, the less nucleophilic ylides APPY[24] and BPPY[24] are bonded through the ylidic carbon atom and through the carbonyl oxygen, both forms probably being involved in an exchange equilibrium; the more nucleophilic ylides CMPPY[24] and DMPPY[26] are selectively bonded through the ylidic carbon in *trans* position to the nitrogen atom of the NMe$_2$ group **7** (Scheme 1). In all cases, the remaining NCMe molecule can not be displaced from the complex without decomposition. The cyano-stabilized ylide CPPY[25] behaves differently towards the same bis-solvate precursor since the reaction in a 1 : 1 molar ratio gives the dinuclear [Pd(dmba)(μ-NCC(H)PPh$_3$)]$_2$[ClO$_4$]$_2$ **8** (Scheme 2) by displacement of both NCMe molecules and coordination of the ylide as a C,N-bridging while the reaction in a 1 : 2 ratio (Pd : ylide) gives the mononuclear [Pd(dmba)(NCC(H)PPh$_3$)$_2$][ClO$_4$] **9**, in which two ylides are coordinated: one is C-coordinated *trans* to the NMe$_2$ group and the other one is N-coordinated *trans* to the orthometallated carbon atom. Although at least four different isomers would be expected for this complex, only that described is observed. This complex represents a noteworthy example of linkage isomerism (Scheme 2).

When the starting complex contains another auxiliary ligand other than the NCMe group [Pd(dmba)(L)(THF)][ClO$_4$], the coordination mode of the ylide depends on two main factors: (i) the strength of the Pd-L bond and (ii) the nucleophilicity of the ylidic carbon. With weakly bonded L ligands such as pyridine, the less nucleophilic ylides APPY and BPPY are O-bonded *trans* to the aryl carbon of the dmba ligand **2**. With the more nucleophilic ylides CMPPY and DMPPY, however, the ylide coordinates through the carbon atom *trans* to the N atom of the NMe$_2$ group, promoting the displacement of the pyridine ligand from the *cis* position to the aryl carbon to the *trans* position to the same arylic carbon **10**. It must be noted that the starting complexes [Pd(dmba)(L)(THF)][ClO$_4$] are obtained as single isomers with the L ligand *trans* to the NMe$_2$ group and that the ylide compounds [Pd(dmba)(L)(YLIDE)][ClO$_4$] are also obtained as single isomers with the reported stereochemistry. The CPPY ylide promotes the irreversible displacement of the py ligand and the formation of the dinuclear [Pd(dmba)(μ-NCC(H)PPh$_3$)]$_2$[ClO$_4$]$_2$ **8**.

With strongly bonded L ligands such as phosphines or phosphites, the types of behaviour are more uniform than the preceding types. APPY, BPPY and CMPPY ylides coordinate through the carbonyl oxygen *trans* to the aryl carbon **11** and the CPPY ylide coordinates through the N atom also *trans* to the orthometallated carbon **12** (Scheme 1). At this point the ambidenticity of these ylides is unambiguously established; they can coordinate through the carbon atom or through the carbonyl oxygen (or the nitrilic nitrogen) indistinctly. We will come back to this point later.

When the orthometallated ligand is changed this behaviour does not change appreciably. We thus explored the reactivity of the ylides towards the C,P-cyclometallated[27] complexes $\{Pt[CH_2C_6H_4P(o\text{-}tol)_2](L)(L')\}^{n+}$ and we found that when the ylide is C-bonded it is located *trans* to the P atom **13** and when it is bonded through the heteroatom the coordination occurs *trans* to the carbon atom **14** (Chart 1).

Ligands containing an end-phosphine group and an ylide moiety were prepared and their reactivity towards different Pd(II) compounds explored. The APPY ylide can be easily deprotonated at the methyl group, this reaction being the base for subsequent transformations of the ylide. For instance, $Ph_3P{=}C(H)C(O)CH_2PPh_2$ is synthesized[28] in moderate yields by reaction of APPY with two equivalents of LiBu^n and 1 equivalent of ClPPh$_2$. The reaction of this phosphino-ylide with the cyclometallated [Pd(μ-Cl)(dmba)]$_2$ affords the cationic [Pd(dmba)(*P*PPh$_2$CH$_2$C(*O*)C(H)=PPh$_3$)]Cl **15** (Chart 1) in which the ligand is P,O-coordinated. Only one geometric isomer is detected for this complex and its spectroscopic data reveal that the ligand arrangement is P-*trans*-to-N, thus O-*trans*-to-C$_{\text{aryl}}$. These results are very similar to those obtained with the iminophosphorane[29] NC$_5$H$_4$–2–C(O)–N=PPh$_3$. The reaction of [Pd(dmba)(NCMe)$_2$][ClO$_4$] with 1 equivalent of the iminophosphorane results in the formation of [Pd(dmba)(*N*C_5H_4–2–C(*O*)–N=PPh_3)]$^+$ **16**, in which the iminophosphorane is N(py),O-coordinated, with the pyridine N atom *trans* to the N atom of the NMe_2 group and the carbonyl oxygen *trans* to the aryl carbon. The reaction of the C,P-chelate [M(*C*$H_2C_6H_4$*P*(o-tol)$_2$)$(NCMe)_2$][ClO_4] (M = Pd, Pt) with the iminophosphorane (1 : 1 molar ratio) similarly gives [Pd(*C*$H_2C_6H_4$*P*(o-tol)$_2$)(*N*C_5H_4-2-C(*O*)–N=PPh_3)]$^+$, which shows a P-*trans*-to-N(py), O-*trans*-to-C, ligand arrangement. However, the same ligand behaves as a N,N-chelating ligand towards MCl_2 units, and the reaction of *trans*-$PdCl_2(NCMe)_2$ or $PtCl_2$ with NC_5H_4-2-C(O)–N=PPh_3 (1 : 1 molar ratio) gives *cis*-Cl_2M(*N*C_5H_4-2-C(O)–*N*=PPh_3) (M = Pd, Pt).

The phosphino-ylides $Ph_2PCH_2PPh_2$=C(H)C(O)R′ (R′ = Me, Ph, OMe) are related ligands which can be prepared in good yield by the reaction of dppm ($Ph_2PCH_2PPh_2$) with the corresponding halo-derivatives X–CH_2C(O)R′ and deprotonation of the resulting phosphonium-phosphine with NEt_3. The reaction of $Ph_2PCH_2PPh_2$=C(H)C(O)R′ with the bis-solvate [Pd(*R*-dmphea)$(NCMe)_2$][ClO_4] (*R*-dmphea = *R*-C_6H_4C(H)-(Me)NMe_2-2) results[30] in the formation of [Pd(*R*-dmphea)-(*P*$Ph_2CH_2PPh_2$*C*(H)C(O)R′)][ClO_4] **17**. In these complexes the ylide ligand is coordinated in a *P,C*-chelate form, in such a way that the P atom is *trans* to the NMe_2 group and the ylide carbon is *trans* to the orthometallated carbon. These products can also be obtained by the reaction of the acac derivative [Pd(*R*-dmphea)(acac)] (acac = acetylacetonate) with [Ph_2PCH_2-PPh_2CH_2C(O)R′][ClO_4]. The synthesis of [Pd(*R*-dmphea)-(*P*$Ph_2CH_2PPh_2$*C*(H)C(O)R′)][ClO_4] **17** (R′ = Me, Ph, OMe) is remarkable due to two facts: (i) it is the first example of a C-*trans*-C in which an ylidic carbon is involved and (ii) the synthesis is highly stereoselective: the ylidic carbon, after coordination, becomes chiral and the products are obtained as the mixture of the two diastereoisomers, and diastereomeric excess (*RR-RS*) of 71% can be reached. The origin of this stereoselectivity seems to be related to the mutually *cis* arrangement of the NMe_2 group and the ylidic carbon and to the role of the NMe_2 unit as a mirror of the chirality of the stereogenic center of the *R*-dmphea ligand.

More complex ylides Ph_3P=C(H)C(O)R (R = 2-thiazolyl) have been recently described[31,32] and their coordinating properties towards niobium(III) derivatives explored. As expected for a strong oxophilic metal, the reactions of $[NbCl_3(dme)]_n$ or [$NbCl_3$(dme)(alkyne)] with the ylide (1 : 1 molar ratio) result in the formation of dinuclear [$NbCl_3$(N,O-ylide)]$_2$ **18** or mononuclear [$NbCl_3$(N,O-ylide)(alkyne)] compounds.[31] In these, the ylide acts as a chelating ligand through the carbonyl oxygen and the heterocyclic nitrogen. The mononuclear complex [$NbCl_3$(N,O-ylide)(PhCCMe)] undergoes internal orthometallation of one of the phenyl groups of the PPh_3 fragment when treated with MeLi.[32] This N,O-bonded ylide can also use the electron density at the ylide carbon and at the heterocyclic sulfur to coordinate to a second metal center, resulting in the formation of tetrametallic derivatives in which the ylide acts as a N,O,C,S-tetradentate ligand [$Nb_2Cl_6(ML_n)_2$(N,O,C,S-ylide)$_2$](CF_3SO_3)$_2$ (ML_n = $AuPPh_3$, Ag).[32]

The ambidenticity of the phosphino-ylides [Ph_2PCH_2P-Ph_2=CHC(O)R′] can also become polydenticity if, following coordination, the ligand is subjected to a deprotonation process which transforms it into a methanide group.[33] For instance, the treatment of the phosphonium [X=$Ph_2PCH_2PPh_2CH_2$-C(O)Me]ClO_4 (X = O, S) with 2 equivalents of (acac)$AgPPh_3$ gives[34] the dinuclear [$Ag_2(PPh_3)_2$(*X*PPh_2*C*HPPh_2*C*HC(*O*)-OMe)]ClO_4. In this complex the methanide group generated acts as a tetradentate ligand, through the heteroatom X, the methanide carbon, the ylide carbon and the carbonyl oxygen, in an unprecedented coordination mode. However, these multiple coordination modes do not come within the scope of our purposes and they will not be analyzed further.

1.2. Control of the position and the coordination mode and the antisymbiotic effect: an old concept which is always current

The preference of stabilized ylides to bind to a given metal through one specific donor atom is closely related to the hard or soft nature of the metal, according to the HSAB rules (Hard and Soft Acid and Bases) given by Pearson.[35] We have thus seen that α-keto stabilized phosphoylides are coordinated through the "hard" oxygen atom[35,36] towards very hard, oxophilic metals such as Sn(IV), Pb(IV),[18] Ti(IV), Zr(IV), Hf(IV)[20] or Nb(III).[32] In almost all cases the other ligands around the metal center are "hard" halides.[36] It is clear that this is a good example of the rule "hard acids prefer to bind to hard bases" and, moreover, it is reasonable to propose a *symbiotic* behaviour for these metals. It was Jørgensen who coined the term "symbiosis" to describe the fact that soft bases tend to group together on a given central atom and hard ligands tend to group together ("birds of a feather flock together") resulting in a mutual stabilizing effect.[37]

What happens with "soft" metals? From the preceding paragraphs (Section 1.1) it seems that, at least in Pd(II) and Pt(II) complexes, there is a certain preference for the aforementioned C-bonded ylides to be coordinated *trans* to a heteroatom (usually N or P) but not *trans* to another carbon atom (with exceptions). Moreover, when ylides are bonded through heteroatoms (either the carbonyl oxygen or the nitrile nitrogen) the preferred coordination site is, mainly, that *trans* to an aryl or alkyl carbon atom. Although Pd(II) and Pt(II) complexes follow the rule that "soft acids prefer to bind to soft bases", the behaviour observed is opposite to that described as symbiosis, since in a *trans* position to a soft donor atom (the ylidic C atom) a hard donor atom (the N atom, for instance) is preferred. This behaviour has been called *antisymbiosis*[36,38] and it has been defined by Pearson as: *two soft ligands in mutual* trans *position will have a destabilizing effect on each other when attached to class b metal atoms*. The antisymbiotic effect has been explained in a qualitative way[36] and there are a great number of examples reported in the literature on this phenomenon (see Fig. 2).[39] A very clear example of antisymbiotic behaviour is found in the complex [Pd($PPh_2CH_2CH_2CH_2NMe_2$)(*N*CS)(*S*CN)] (Fig. 2) which is obtained as a single isomer.[39a] This complex contains two anionic [SCN]$^-$ ligands coordinated, one through the nitrogen atom and the other one through the sulfur atom, in such a way that the soft *S*CN ligand is bonded *trans* to the "hard" N atom of the NMe_2 unit and the "hard" *N*CS ligand is coordinated *trans* to the soft PPh_2 group. Moreover, in an excellent recently published paper,[40] Vicente *et al.* describe the difficulty in preparing *cis*-[Pd(Ar)X$(PPh_3)_2$] complexes (a soft phosphine ligand will be destabilized *trans* to a soft aryl carbon atom) and, using the antisymbiotic effect, establish a sequence of destabilizing effects for *trans* ligands Ar/Ar > Ar/PR_3 > PR_3/PR_3 which they call *transphobia*. They also point out that this destabilizing effect is greater for palladium than for platinum and that the destabilization increases with the *trans* influence of the ligands.

We can now analyze the structures found in complexes **1**–**17** (Chart 1, Schemes 1 and 2) in the light of all these concepts: the

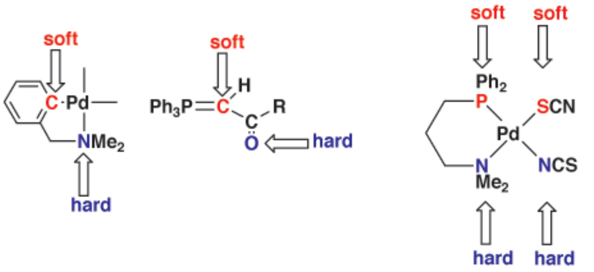


Fig. 2

antisymbiotic effect, the transphobia, and the different nature of the donor atoms of the ylides (a soft donor atom such as the ylidic carbon and a more or less hard atom such as are the carbonyl oxygen or the nitrile nitrogen, see Fig. 2). It must be noted that there will always be a balance between the nucleophilic ability of the donor atoms of the stabilized ylide, the steric requirements of the starting compound, the nature of the metal center and that of the donor atom in the *trans* position to that in which the ylide is coordinated. This delicate balance between electronic *and* steric factors will result in a specific coordination mode and only by considering all these items can a reasonable explanation of the observed chemical behaviour be established.

Complex **1** shows an O-bonded APPY ylide *trans* to a carbon atom of the C_6F_5 group, as predicted by the antisymbiotic effect. The soft ylidic C donor will be destabilized when *trans* to the aryl soft C donor and then the hardest oxygen will be preferred as a donor atom. Moreover, this coordination mode is less sterically demanding than C-coordination, but the steric repulsion cannot be the only factor responsible for this orientation since the position *trans* to the C_6F_5 group in the unit *trans*-$[Pd(C_6F_5)(PR_3)_2]^+$ can be occupied by crowded ligands such as PPh_3. In the same contribution,[17b] the synthesis of $[Pd(C_6F_5)(bipy)(O\text{-}APPY)][ClO_4]$ is also described. Here the fragment $[Pd(C_6F_5)(bipy)]^+$ would offer a better possibility to the ylide to adopt a C-bonding mode since it has lower steric requirements than those of *trans*-$[Pd(C_6F_5)(PR_3)_2]$, but even in this case the ylide coordinates through the oxygen *trans* to the borderline N atom. The alternance in the O- and C-bonding modes in complexes **3**–**6** is reported to be due exclusively to steric factors. In complexes **3**, the low steric requirements of the η^3-allyl ligand favour C-bonding (we must not forget that stabilized ylides behave essentially as C-donors towards soft metals) but the reasons for which **4** contain an O-bonded ylide seem to be very similar to those described for **1**. The appearance of both coordination modes in **5** (R = Me, Ph) and **6** (R = OMe) suggests that other factors must be taken into account. Thus, the low nucleophilic APPY or BPPY ylides, which show similar donating abilities at the ylidic carbon and at the carbonyl oxygen,[24] will be more stabilized O-bonded *trans* to a soft P atom **5** while the more nucleophilic CMPPY shows a C-bonding mode **6**. Obviously, in this case, steric repulsion does not play an important role in the bonding mode, since the "volume" required for the C-coordination of CMPPY is more or less the same as that required for APPY or BPPY, if not higher. It is the different nucleophilic ability of the carbon atom in the ylide which seems to be the crucial factor (Chart 1).

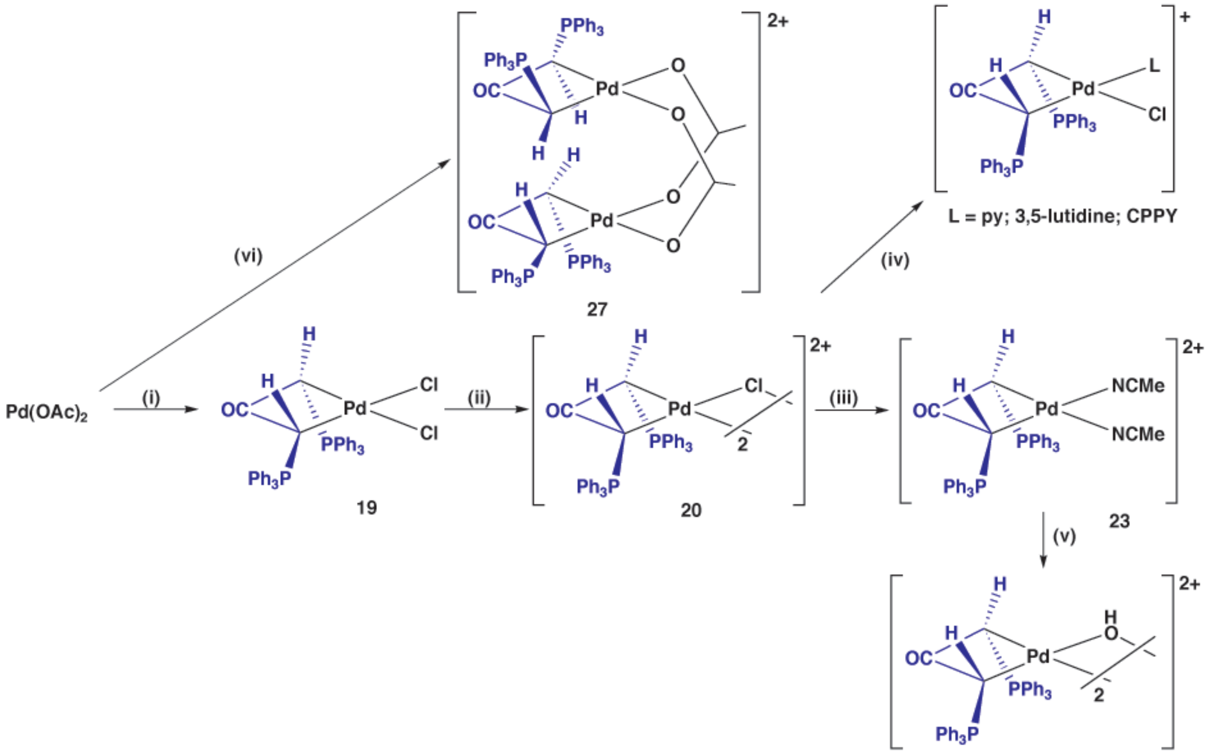
Similar behaviour to that observed in **5** and **6** was found when we compared **2** and **10** (Scheme 1). The reaction of the starting compound, $[Pd(dmba)(py)(THF)][ClO_4]$ (N-*trans*-to-N), with APPY or CMPPY not only gives different coordination modes, but these are also at different coordination sites. In the case of **2**, the hard O-bonded ylide is located *trans* to the softer atom of the dmba ligand (the aryl C atom) and the arrangement around the Pd atom is retained. However, the most nucleophilic CMPPY in **10** coordinates through the soft ylidic C atom (as in **6**) but not *trans* to the soft aryl C atom. Instead, it promotes the displacement of the pyridine ligand to the position *trans* to the aryl C atom and it coordinates *trans* to the harder N atom of the dmba group. In this way the full antisymbiotic effect occurs and the hard-*trans*-to-soft arrangement is achieved. Similar considerations can be proposed for the structure of complex **9** (Scheme 2), a good example of linkage isomerism: the soft C-bonded ylide is *trans* to the harder atom of the dmba (the N atom) and the harder N atom of the ylide CPPY is *trans* to the soft aryl C atom of the dmba. Complexes **11** and **12** have been synthesized by reaction of $[Pd(dmba)(PR_3)(THF)][ClO_4]$ with the APPY or CPPY ylides (Scheme 1). The starting compound shows a defined stereochemistry in which the phosphine ligand is *trans* to the N atom of the NMe_2 group, the reason why a single isomer is obtained for this product also lies in the antisymbiotic effect. Since the phosphine ligand is strongly bonded to the Pd atom we do not expect its displacement during reaction with the ylide, thus the only vacant coordination site is *trans* to the soft aryl C atom. Accordingly, all ylides coordinate through the "hard" heteroatom, the keto-stabilized through the carbonyl oxygen **11** or the cyano-stabilized through the nitrile N atom **12**. With respect to complexes **13** and **14**, we have observed the same trends as those described previously (Chart 1).

The case of complexes **15** and **16** (Chart 1) is also worth noting. In **15** the phosphine-ylide has three potential donor atoms: the phosphine P atom (soft), the ylidic C atom (soft) and the carbonyl oxygen (hard). The reaction is driven by the phosphine P atom, which forms a strong bond with the Pd centre and, in accordance with the antisymbiotic effect, it coordinates *trans* to the harder atom of the dmba, the N atom of the NMe_2 group. Both the coordination of the ylidic C atom or the carbonyl oxygen would result in the formation of a five-membered metallacycle and we would expect a similar stabilization by chelate effect. However, since the vacant site is *trans* to the soft aryl C atom, O-bonding is preferred. In addition, this results in lower steric repulsions between the NMe_2 group and its *cis* position, although this is not the only factor responsible for the observed bonding mode (see the structure of complex **17**). Similar arguments can be used to explain the stereochemistry of **16**: the N coordination of the py fragment is more stabilized *trans* to the NMe_2 group[41] and once again, an O-bonding mode (in this case of a keto-stabilized iminophosphorane) is observed *trans* to the aryl group. The synthesis of complex **17**, which contains a P,C-coordinated phosphine-ylide, initially follows the same steps as **15**, that is, the reaction is driven by the P coordination of the phosphine end *trans* to the NMe_2 group. However, the coordination of the ylidic C atom or the carbonyl O atom now results in different metallacycles, five-membered in the case of C-bonding and seven-membered in the case of O-bonding. The additional stabilization provided by the formation of a five-membered ring counterbalances the destabilization resulting from the C-*trans*-to-C situation and shows that the position *cis* to the NMe_2 group has sufficient "volume" to accommodate a C-bonded ylide. This fact is important, since it shows that the O-bonding in **15** is preferred mainly for electronic reasons (as is the case in **16**), which have a similar chelate effect. We think that similar conclusions can be extrapolated for complexes **7**, **9** and **10** in which the ylides are C-bonded *trans* to the NMe_2 group for electronic reasons, not due to steric repulsions, although in these cases there is not the additional stabilization of the chelate effect.

We have thus shown how the consideration of very simple, "old" arguments provides a clear interpretation of the molecular stereochemistry of ylide complexes. Obviously, there is much more scope for research into this field of the coordination chemistry of "simple", stabilized ylides, and we think that new, more interesting results are awaiting study.

2.1. Bis-ylide complexes: synthesis and structure

The study of the coordination chemistry of bis-ylides represents one step further in the investigation into the complexity of ylidic systems. Some reports have appeared in the literature to date, containing non-stabilized bis-ylides such as $[Ph_3PCH\text{–}(CH_2)_n\text{–}CHPPh_3]$ (Ni-complexes)[42a] or $[\textit{ortho}\text{-}(C_6H_4)\textit{C}H{=}PR_2\text{-}CH{=}PR_2\text{-}\textit{C}H_2]$ (Zn, Mn, Fe, Co and Cd-complexes)[42b,c] and stabilized bis-ylides such as $[Ph_2P(CHCOOR)_2]^-$ in Ag,[43a] Au[43b] and Pd[43c] complexes, $[Ph_3PC(R)CO\text{–}(CH_2)_n\text{–}COC(R)PPh_3]$ (Sn-complexes),[44] and $[Ph_3PC(H)C(O)C(H)PPh_3]$[45] (Ag and Au complexes) (see Fig. 3 for representative examples). This latter ylide is a good candidate for the investigation of its coordination behaviour since its chemistry with palladium is yet



Scheme 3 (i) +[$Ph_3PCH_2COCH_2PPh_3$]Cl_2, −2 HOAc, CH_2Cl_2, r.t. (ii) +$TlClO_4$, −TlCl, CH_2Cl_2, r.t. (iii) +2 $TlClO_4$, −2 TlCl, NCMe, r.t. (iv) +2 L, CH_2Cl_2, r.t. (v) +2 NBu_4OH, MeOH/H_2O, r.t. (vi) +[$Ph_3P{=}C(H)COCH_2PPh_3$](ClO_4), −HOAc, CH_2Cl_2, r.t.

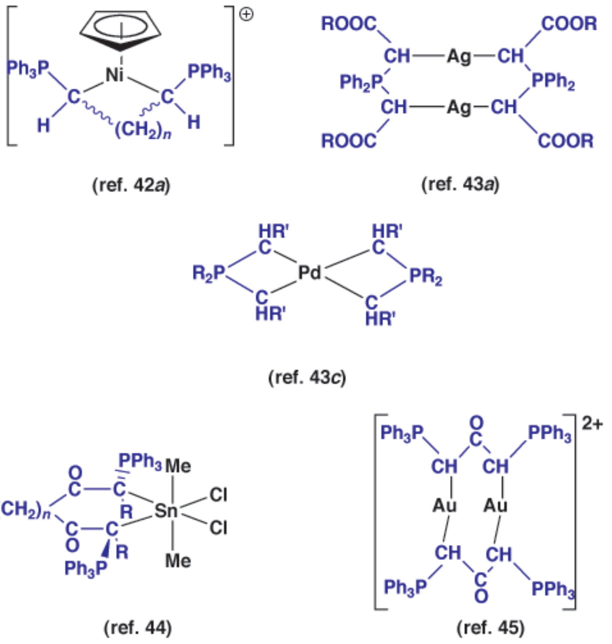

(ref. 42*a*)
(ref. 43*a*)
(ref. 43*c*)
(ref. 44)
(ref. 45)

Fig. 3

to be explored, it is closely related to the stabilized ylides described in Section 1.1 and it provides three potential donor atoms (two carbons and one oxygen) and it can coordinate in at least three different ways (monodentate, bidentate chelate and bidentate bridging).

In spite of its similarity to the α-stabilized ylides $Ph_3P{=}C(H)COR$ already described, which are not air and moisture sensitive, the bis-ylide [$Ph_3PC(H)C(O)C(H)PPh_3$] is very reactive towards aerial oxygen and water.[46] The best starting point for the synthesis of complexes with this ylide was found to be the reaction of [$Pd(OOCCH_3)_2$]$_3$ with the bis-phosphonium salt [$Ph_3PCH_2C(O)CH_2PPh_3$]Cl_2, which results in the formation of the neutral *cis*-$Cl_2Pd\{[C(H)PPh_3]_2CO\}$ **19** in good yields (see Scheme 3).[47] Complex **19** reacts with $TlClO_4$ to give the dinuclear cationic [$Pd(\mu\text{-}Cl)\{[C(H)PPh_3]_2CO\}]_2[ClO_4]_2$ **20**. These complexes provide ideal starting materials for subsequent reactions, such as the synthesis of bis-solvate derivatives, reactions of cleavage of the chlorine bridging system by neutral ligands L, and metathesis of the bridging ligands by other monodentate or chelating groups, *etc*. (see Scheme 3).[47] With respect to the stereochemistry of these complexes, the crystal structure of **20** shows the bis-ylide acting as a C,C-chelating ligand through the two ylidic carbon atoms. Only one diastereoisomer is obtained (one of the *meso* forms) and this structure should be maintained in solution since only one diastereoisomer, with *RS* configurations within each fragment [Pd(C,C-ylide)], is observed for **19**, **20** and its derivatives in their NMR spectra. However, we have never observed the *RR*/*SS* forms, although these are preferred in other four-membered metallacycles containing a carbonyl group[48] (see below).

There are some remarkable facts concerning the reactivity of complex **20**. The first is that all of the complexes similar to type [$PdCl\{[C(H)PPh_3]_2CO\}L$]$^+$ possess, *trans* to the bis-ylide, L ligands with donor atoms which behave as borderline or hard bases (pyridines, N-bonded ylides). The same applies for [$Pd(\{[C(H)PPh_3]_2CO\}L_2$]$^{2+}$ (L or L_2 = acac, NCMe, N-bonded ylides) and [$Pd(\mu\text{-}X)\{[C(H)PPh_3]_2CO\}$]$_2^{2+}$ (X = OH, OOCMe). For instance, the cyano-stabilized ylide CPPY coordinates systematically through the N atom (never through the C atom) and other strong C-donor ylides such as CMPPY or DMPPY were not able to break the chlorine bridging system in **20**, nor even to displace the NCMe ligands from the bis-solvate [$Pd\{[C(H)PPh_3]_2CO\}(NCMe)_2$]$^{2+}$ **23**. In the same way, the μ-hydroxo ligands in the dimer [$Pd(\mu\text{-}OH)\{[C(H)PPh_3]_2CO\}$]$_2^{2+}$ appear to be truly stabilized. Once again, it seems that the soft nature of the ylidic carbons and the antisymbiotic effect are responsible for the aforementioned facts.

The second remarkable fact is the permanence of the *RS* configurations at the ylidic carbon atoms of the C,C-chelating bis-ylide in all the complexes obtained, that is, the chelate ligand seems to be configurationally stable, in spite of the ring strain present in four-membered metallacycles. The carbonyl oxygen is non-coplanar with the puckered Pd–C–C–C chelate ring and examination of the relative arrangement of the substituents at the chiral ylidic carbon in the crystal structure of **20** reflects the pseudo-equatorial location of the PPh_3 groups and the eclipsed axial arrangement of the ylidic H atoms. These *RS* configurations have also been observed in gold complexes in which the bis-ylide acts as a bridging ligand.[45] However, the configurations observed in other related chelating four-membered metallacycles containing a carbonyl group, for instance cyclobutanones[48] of stoichiometry [M(C(H)RC(O)-C(H)R)L_2] (M = Pd, Pt; R = CO_2Me, CO_2Et, Ph; L = neutral ligand), show similar deviations of planarity but also reveal that the preferred arrangement of the R substituents is one axial and one equatorial[48a–c,e] except in the case of R = Ph,[48d] in which both Ph groups are pseudo-equatorially arranged, probably due to the conjugation of the phenyl substituents with the π system of the oxodimethylenemethane ligand. Obviously, we cannot invoke a similar delocalization in our case to explain the stereochemistry observed, and we are currently researching in this area to determine why such an arrangement is adopted. The *RS* arrangement in metallated ylidic carbon atoms is a general phenomenon, probably related to the presence of short intramolecular P···O contacts.

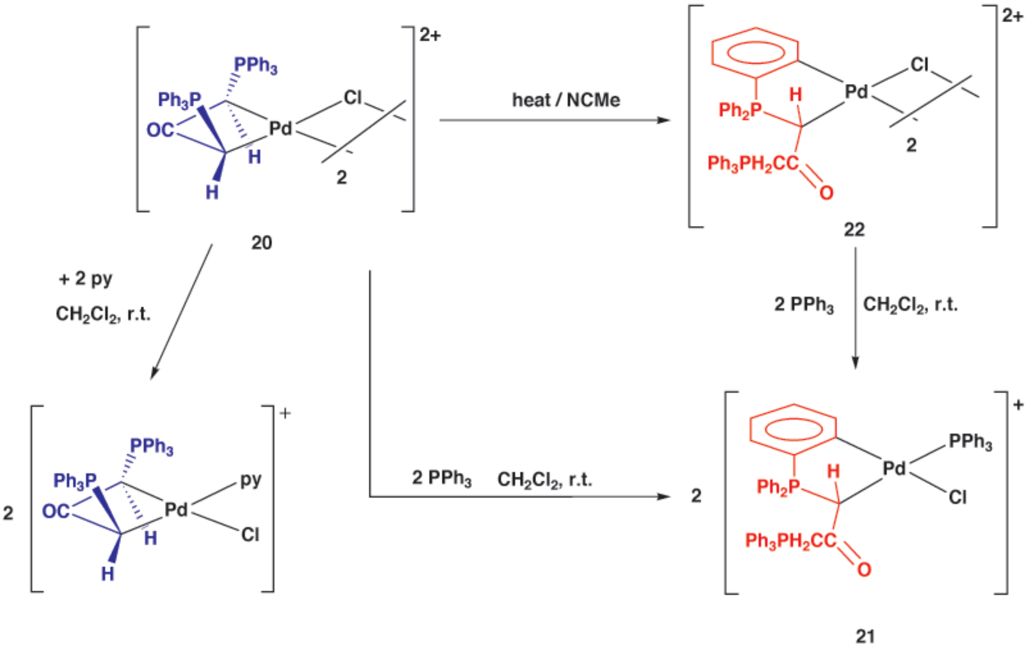
Finally, the third noteworthy aspect is the reactivity of **20** with strong soft donor ligands, such as phosphines, which promote a dramatic intramolecular rearrangement.

2.2. Orthometallation of bis-ylide complexes and reactivity

The reaction of **20** with two equivalents of PPh_3 results in the formation of the orthometallated derivative [PdCl{C_6H_4-2-PPh_2-*C*(H)C(O)CH_2PPh_3}(PPh_3)][ClO_4] **21** in which the metallated ligand is coordinated through the remaining ylidic carbon atom and one aryl carbon atom of a PPh_3 group (see Scheme 4). Although the orthometallation of an ylide ligand is not an unknown phenomenon,[49] the extremely easy rearrangement of the bis-ylide $[C(H)PPh_3]_2CO$ into the orthometallated group [C_6H_4-2-PPh_2-C(H)C(O)CH_2PPh_3] was unexpected.[50] The orthometallation of other keto-stabilized ylides has been performed either by thermal treatment of the metal-coordinated ylides[49b–f,j] or through their deprotonation with bases[49h] but we have not found similar examples of such ligand-promoted orthometallation. As expected, the thermal induction of the orthometallation is another plausible pathway. Thus, thermal treatment in refluxing NCMe of **20** results in the formation of the corresponding dinuclear orthometallated derivative [Pd(μ-Cl){C_6H_4-2-PPh_2-C(H)C(O)-CH_2PPh_3}]$_2$[ClO_4]$_2$ **22**, obtained as the mixture of diastereoisomers (*RR*/*SS*) and (*RS*/*SR*). Obviously, treatment of **22** with two equivalents of PPh_3 gives **21** by the simple cleavage of the chlorine bridging system (see Scheme 4).

The mechanism of the thermal rearrangement **20**→**22** has been studied in some detail and there are several parameters that control the global process.[50] The role of the phosphonium group, the solvent, the temperature, the net charge of the starting complex and the addition of halide ligands have been examined. The results obtained show that an increase in the number of alkyl groups on the P atom notably decreases the percentage of the orthometallated product and that the solvent must have a relatively high coordinating strength and a moderately high boiling point. Moreover, the comparison of the orthometallation of the species **20** and **19** (by monitoring the reaction by ^1H and $^{31}P\{^1H\}$ NMR) showed that the "active" species is the mononuclear [PdCl{$[C(H)PPh_3]_2CO$}(NCMe)]$^+$. In this intermediate complex an electrophilic attack by the metal on a phenyl group takes place and this is followed by an intramolecular acid–base reaction in which the proton resulting from the electrophilic substitution is captured by one of the ylidic carbon atoms (the C–H activation is assisted by a coordinated base), generating the phosphonium moiety. It seems that the driving force for this reaction is related to the steric repulsions between the two PPh_3 fragments and to the transformation of a four-membered ring into a more stable five-membered ring.

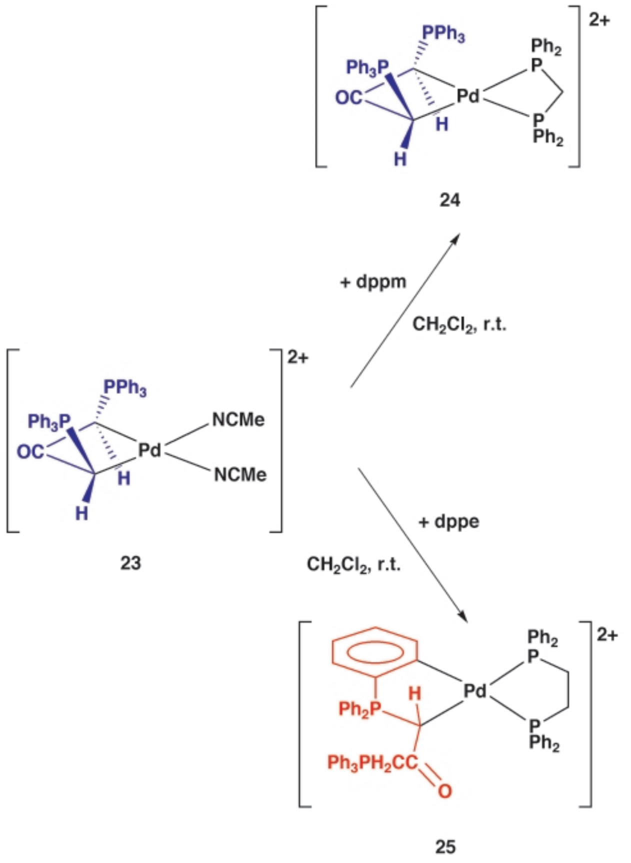
Taking advantage of these steric repulsions, we have investigated the reactivity of **20** and that of the solvate [Pd{$[C(H)PPh_3]_2CO$}$(NCMe)_2$][ClO_4]$_2$ **23** towards different neutral monodentate or bidentate ligands. Our purpose was to study (i) the influence of the nature of the donor atom and (ii) that of the steric requirements of the incoming ligands in the orthometallation reaction. With monodentate N-donor ligands (pyridine or lutidine) **20** reacts through cleavage of the bridging system, affording [PdCl{$[C(H)PPh_3]_2CO$}(L)][ClO_4] type compounds while reaction with monodentate P-donor ligands (phosphines), affords **21** type compounds by orthometallation



Scheme 4

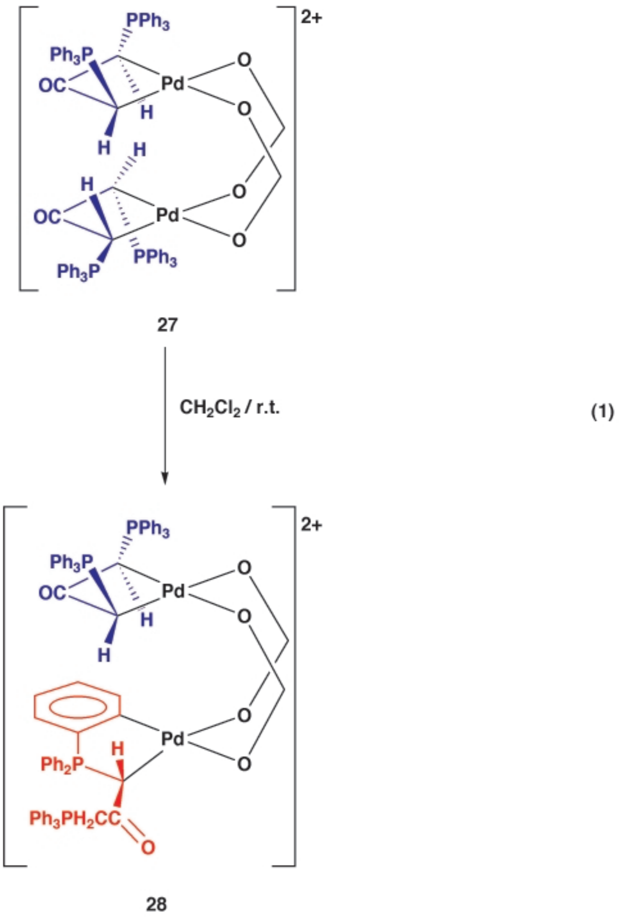
(see Scheme 4). Both reactions were performed in mild conditions (CH_2Cl_2, r.t.). One can thus assume that hard ligands (pyridines) are able to stabilize the chelating bis-ylide while soft ligands (phosphines) would not be stable and would encourage orthometallation. It must, however, be taken into account that pyridines can accommodate in a plane perpendicular to the molecular plane, and thus do not exert any considerable influence upon the ylidic $C(H)PPh_3$ group in a *cis* position, while the volume occupied by phosphines is considerably larger and such ligands may crowd the two *cis* ylidic $C(H)PPh_3$ fragments. As a result, in the case of pyridines the molecule remains stable while in the case of phosphines the molecule evolves to give a less hindered situation.

The reactions of **23** towards bidentate ligands under mild conditions (CH_2Cl_2, r.t.) are definitive proof of the importance of the steric interactions. Thus, **23** reacts with $Ph_2PCH_2PPh_2$ (dppm) to give $[Pd\{[C(H)PPh_3]_2CO\}(dppm\text{-}P,P')][ClO_4]_2$ **24** in which the bis-ylide remains intact and the dppm ligand is P,P-bonded (see Scheme 5). However, the reaction of **23** with $Ph_2PCH_2CH_2PPh_2$ (dppe) results in the formation of $[Pd\{C_6H_4\text{-}2\text{-}PPh_2\text{-}C(H)C(O)CH_2PPh_3\}(dppe\text{-}P,P')][ClO_4]_2$ **25**. Moreover, **23** reacts with 1,10-phenanthroline to give $[Pd\{C_6H_4\text{-}2\text{-}PPh_2\text{-}C(H)C(O)CH_2PPh_3\}(phen)][ClO_4]_2$ **26**, showing that the nature of the donor atom is not a determining factor in orthometallation, but that the size of the resulting metallacycle after coordination of the incoming ligand is critical. The dppm ligand shows a bite angle of about 74°,[51] while that of the dppe is about 86°.[52] Thus, the interactions between the Ph groups of the dppm ligand and the ylidic fragments $C(H)PPh_3$ are not strong enough to promote orthometallation, while in the case of dppe the two groups are in close proximity, as a result of the increase of the bite angle, and the orthometallation can easily be induced.

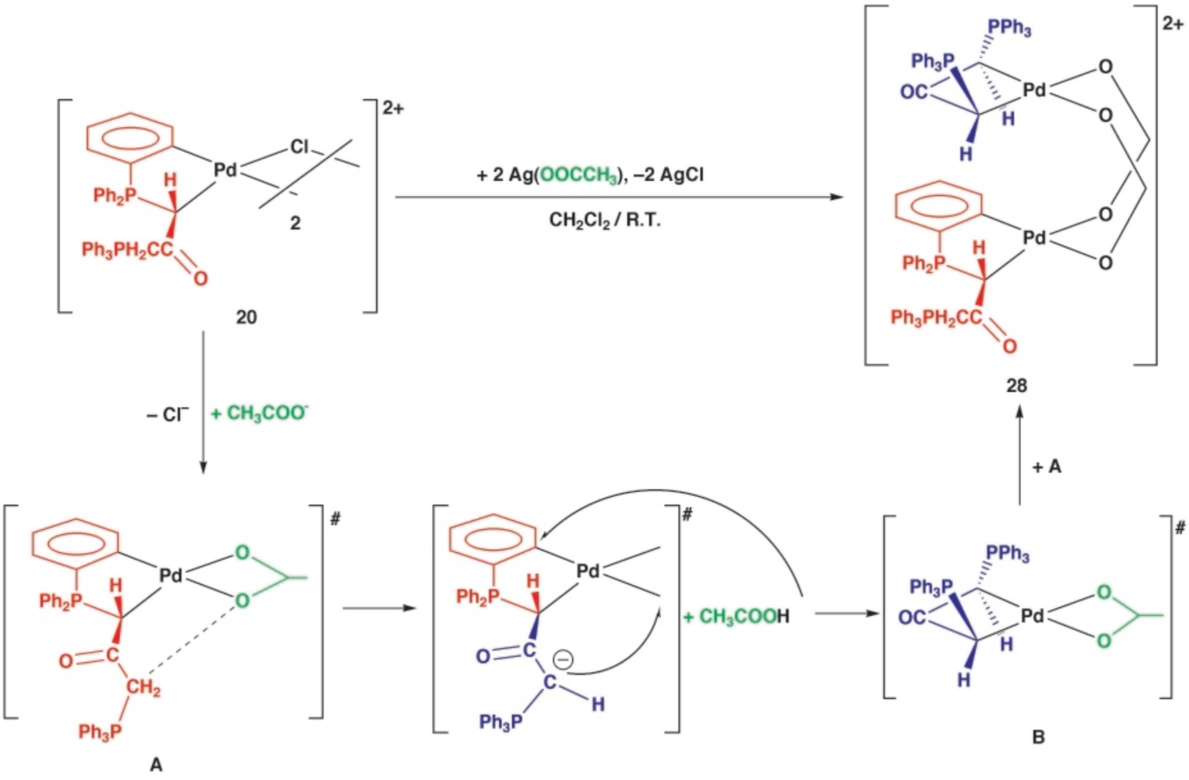


Scheme 5

Another interesting example is that represented by the spontaneous orthometallation of $[Pd(\mu\text{-}OOCMe)\{[C(H)PPh_3]_2CO\}]_2[ClO_4]_2$ **27** which evolves in solution to $[\{C_6H_4\text{-}2\text{-}PPh_2\text{–}C(H)C(O)CH_2PPh_3\}Pd(\mu\text{-}OOCMe)_2Pd\{[C(H)PPh_3]_2CO\}][ClO_4]_2$ **28** in quantitative yield [see eqn. (1)]. This reaction has two striking features. The first is the spontaneity of the reaction, since neither incoming ligands nor heating is required, and for which only the steric crowding in **27** (with an "open-book" structure) appears to be the driving force for orthometallation. The second is the fact that **28** contains only one orthometallated group. We have attempted the synthesis of the corresponding acetate-bridging orthometallated by the trivial reaction of **22** with two equivalents of AgOOCMe but, to our surprise, the reaction affords exclusively **28**; that is, we have induced, at some point, the reversibility of the orthometallation, probably by protonation of the $Pd–C_{aryl}$ bond with the acetic acid resulting from the reaction of the acetate anion and the phosphonium moiety (see Scheme 6).



We have also explored the reactivity of **22** towards deprotonating reagents of different natures,[53] and we have found new coordination modes of the bis-ylide, in addition to those already presented: (i) the C,C-chelating $[C(H)PPh_3]_2CO$ and (ii) the C,C-chelating orthometallated $[C_6H_4\text{-}2\text{-}PPh_2\text{-}C(H)C(O)CH_2\text{-}PPh_3]$ (see Fig. 4). The reaction of **22** with $Hg(OOCMe)_2$ gives $[Pd_2Hg(\mu\text{-}Cl)_2\{C_6H_4\text{-}2\text{-}PPh_2\text{-}\mathit{C}(H)CO\mathit{C}(H)PPh_3\}_2][ClO_4]_2$ **29** (Scheme 7) together with small amounts of **28**. The presence of **28** in the reaction mixture can be derived following the same considerations as those described in Scheme 6. Complex **29** contains a new and unprecedented bonding mode for the ylide (terdentate-C,C,C; see Scheme 7 and Fig. 4) since it is coordinated to the palladium center through the aryl carbon and through one ylidic carbon and it is also coordinated to the mercury center through the ylidic carbon generated by deprotonation of the phosphonium moiety present in **22**. The synthesis of this complex shows two interesting features. Firstly, the easy deprotonation of the methylene group bonded to the phosphonium by the acetate anion and the subsequent coordination of the ylide to the mercury center, avoiding the transmetallation which should occur by mercury-halide



Scheme 6

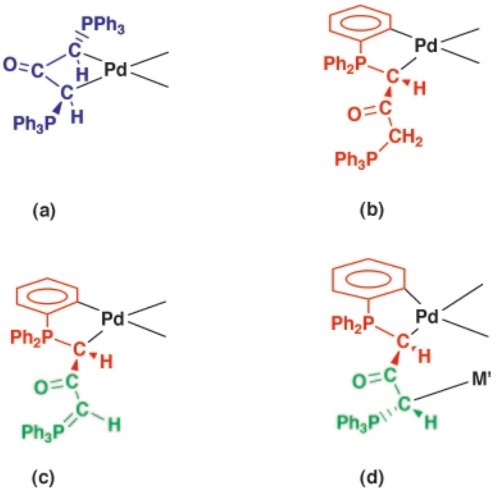


Fig. 4

abstraction (Hg(II) derivatives are good transmetallating reagents). Secondly, **29** is obtained as a single diastereoisomer (mixture of the two enantiomers) in spite of the presence of four chiral centers in the molecule. The synthesis is completely stereoselective and occurs in such a way that a given configuration in the carbon bonded to Pd induces a specific chirality at the ylidic carbon bonded to Hg ($R_{C(Pd)}$ induces $S_{C(Hg)}$ and $S_{C(Pd)}$ induces $R_{C(Hg)}$). Moreover, this stereoselective induction occurs *at reaction time* and resembles the situation found during the synthesis of complexes **19** and **20**, and their derivatives, and also that found in gold complexes with the bis-ylide acting as a bridging ligand.[45] This systematic arrangement of the $Ph_3P\text{–}C(H)(M)\text{–}C(O)\text{–}C(H)(M)\text{–}PPh_2R$ unit (R = Ph, C_6H_4-2) resembles that described in the case of the C,C-chelating $[C(H)PPh_3]_2CO$ bis-ylide and we are at present concentrating our efforts on discovering the driving force behind this stereoselectivity.

Other deprotonating reagents do not behave as $Hg(OOCMe)_2$ does towards **22**. Thus, $(NBu_4)[Au(acac)_2]$ or $(acac)AuPPh_3$ react with **22** giving the transmetallation of the acac ligand from the gold to the palladium center. However, dinuclear derivatives of stoichiometry $[Pd\{C_6H_4\text{-2-}PPh_2\text{-}C(H)COC(H)(AuPPh_3)PPh_3\}(L\text{-}L)]^{n+}$ can be obtained by reaction of $[Pd\{C_6H_4\text{-2-}PPh_2\text{-}C(H)COCH_2PPh_3\}(L\text{-}L)]^{n+}$ with $(acac)AuPPh_3$ (see Scheme 7, L–L = Cl, PPh_3; phen). These dinuclear compounds in which the ylide acts as C,C,C-terdentate are also obtained as a single diastereoisomer ($R_{C(Pd)}/S_{C(Au)}$) and ($S_{C(Pd)}/R_{C(Au)}$) showing, once again, the selectivity that exists in the replacement of one methylenic proton of the $\text{–}CH_2PPh_3$ unit by a metal center. The isolation of complexes containing the orthometallated moiety and a "free" ylide group is easily accomplished by treatment of the complexes $[Pd\{C_6H_4\text{-2-}PPh_2\text{-}C(H)COCH_2PPh_3\}(L\text{–}L)]^{n+}$ with strong bases such as $Na[N(SiMe_3)_2]$ or NBu_4OH. This deprotonation reaction results in the formation of complexes of stoichiometry $[Pd\{C_6H_4\text{-2-}PPh_2\text{-}C(H)COC(H)\text{=}PPh_3\}(L\text{–}L)]^{(n-1)+}$ (see Scheme 7) which, in turn, react with electrophilic metal centers, for instance ClAuL, affording $[Pd\{C_6H_4\text{-2-}PPh_2\text{-}C(H)COC(H)(AuCl)(PPh_3\}(L\text{–}L)]^{(n-1)+}$ with complete stereoselectivity (only one stereoisomer observed).

Throughout this second section, we have briefly described the coordination chemistry of the bis-ylide $[C(H)PPh_3]_2CO$ and some of its possible transformations. Four different structural possibilities have been fully characterized to date [C,C-chelate; C,C-orthometallated; C,C-orthometallated + "free" ylide; and C,C,C-terdentate (Fig. 4)] while, in the most favorable of cases, we had proposed three. As we concluded at the end of Section 1.2, this field is still open and we are now working on the reactivity of complex **22** towards other deprotonating reagents, aiming to obtain new coordination modes and structural situations.

Acknowledgements

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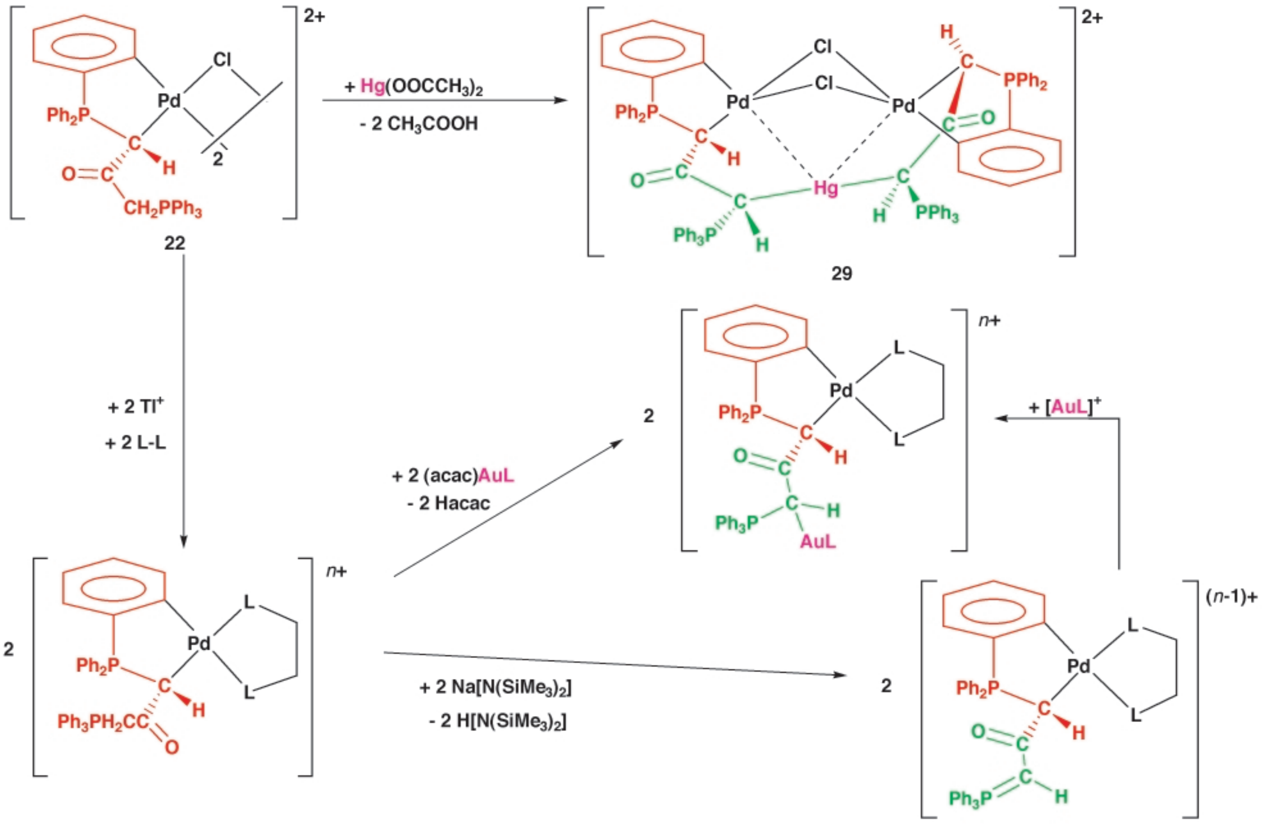

Scheme 7

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