Synthesis and reactivity of Pt^{II} complexes containing the orthometallated ligand [C_6H_4-2-$PPh_2C(H)COCH_2PPh_3$]

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The reaction of $PtCl_2(NCPh)_2$ with the ylide [Ph_3P=C(H)$COCH_2PPh_3$]ClO_4 (1 : 1 molar ratio, refluxing $CHCl_3$) affords *trans*-[$PtCl_2$(NCPh){C(H)PPh_3C(O)CH_2PPh_3}]ClO_4 **1**. However, the reaction of $PtCl_2$ (CH_2Cl_2, r.t.) or $PtCl_2(NCMe)_2$ (2-methoxyethanol, reflux) with the ylide [Ph_3P=C(H)$COCH_2PPh_3$]ClO_4 (1 : 1 molar ratio) affords the orthometallated [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(μ-Cl)]$_2$(ClO_4)$_2$, **2**, as a mixture of diastereoisomers **2a**–**d**. Treatment of **2** with PPh_3 (1 : 2 molar ratio) affords [PtCl{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(PPh_3)](ClO_4), **3**, as a single geometric isomer. The reaction of **2** with $AgClO_4$ (1 : 2 molar ratio) in NCMe gives the solvato complex [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(NCMe)$_2$](ClO_4)$_2$, **4**, while the reaction of **2** with Tl(acac) (1 : 2 molar ratio) gives [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(acac)](ClO_4), **5**. The dicationic complexes [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(dppe)](ClO_4)$_2$, **6**, and [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}(phen)](ClO_4)$_2$, **7**, can be obtained by reaction of **2** with $AgClO_4$ followed by addition of the appropiate ligand (1 : 2 : 2 molar ratio). The reaction of **6** with NaH gives [Pt{C_6H_4-2-PPh_2C(H)COCH=PPh_3}(dppe)](ClO_4), **8**, while the reaction of **4** with PPh_3 and NaH gives [Pt{C_6H_4-2-PPh_2C(H)COCH=PPh_3}(PPh_3)$_2$](ClO_4), **9**. Complexes **8** and **9**, which contain a "free ylide" functionality, react with ClAu(tht) to give [Pt{C_6H_4-2-PPh_2C(H)CO*C*H(AuCl)PPh_3}(dppe)](ClO_4), **10**, and [Pt{C_6H_4-2-PPh_2C(H)COCH(AuCl)PPh_3}(PPh_3)$_2$](ClO_4), **11**. In the heterobimetallic complexes **10** and **11** the ylide ligand acts as a *C*,*C*,*C*-terdentate ligand and, in spite of the presence of two chiral centers, only one diastereoisomer (as the mixture of two enantiomers) is observed. All complexes were characterized on the basis of their spectroscopical and analytical parameters.

One of our main current resarch subjects is the coordination chemistry of Pd^{II} and Pt^{II} with α-stabilized phosphoylides.[1] Amongst them, the neutral bis-ylide [C(H)=PPh_3]$_2$CO has shown a notable reactivity, not only in Pd^{II} derivatives[2–5] but also in gold and silver complexes, as it has been reported by other research groups.[6] One of the most interesting reactions of this bis-ylide is its intramolecular rearrangement from the *C*,*C*-chelating form [*C*(H)PPh_3]$_2$CO to the C,C-orthometallated form [C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$],[3] which can be induced through a variety of methods. This rearrangement occurs through a C–H bond activation process in one Ph group of a PPh_3 fragment, followed by an acid-base intramolecular reaction.[3] Pt^{II} complexes have been employed frequently to promote C–H bond activation,[7] and interest in cycloplatination reactions is growing continuously (as evidenced by the number of contributions that have appeared in this field[8–20]), because of their practical importance.[21] On the other hand, although the orthometallation of ylide ligands is a known reaction, not only for the platinum group metals[22–29] but also in early transition metals such as Nb,[30] the subsequent reactivity of the orthometallated ylide ligands has been rarely reported.[4,5,24]

Due to our interest in C–H bond activation processes and in orthometallated systems derived from ylide groups, we have decided to explore the reactivity of some simple complexes of Pt^{II} such as $PtCl_2$ or $PtCl_2(NCR)_2$ (R = Me, Ph) towards the phosphonium ylide salt [Ph_3P=C(H)C(O)CH_2PPh_3]ClO_4. In the case of the nitrile complexes one should expect, at a first glance, a simple displacement of the coordinated nitrile by the incoming ylide, but it has been previously reported that the reactions of $PtCl_2(NCR)_2$ (R = Me, Ph, C_6F_5) with stabilized ylides are actually more complicated, giving different types of C–C bond coupling products,[31–33] resulting from the nucleophilic attack of the C_α of the ylide on the nitrilic carbon. Thus, several reactivity patterns should be considered in this kind of reaction.

In this paper, we report different synthetic methods to achieve the orthometallation of the phosphonium ylide [Ph_3P=C(H)C(O)CH_2PPh_3]ClO_4 promoted by Pt^{II} complexes. Interestingly, the reactions of the nitrile precursors $PtCl_2(NCPh)_2$ and $PtCl_2(NCMe)_2$ with the aforementioned phosphonium ylide proceed without attack over the coordinated nitriles and, in some cases, afford the orthometallated derivatives under very mild conditions (CH_2Cl_2, r.t.). We have also studied the reactivity of the *C*,*C*-orthometallated derivatives [Pt{C_6H_4-2-PPh_2C(H)$COCH_2PPh_3$}L_n]$^{n+}$ towards deprotonating reagents, which results in the synthesis of "free-ylide"-containing complexes [Pt{C_6H_4-2-PPh_2C(H)COCH=PPh_3}L_n]$^{(n-1)+}$ and their subsequent reactivity towards electrophilic reagents, such as ClAu(tht) (tht = tetrahydrothiophene), to afford the heterobimetallic species [Pt{C_6H_4-2-PPh_2C(H)CO*C*H(AuCl)PPh_3}L_n]$^{(n-1)+}$, in which the orthometallated ylide group acts as a *C*,*C*,*C*-terdentate ligand.

Results and discussion

Reactivity of $PtCl_2(NCR)_2$ and $PtCl_2$ with [Ph_3P=C(H)C(O)CH_2PPh_3]ClO_4

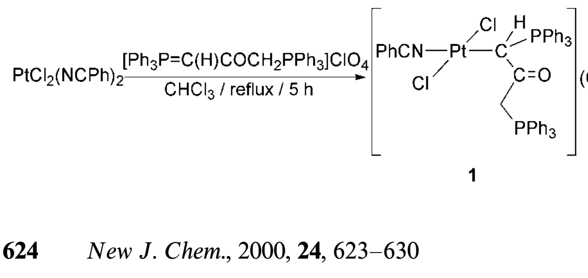
The reaction of $PtCl_2(NCPh)_2$ with [Ph_3P=C(H)C(O)CH_2PPh_3]ClO_4 (1 : 1 molar ratio, $CHCl_3$, reflux, 5 h) results in the formation of *trans*-[$PtCl_2$(NCPh)- {C(H)PPh_3-

$C(O)\text{-}CH_2PPh_3\}]ClO_4$, **1**, eqn. (1), according to its analytical and spectroscopic data (see Experimental). The reaction occurs by simple displacement of only one coordinated nitrile and its substitution by the ylide, which coordinates through the ylidic C atom. This result contrasts with related reports of the reactivity of Pt^{II}-nitrile complexes with α-keto-stabilized ylides $R_3P{=}C(H)CO_2R$, which result in the attack of C_α on the coordinated nitrile.[31–33] The difference in the observed reactivity could be related to the different basicity associated with the ylidic carbon.

The stretching ν(CO) band appears at 1654 cm^{-1} in the IR spectrum, clearly shifted to higher frequencies with respect to the starting ylide (1590 cm^{-1})[6] and suggesting its *C*-coordination. The Cl-*trans*-to-Cl geometry of **1** can be inferred from the observation of only one Pt–Cl absorption (309 cm^{-1}), and the presence of coordinated NCPh from the absorption located at 2300 cm^{-1}. The ^1H NMR spectrum shows the resonance attributed to the ylidic CH proton at 6.22 ppm, as a broad singlet, and flanked by ^{195}Pt satellites. The value of the coupling constant $^2J_{Pt\text{-}H} = 117$ Hz is in good agreement with previously reported values for Pt^{II} C-bonded ylides.[26,34] This spectrum shows also the presence of the AB part of an ABX spin system, attributed to the methylene protons of the $–CH_2PPh_3$ group (see Experimental). In addition, the $^{31}P\{^1H\}$ NMR spectrum shows the two chemically inequivalent P atoms as two doublets ($^4J_{P\text{-}P} = 10$ Hz), one of them showing ^{195}Pt satellites ($^2J_{Pt\text{-}P} = 76$ Hz), and the $^{13}C\{^1H\}$ NMR spectrum confirms the C-bonding of the ylide $[Ph_3PC(H)C(O)CH_2PPh_3]ClO_4$ since the ylidic carbon appears at 21.52 ppm as a doublet of doublets, although due to the low intensity of the resonance we were unable to find the corresponding platinum satellites. The presence of coordinated NCPh was also evident from the $^{13}C\{^1H\}$ NMR spectrum since the nitrilic carbon appears at 114.99 ppm, typical for coordinated nitriles.[35]

Complex **1** has the ylide $[Ph_3PC(H)C(O)CH_2PPh_3]ClO_4$ selectively coordinated through the ylidic carbon. This result contrasts with those obtained in Pd^{II} complexes, in which we were unable to obtain this coordination mode.[2] As far as we know, only one example of this bonding mode has been reported, the gold(I) derivative $[AuCl\{CH(PPh_3)\text{-}COCH_2PPh_3\}]ClO_4$.[6] Owing to the presence of the phosphonium moiety in **1**, and due to our recent experience in the deprotonation of related systems,[4,5] we have performed several reactions in order to obtain Pt^{II} derivatives with the *C*,*C*-chelating ligand $[C(H)PPh_3]_2CO$, which should arise from direct deprotonation of **1** and simultaneous abstraction of one chloride ligand. However, the reactivity of **1** towards deprotonating reagents such as NaH (1 : 1 molar ratio, THF, r.t.), NBu_4OH (1 : 1 molar ratio, MeOH, r.t.), Tlacac (1 : 1 or 1 : 2 molar ratio, $CHCl_3$, r.t. or reflux) or $(acac)AuPPh_3$ (1 : 1 molar ratio, CH_2Cl_2, r.t.) only gave intractable mixtures of several products, which were not analyzed further.

Other reactions were performed in order to obtain complexes related to **1** with the ylide C-bonded. However, $PtCl_2(NCMe)_2$ does not react with $[Ph_3P{=}C(H)\text{-}C(O)CH_2PPh_3]ClO_4$ under the same conditions (1 : 1 molar ratio, $CHCl_3$, reflux, 5 h) and the starting materials were recovered. Probably, the different lability of the two nitrile ligands accounts for this different reactivity. Moreover, $PtCl_2$ reacts with $[Ph_3P{=}C(H)C(O)CH_2PPh_3]ClO_4$ (1 : 1 molar ratio, CH_2Cl_2, r.t., 4 days) but gives a very different complex. At the end of the reaction time, the $PtCl_2$ is almost completely dissolved. After filtration, removal of the solvent and Et_2O addition, the mixture of the orthometallated complexes **2a–d** is obtained as a cream solid [see eqn. (2) (top)]. The presence of four isomers can be inferred from the NMR spectra (see below and Experimental) but two of the isomers, **2a** and **2b**, are always present in higher amounts than the other two, **2c** and **2d**.



(1)

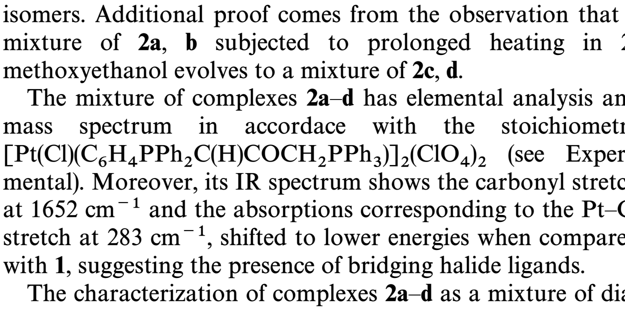
1

The mild conditions employed in the cycloplatination of the phosphonium ylide $[Ph_3P{=}C(H)C(O)CH_2PPh_3]ClO_4$ contrast with the previous reports of orthometallation of stabilized ylides. Thus, the ylide $Ph_3P{=}C(H)COMe$ is orthometallated by reaction with $PtCl_2$ in refluxing NCMe for 44 h,[22] while the complex *trans*-$PtCl_2\{C(H)PPh_3C(O)Me\}_2$ evolves in refluxing THF (8 h) or refluxing NCMe (44 h), resulting in the formation of $\{PtCl_2[CH(COCH_3)PPh_2(o\text{-}C_6H_4)]\text{-}[Ph_3PCH_2COCH_3]\}$.[26] However, the authors also reported that the latter transformation can also be performed in CH_2Cl_2 at room temperature for several days.[26]

In order to shed light on the kinetic or thermodynamic nature of the different pairs of isomers **2a**, **b** and **2c**, **d** obtained and since the orthometallation of the ylides is usually promoted at high temperatures, we have refluxed equimolar amounts of $PtCl_2(NCMe)_2$ and $[Ph_3P{=}C(H)C(O)CH_2PPh_3]ClO_4$ in different solvents. The best results were obtained in 2-methoxyethanol, a solvent that has been employed in the orthometallation of bulky tertiary phosphines.[36] The reaction of $PtCl_2$ with $[Ph_3P{=}C(H)C(O)CH_2PPh_3]ClO_4$ in 2-methoxyethanol [1 : 1 molar ratio, reflux, 5 h, see eqn. (2) (bottom)] results in the almost exclusive formation of the isomers **2c**, **d** according to the NMR data. Thus, it seems that the isomers obtained at room temperature, **2a**, **b**, are the kinetic isomers and those obtained at higher temperatures, **2c**, **d**, are the thermodynamic isomers. Additional proof comes from the observation that a mixture of **2a**, **b** subjected to prolonged heating in 2-methoxyethanol evolves to a mixture of **2c**, **d**.

The mixture of complexes **2a–d** has elemental analysis and mass spectrum in accordace with the stoichiometry $[Pt(Cl)(C_6H_4PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ (see Experimental). Moreover, its IR spectrum shows the carbonyl stretch at 1652 cm^{-1} and the absorptions corresponding to the Pt–Cl stretch at 283 cm^{-1}, shifted to lower energies when compared with **1**, suggesting the presence of bridging halide ligands.

The characterization of complexes **2a–d** as a mixture of diastereoisomers containing the orthometallated $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3]$ ligand has been made on the basis of their NMR data. The ^1H NMR spectrum of **2a–d** shows the presence of four different resonances attributed to the ylidic Pt–C*H* protons and four AB parts of ABX spin systems, attributed to the methylene protons of the $–CH_2PPh_3$ groups (X = ^{31}P nucleus). The $^{31}P\{^1H\}$ NMR of **2a–d** shows also the presence of four sets of AX spin systems: the part A of the resonances appears centered around 20 ppm ($–CH_2PPh_3$) and the part X appears spread from 24 to 30 ppm (PPh_2). The $^{13}C\{^1H\}$ NMR spectrum provides fundamental evidence for the presence of the orthometallated *C*,*C*-chelating ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3]$. Thus, the APT spectrum (attached proton test) shows negative doublet resonances in



(2)

2a-d

syn (*RR*/*SS*) } **2a, 2b**
syn (*RS*/*SR*)

anti (*RR*/*SS*) } **2c, 2d**
anti (*RS*/*SR*)

the range 135–144 ppm, the typical region for the appearance of the orthometallated C_1 carbon atom {the reported value for $[Pt(\mu\text{-}Cl)CH_3COCHP(C_6H_4)(C_6H_5)_2]_2 \cdot 2\ CDCl_3$ is 136.9 ppm).[22]

Once the orthometallated dinuclear nature of complexes **2** is established, the explanation of the presence of four different isomers could be explained by assuming that we have two different arrangements of the $[Pt(Cl)(C_6H_4PPh_2\text{-}C(H)COCH_2PPh_3)]$ fragments: *syn* and *anti*. In turn, the *syn* isomer possess two chiral centers (the two ylidic carbon atoms bonded to the Pt center) and thus we have again two possibilities: *syn* (*RR*/*SS*) and *syn* (*RS*/*SR*), which appear as two different products. In the same way, we could have *anti* (*RR*/*SS*) and *anti* (*RS*/*SR*) thus giving four different diastereoisomers, each as the racemic mixture of two enantiomers. The assignment of the *anti* isomers to the products **2c**, **d** has been made by similarity of the chemical shifts, and of the shape of the resonances of the ^1H NMR spectrum of the mixture, with those observed in the corresponding Pd^{II} complex[3] $[Pd(\mu\text{-}Cl)\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}]_2(ClO_4)_2$, which proved to be the *anti* isomers.[4] Thus, the compounds **2a**, **b** have been assigned to the *syn* isomers.

With respect to the mechanism of the orthometallation, we have some evidence to believe that the reaction in CH_2Cl_2 occurs in a similar way to that described[26] for the cycloplatination of $[PtCl_2\{C(H)PPh_3C(O)Me\}_2]$. In this report, the intramolecular metallation seems to be promoted by the presence of traces of HCl and it is completely inhibited in the presence of K_2CO_3. In the same way, we have performed the reaction of $PtCl_2$ with equimolar amounts of $[Ph_3P\mathbf{2}C(H)C(O)CH_2PPh_3]ClO_4$ in CH_2Cl_2 and in THF, in the presence or absence of Na_2CO_3, and we have observed cycloplatination only in the reaction carried out in CH_2Cl_2 in the absence of Na_2CO_3 (all reactions at room temperature). We have not performed experiments in order to ascertain which mechanism operates in the thermal orthometallation in 2-methoxyethanol.

Reactivity of the cycloplatinated derivatives 2a–d

Obviously, the reactivity of the four isomers in cleavage reactions of the chloride bridging system is the same. The reaction of **2a**–**d** (different molar ratios **a** : **b** : **c** : **d**) with PPh_3 (1 : 2 molar ratio) gives $[Pt(Cl)\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2\text{-}PPh_3\}(PPh_3)](ClO_4)$, **3**, as a single isomer and in good yields (see Scheme 1). When the reaction is monitored by $^{31}P\{^1H\}$ NMR (CD_2Cl_2, r.t.) the spectroscopic yield of **3** is 100%, and we have not detected unreacted **2** in the solution, nor other isomers of **3**. Complex **3** was obtained, in preparative scale, after evaporation of the solvent to dryness and addition of MeOH or Et_2O as a white solid. Its elemental analysis and mass spectrum are in good agreement with the proposed stoichiometry. The IR spectrum of **3** shows the carbonyl absorption at 1643 cm^{-1} and the Pt–Cl stretch at 283 cm^{-1}, typical for a terminal chloride trans to a carbon atom.[26] Further characterization of **3** comes from the analysis of its NMR data. The ^1H NMR spectrum shows only one set of resonances, suggesting the presence of a single geometric isomer. The ylidic CH proton appears at 4.84 ppm as a doublet of doublets of doublets, due to its coupling with three different P atoms, and suggesting that the PPh_3 ligand is trans to the ylidic carbon, as it has been observed in its Pd homolog. The methylenic CH_2P protons appear at 4.95 and 5.73 ppm, as the AB part of an ABX spin system ($X = {}^{31}P$). The $^{31}P\{^1H\}$ NMR spectrum of **3** shows the presence of only one set of three resonances, corresponding to the three chemically inequivalent P nuclei of the molecule. The coordinated PPh_3 appears at 24.10 ppm as a doublet with ^{195}Pt satellites ($^1J_{Pt\text{-}P} = 3623$ Hz), the P atom in the cycloplatinated ring appears at 21.90 ppm as a doublet of doublets with unresolved ^{195}Pt satellites (a broadening of the base of the signal) and the phosphonium group appears at 20.17 ppm as a doublet.

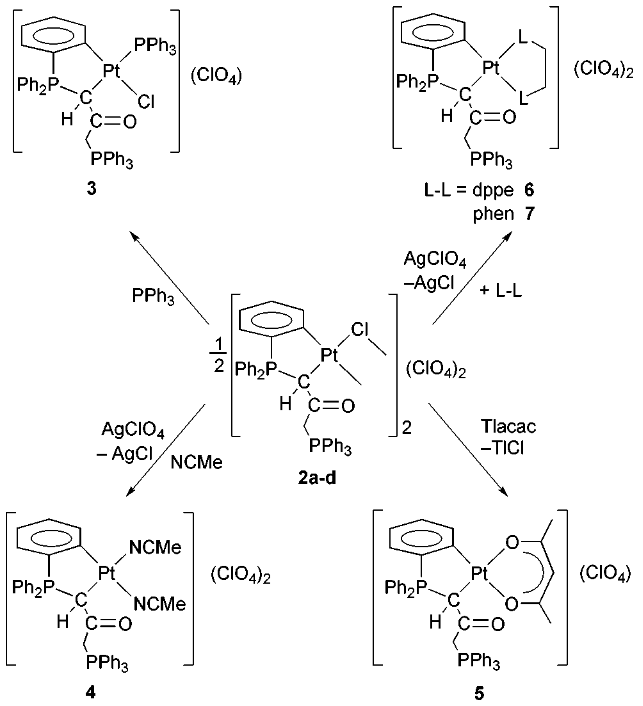
The synthesis of **3** as a single isomer resembles that of the related Pd(II) derivative $[Pd(Cl)\{C_6H_4\text{-}2\text{-}PPh_2C(H)\text{-}COCH_2PPh_3\}(PPh_3)](ClO_4)$.[3] In the Pd(II) complex, this selectivity was explained taking into account the antisymbiotic behavior of the soft Pd(II) metal center,[1,37–41] and similar arguments can be invoked here to explain this similar selectivity of the soft Pt(II) center.[37,39] In our experience, in all complexes of Pd^{II} and Pt^{II} containing the *neutral* orthometallated ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3]$, the coordination of an incoming phosphine ligand always occurs at the trans position to the ylidic carbon. It has been recently reported that the mutual destabilizing effect of trans ligands increases with their trans influence.[41] According to this effect, and taking into account that the trans influence of the aryl group is higher than that of the phosphine ligand ($Ar > PR_3$), the decreasing order of destabilizing effects should be $Ar/Ar > Ar/PR_3 > PR_3/PR_3$.[41] This effect has been called *transphobia*.[41,42]

We can now propose the inclusion of a new member in this sequence, according to our experimental data. Since it seems that the trans influence decreases in the order $Ar > C_{ylide} > PR_3$, the latter sequence of destabilizing effects could be extended as follows: $Ar/Ar > Ar/C_{ylide} > Ar/PR_3 > C_{ylide}/PR_3 > PR_3/PR_3$, though we do not yet have experimental evidence to include in a precise position the term C_{ylide}/C_{ylide}. The trends described here have found wide support in the experimental work.

Nevertheless, we are aware of the existence of exceptions to this rule, some of which have been reported by us[4] and by other authors,[25] but, in general, the *transphobia* rule gives accurate predictions. It is clear that antisymbiosis and the trans influence are not the sole parameters governing the final stereochemistry of a given complex. For instance, subtle variations in the ligands can alter dramatically the predicted stereochemistry, as in the case of $[Pd(Cl)\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(PPh_3)](ClO_4)$ (1 isomer)[3] and $[Pd(Cl)\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3\}(PPh_3)]$ (2 isomers),[4] for which the only difference is the presence of a phosphonium fragment or an ylide group, respectively, or in the case of the complex $[PdCl\{\kappa^2\text{-}C_6H_3[PTo_2\text{-}CH(Py\text{-}2')\text{-}2]Me\text{-}4\}(PEt_3)]$,[25] which is obtained as a mixture of two isomers (PEt_3 *trans* C_{aryl} and PEt_3 *trans* C_{ylide}).

On the other hand, the solvate $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(NCMe)_2](ClO_4)_2$, **4**, can be obtained, as a white solid, by reaction of the mixture **2a**–**d** with $AgClO_4$ (1 : 2 molar ratio) in NCMe at room temperature, filtration of the precipitated AgCl, evaporation of the solvent to dryness and treatment of the oily residue with *n*-hexane. The elemental analysis and mass spectrum of **4** are in good agreement with the proposed stoichiometry. The presence of two NCMe ligands can be inferred from the IR spectrum (absorptions at 2322 cm^{-1}), which also shows the $\nu(CO)$ band at 1670 cm^{-1}. The ^1H NMR spectrum shows the presence of resonances attributed to two nitrile ligands (two singlets at 2.46 and 2.41 ppm), to the ylidic CH proton (a doublet at 5.33 ppm) and to the methylene protons. The last resonance appears as a doublet (instead of a well-resolved AB spin system), probably due to isochrony of the two protons, which transforms the AB spin system into an A_2 system.[43] This deceptively simple A_2 spin system is coupled with the ^{31}P nucleus with the same coupling constant ($^2J_{P\text{-}H} = 12.3$ Hz). The $^{31}P\{^1H\}$ NMR spectrum shows, as expected, an AX spin system (30.03 and 21.06 ppm).

The chlorine ligands in **2** can be substituted by the acac ligand (acac = acetylacetonate) by reaction of **2** with Tl(acac) (1 : 2 molar ratio, CH_2Cl_2, r.t.). After removal of the TlCl and solvent evaporation, the complex $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(acac)](ClO_4)$, **5**, (see Scheme 1) was



Scheme 1

obtained, according to its elemental analysis and mass spectrum. The spectroscopic data of **5** are also in keeping with the proposed stoichiometry. The IR spectrum shows absorptions attributed to the carbonyl stretch of the ylide (1656 cm^{-1}) and to the acac ligand (1558 and 1520 cm^{-1}). The ^{1}H NMR shows the expected resonances for the CH (acac) proton (5.24 ppm), the CH_2P protons (5.25 ppm), the CH (ylide) proton (4.71 ppm) and the methyl (acac) protons (1.89 and 1.58 ppm). Once again, the $^{31}P\{^{1}H\}$ NMR spectrum shows an AX spin system (30.36 and 21.12 ppm).

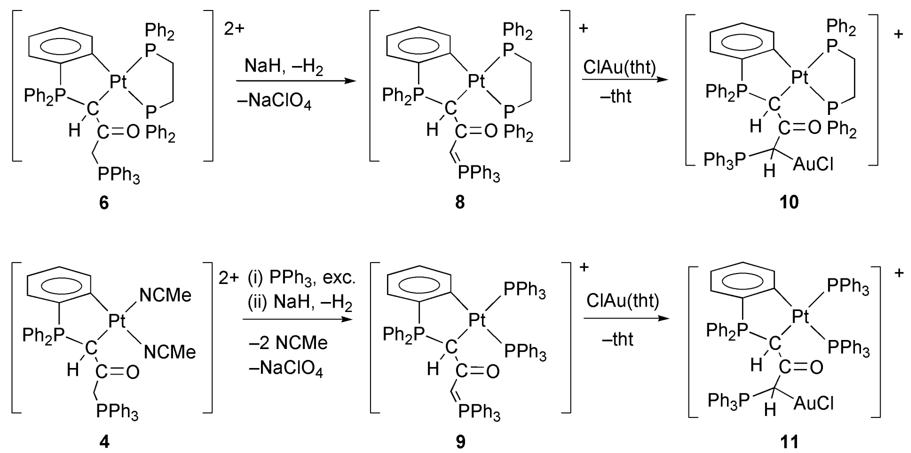
Finally, dicationic complexes of stoichiometry $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(L\text{-}L)](ClO_4)_2$ (L-L = dppe **6**, phen **7**) can be obtained by reaction of **2** with $AgClO_4$ (1 : 2 molar ratio, THF, r.t) (see Scheme 1), filtration of the AgCl, and subsequent addition of the L-L ligands (molar ratio **2** : L-L = 1 : 2) to the resulting solution of the solvated species $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(THF)_x](ClO_4)_2$. The analytical and spectroscopic data of **6** and **7** are in good agreement with the proposed stoichiometry. The IR spectra show absorptions attributed to the carbonyl stretch of the ylide, which in both cases appears at 1657 cm^{-1}. The ^{1}H NMR spectra shows the expected resonances for the dppe or the phen groups in an asymmetric environment (inequivalence of the two halves of each ligand). In addition, the ^{1}H NMR spectrum of **6** shows the CH (ylide) as a triplet (5.36 ppm, $^{2}J_{P\text{-}H} = {^{3}J_{Ptrans\text{-}H}} = 6.3$ Hz) with ^{195}Pt satellites ($^{2}J_{Pt\text{-}H} = 80$ Hz) and the diastereotopic CH_2P protons (4.29 and 3.78 ppm) as the AB part of an ABX spin system. The $^{31}P\{^{1}H\}$ NMR spectrum of **6** shows the presence of four resonances corresponding to the four chemically inequivalent P atoms of the molecule. For complex **7**, the CH (ylide) proton appears at 5.80 ppm and the CH_2P protons at 5.47 and 5.15 ppm. As expected, the $^{31}P\{^{1}H\}$ NMR spectrum of **7** shows an AX spin system (26.55 and 20.79 ppm).

Deprotonation of complexes 3–7

Owing to the presence of the phosphonium group $-C(O)CH_2PPh_3$ in complexes **3**–**7**, we have attempted the deprotonation of these compounds with a variety of bases in order to obtain neutral or monocationic derivatives containing the free ylide unit $-C(O)C(H){=}PPh_3$, in a similar way to that described for Pd complexes.[4] However, the reactivity of **3**–**7** with bases such as NBu_4OH, which have given excellent results in Pd complexes,[4] did not give clean reactions in this case and complex mixtures were obtained. The same results were observed in the reaction of **3** with NaH, and the reaction of **4** or **5** with NaH was not attempted.

The reactivity of **6** with NaH was more successful. Thus, the treatment of a THF suspension of **6** with an excess of NaH affords the monocationic derivative $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3\}(dppe)](ClO_4)$, **8**, (see Scheme 2) according to its elemental analysis and mass spectrum (see Experimental). The IR spectrum of **8** shows the carbonyl absorption at 1529 cm^{-1}, that is, shifted 128 cm^{-1} to lower energies with respect to the starting compound **6** and in good agreement with the presence of the free ylide unit $-C(O)C(H){=}PPh_3$. The NMR spectra provide further characterization. The ^{1}H NMR spectrum shows, in addition to the aromatic resonances and those expected for the methylene protons of the dppe ligand, a triplet centered at 4.15 ppm (attributed to the Pt–CH proton) and a new doublet at 3.09 ppm (relative intensity 1 : 1). This last resonance showing a value of the coupling constant $^{2}J_{P\text{-}H}$ of 25.2 Hz, very similar to those observed for the free ylides, and which is attributed to the ylidic proton of the "free ylide" group. The $^{31}P\{^{1}H\}$ NMR is also in good agreement with the proposed stoichiometry, since the resonance at 21.13 ppm in the starting product **6** is not observed and a new resonance at 13.60 ppm appears, corresponding to the free ylide phosphorus.

The synthesis of complex $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)\text{-}COCH{=}PPh_3\}(PPh_3)_2](ClO_4)$, **9**, (see Scheme 2) is not as straightforward as that described for complex **8**. The reaction of the bis-acetonitrile complex **4** with an excess of PPh_3 should result in the replacement of the two NCMe ligands by two PPh_3 groups or, at least, in the exchange of one NCMe by one PPh_3, giving the complex $[Pt\{C_6H_4\text{-}2\text{-}$



Scheme 2

$PPh_2C(H)COCH_2PPh_3\}(PPh_3)(NCMe)](ClO_4)_2$, by analogy to the observed behavior in Pd(II) complexes.[3] Thus, although the bis-phosphine derivative $[Pd\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(PPh_3)_2](ClO_4)_2$ could not be obtained, the complex $[Pd\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}(PPh_3)(NCMe)](ClO_4)_2$, containing one PPh_3 group, was synthesized in high yield and characterized crystallographically.[3] However, by reaction of **4** with PPh_3 in different molar ratios, we have not been able to obtain a compound with a defined stoichiometry by simple exchange of ligands.

Nevertheless, we have attempted the deprotonation of **4** in the presence of PPh_3. Thus, a suspension of **4** in THF was treated with an excess of PPh_3, resulting in the gradual dissolution of the starting compound. This solution was then allowed to react with NaH, and the subsequent workup (see Experimental) gives the desired deprotonated compound $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH\mathbf{2}PPh_3\}(PPh_3)_2](ClO_4)$, **9**, although in moderate yield (58%). This behavior is somewhat related to that observed in the palladium complexes. Thus, although $[Pd\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3\}\text{-}(PPh_3)_2](ClO_4)_2$ could not be[3] synthesized, its deprotonated form $[Pd\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3\}(PPh_3)_2](ClO_4)$ can be obtained and it is stable, both in the solid state and in solution.[5]

The elemental analysis and mass spectrum of **9** are in good agreement with the proposed stoichiometry. The IR spectrum shows the carbonyl stretch at 1531 cm^{-1}, in the same region as that observed for **8**. The ^1H NMR spectrum shows the presence of a very complex multiplet with ^{195}Pt satellites at 3.62 ppm, attributed to the ylidic Pt–C(H) proton and a doublet at 3.89 ppm, with a value of the coupling constant $^2J_{P\text{-}H}$ of 26.1 Hz. Both facts are in keeping with the presence of the free ylide group –C(O)–C(H)=PPh_3. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of four chemically inequivalent P atoms, as expected for the proposed stoichiometry and showing that two PPh_3 ligands have replaced two NCMe groups. Moreover, the resonance located at 14.37 ppm provides additional evidence for the presence of the free ylide group –C(O)–C(H)=PPh_3.

Synthesis of heterobimetallic complexes

We have also attempted the synthesis of bimetallic derivatives through two different methods. The first one is the reaction of the phosphonium-containing complexes **3–7** with $(acac)AuPPh_3$ (a method that had proved to be very efficient in palladium complexes)[4] and the second one is the reaction of the ylide complexes **8** and **9** with ClAu(tht). To our surprise, the reactivity of **3–7** with $(acac)AuPPh_3$ did not give the expected results, and very complex mixtures of products were obtained.

The reactivity of **8** and **9** with ClAu(tht) (1 : 1 molar ratio) was more succesful, and the heterodinuclear complexes $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH(AuCl)PPh_3\}(dppe)](ClO_4)$, **10**, and $[Pt\{C_6H_4\text{-}2\text{-}PPh_2C(H)COCH(AuCl)PPh_3\}(PPh_3)_2]\text{-}(ClO_4)$, **11**, were obtained (see Scheme 2). These complexes show correct elemental analyses and mass spectra for the proposed stoichiometries.

The IR spectra of **10** and **11** show the carbonyl stretch at 1621 (**10**) and at 1631 cm^{-1} (**11**), that is, shifted to higher energies when compared with the respective starting compounds **8** and **9**, and slightly shifted to lower energies when compared with the parent phosphonium derivatives **6** and **4**, respectively (although in the case of **4** this is not rigorous, since they do not have the same ancillary ligands). Thus, we have the sequence ν(CO, phosphonium) > ν(CO, C-bonded ylide) > ν(CO, free ylide). This trend has already been observed in similar situations.[6,44] The presence of the [Au–Cl] fragment can be clearly inferred from the observation in the IR spectra of the ν(Au–Cl) stretch at 340 (**10**) and at 329 cm^{-1} (**11**), the typical region for the Cl trans to C(ylide).[6] The ^1H and $^{31}P\{^1H\}$ NMR spectra of **10** and **11** show the expected changes for the new stereochemistry. The resonances at 13.60 (**8**) or 14.37 ppm (**9**) in ^{31}P have moved to 25.49 (**10**) and 27.12 ppm (**11**), respectively, suggesting the C-bonding to the [AuCl] fragment. Moreover, and this fact was somewhat expected, complexes **10** and **11** have been obtained as single diastereoisomers, in spite of the presence of two chiral centers (one ylidic carbon C-bonded to platinum and one ylidic carbon C-bonded to gold). In fact, only one set of signals is observed in the NMR spectra (within the detection limits of the spectrometer), suggesting the presence of only one diastereoisomer. This behavior has already been observed in gold[6] complexes with the bis-ylide $Ph_3P{=}C(H)$–C(O)–C(H)=PPh_3, in palladium complexes with the same bis-ylide[2], and in heterodinuclear PdAu and trinuclear Pd_2Hg complexes with the *C,C,C*-terdentate orthometallated ligand $C_6H_4\text{-}2\text{-}PPh_2C(H)COCH(ML_n)PPh_3$.[4] According to these precedents, we can propose that the absolute configurations of the diastereoisomers obtained in **10** and **11** are the *meso* forms ($R_{C\text{-}Pd}S_{C\text{-}Au}/S_{C\text{-}Pd}R_{C\text{-}Au}$).

Conclusions

In conclusion, the reactivity of $PtCl_2$ or $PtCl_2(NCR)_2$ with the phosphonium ylide $[Ph_3P{=}C(H)COCH_2PPh_3]^+$ allows the synthesis of two types of derivatives: the C-bonded complex (**1**) and new cycloplatinated compounds derived from C–H bond activation (**2a–d**). The reactivity of **2a–d** produces cationic complexes containing the orthometallated *C,C*-chelating ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3]$ (**3–7**) which, in turn, can be deprotonated to give Pt^{II} derivatives with the anionic ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCH{=}PPh_3]^-$ (**8**, **9**). The latter are adequate starting materials for the synthesis of bimetallic species (**10**, **11**) with the *C,C,C*-terdentate ligand $[C_6H_4\text{-}2\text{-}PPh_2C(H)COCHPPh_3]^-$.

Experimental

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared and they should be handled with great caution. See ref. 45.

General procedures

Solvents were dried and distilled under nitrogen before use: diethyl ether and tetrahydrofuran over benzophenone ketyl, dichloromethane and chloroform over P_2O_5, acetonitrile over CaH_2, methanol over magnesium and *n*-hexane and toluene over sodium. Elemental analyses were carried out on a Perkin–Elmer 240-B microanalyser. Infrared spectra (4000–200 cm^{-1}) were recorded on a Perkin–Elmer 883 infrared spectrophotometer from nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz) and $^{31}P(^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). Mass spectra (positive ion FAB) were recorded on a VG Autospec spectrometer from CH_2Cl_2 solutions. The starting compound $[Ph_3P{=}C(H)C(O)CH_2PPh_3](ClO_4)$ was prepared according to published methods.[6]

Syntheses

***trans*-[PtCl$_2$(NCPh){C(H)PPh$_3$–C(O)CH$_2$PPh$_3$}](ClO$_4$), 1.** To a solution of $PtCl_2(PhCN)_2$ (0.690 g, 1.47 mmol) in 30 mL of $CHCl_3$, the phosphonium ylide salt $[Ph_3PC(H)COCH_2PPh_3](ClO_4)$ (1.00 g, 1.47 mmol) was added and the resulting solution was refluxed for 5 h. After the reaction time, the solvent was evaporated to dryness and the residue was treated with Et_2O (20 mL), giving **1** as a pale yellow solid, which was filtered and air dried. Obtained: 1.40 g (91% yield).

Anal. calcd. for $C_{46}H_{38}Cl_3NO_5P_2Pt$: C, 52.71; H, 3.65; N, 1.33. Found: C, 52.80; H, 3.61; N, 1.35. IR (cm^{-1}): 1654 (ν_{CO}), 309 ($\nu_{Pt\text{-}Cl}$). FAB-MS [m/z, (%)]: 949 (17%) $[M - ClO_4]^+$ ^1H NMR (CD_2Cl_2): δ 8.00–7.25 (m, 35H, Ph), 6.22 (s, 1H, C*H*Pt, $^2J_{Pt\text{-}H} = 117$ Hz), 5.83 (dd, 1H, CH_2P, $^2J_{H\text{-}H} = 18.3$ Hz, $^2J_{P\text{-}H} = 11.1$ Hz), 5.69 (dd, 1H, CH_2P, $^2J_{P\text{-}H} = 12.3$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 22.99 d, C(H)*P*Ph_3, $^4J_{P\text{-}P} = 10$ Hz, $^2J_{Pt\text{-}P} = 76$ Hz), 18.89 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 197.43 (d, CO, $^2J_{P\text{-}C} = 3.69$ Hz), 134.45 (d, $J_{P\text{-}C} = 10.6$ Hz), 134.02 (s), 134.00 (d, $J_{P\text{-}C} = 2.4$ Hz), 133.87 (s), 130.48 (d, $J_{P\text{-}C} = 13.1$ Hz), 129.75 (d, $J_{P\text{-}C} = 12.5$ Hz), 129.31 (s), 121.69 (d, C_{ipso}, $^1J_{P\text{-}C} = 86$ Hz), 118.76 (d, C_{ipso}, $^1J_{C\text{-}P} = 89$ Hz) (PPh_3), 114.99 (s, C≡N), 110.72 (s, C_{ipso} NC*Ph*), 39.28 (dd, CH_2P, $^1J_{P\text{-}C} = 58.9$ Hz, $^3J_{P\text{-}C} = 12.1$ Hz), 21.52 (dd, CHPt, $^1J_{P\text{-}C} = 48.2$ Hz, $^3J_{P\text{-}C} = 8$ Hz).

[Pt(μ-Cl){C_6H_4-2-PPh_2C(H)COCH_2PPh_3}]$_2$(ClO_4)$_2$, 2a–d. Method (a). Finely ground $PtCl_2$ (0.090 g, 0.36 mmol) was suspended in 50 mL of CH_2Cl_2. To this suspension [Ph_3P=C(H)COCH_2PPh_3](ClO_4) (0.500 g, 0.73 mmol) was added and this mixture was stirred at room temperature for 4 days. The resulting brown suspension was filtered, the filtrate evaporated to dryness and the residue treated with Pr^iOH (25 mL), giving a mixture of the *syn* (**2a**, **2b**) and *anti* (**2c**, **2d**) complexes as a cream solid, which was filtered, washed with additional Pr^iOH (10 mL) and *n*-hexane (20 mL). Obtained: 0.27 g (82% yield). The molar ratios **2a** : **2b** : **2c** : **2d** may be different in different preparations, but the *anti* derivatives always appear as traces. Usually the molar ratio of the *syn* isomers is major : minor = 2 : 1.

Method (b) To a solution of $PtCl_2(NCMe)_2$ (1.00 g, 2.64 mmol) in 25 mL of 2-methoxyethanol, [Ph_3P=C(H)-COCH_2PPh_3](ClO_4) (1.79 g, 2.64 mmol) was added and the resulting suspension was refluxed. After a short induction period, the initial suspension dissolved almost completely and the color of the solution changed gradually to off-white (30 min). An off-white solid precipitated during the remaining reaction time (5 h). This solid was filtered, washed with Pr^iOH (10 mL) and *n*-hexane (15 mL), air dried and identified as a mixture of the *syn* (**2a**) and the *anti* (**2c**, **2d**) isomers (molar ratio *anti* : *syn* = 2.77 : 1; *anti* isomers: molar ratio major : minor = 1.37 : 1). Obtained: 1.39 g (58.5% yield). Further evaporation of the alcoholic solution to a small volume (5 mL) and addition of Pr^iOH (15 mL) yielded a second crop of **2c**, **2d** (0.400 g, 16.7% yield). Total yield: 75.2%.

Anal. calcd. for $C_{78}H_{64}Cl_4O_{10}P_4Pt_2$: C, 51.55; H, 3.55. Found: C, 51.73; H, 3.98. IR (cm^{-1}): 1652 (ν_{CO}), 283 ($\nu_{Pt\text{-}Cl}$). FAB-MS [m/z, (%)]: 1717 (40%) $[M_2 - ClO_4]^+$ ^1H NMR (CD_2Cl_2): δ for the *syn* isomers, 7.67–6.70 (m, Ph, both isomers), 5.81 (dd, CH_2P, **2b**, minor, $^2J_{H\text{-}H} = 16.2$ Hz, $^2J_{P\text{-}H} = 12.6$ Hz), 5.33 (d, CH_{ylide}, **2a**, major, $^2J_{P\text{-}H} = 3.9$ Hz), 5.12 (dd, CH_2P, **2a**, major, $^2J_{H\text{-}H} = 15.6$ Hz, $^2J_{P\text{-}H} = 12.9$ Hz), 4.91 (dd, CH_2P, **2b**, minor, 1H, $^2J_{P\text{-}H} = 13.8$ Hz), 4.90 (dd, CH_2P, **2a**, major, $^2J_{P\text{-}H} = 13.8$ Hz), 4.47 (d, CH_{ylide}, **2b**, minor, $^2J_{P\text{-}H} = 2.7$ Hz). δ for the *anti* isomers, 7.86–7.09 (m, Ph, both isomers), 5.26 (dd, CH_2P, **2c**, major, $^2J_{H\text{-}H} = 19.2$ Hz, $^2J_{P\text{-}H} = 11.4$ Hz), 5.16 (dd, CH_2P, **2c**, major, $^2J_{P\text{-}H} = 10.2$ Hz), 4.89 (dd, CH_2P, **2d**, minor, $^2J_{H\text{-}H} = 17.7$ Hz, $^2J_{P\text{-}H} = 14.1$ Hz), 4.68 (dd, CH_2P, **2d**, minor, $^2J_{P\text{-}H} = 14.10$ Hz), 4.69 (d, CH_{ylide}, **2c**, major, $^2J_{P\text{-}H} = 1.5$ Hz), 4.61 (t, CH_{ylide}, **2d**, minor, $^2J_{P\text{-}H} = {}^4J_{P\text{-}H} = 2.1$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ for the *syn* isomers, 25.89 (d, PPh_2 in ring, **2b**, minor, $^4J_{P\text{-}P} = 5.5$ Hz), 24.88 (d, PPh_2 in ring, **2a**, major, $^4J_{P\text{-}P} = 4.6$ Hz), 20.18 (d, CH_2PPh_3, **2b**, minor), 20.14 (d, CH_2PPh_3, **2a** major). δ for the *anti* isomers, 32.10 (d, PPh_2 in ring, **2d**, minor, $^4J_{P\text{-}P} = 7.9$ Hz), 30.59 (d, PPh_2 in ring, **2c**, major, $^4J_{P\text{-}P} = 7.9$ Hz), 22.96 (d, CH_2PPh_3) 22.91 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ for the *syn* isomers, 188.26 (dd, CO, **2a**, major, $^2J_{P\text{-}C} = 4.8$ Hz, $^2J_{P\text{-}C} = 1.8$ Hz), 186.26 (d, CO, **2b**, minor, $^2J_{P\text{-}C} = 6.1$ Hz), 144.81 (d, C_1, C_6H_4, **2b**, minor, $^2J_{P\text{-}C} = 22.5$ Hz), 141.93 (d, C_1, C_6H_4, **2a**, major, $^2J_{P\text{-}C} = 21.3$ Hz), 136.77–117.02 (m, Ph + C_6H_4, both isomers), 39.88 (d, CH_2P, **2b**, minor, $^1J_{P\text{-}C} = 64$ Hz), 36.77 (dd, CH_2P, **2a**, major, $^1J_{P\text{-}C} = 48$ Hz, $^3J_{P\text{-}C} = 12.1$ Hz), 35.32 (d, CHPt, **2b**, minor, $^1J_{P\text{-}C} = 59.5$ Hz), 35.25 (d, CHPt, **2a**, major, $^1J_{P\text{-}C} = 62$ Hz). The *anti* isomers were too insoluble for ^{13}C measurements, even in CD_2Cl_2.

[PtCl{C_6H_4-2-PPh_2C(H)COCH_2PPh_3}PPh_3](ClO_4), 3. To a solution of **2** (0.25 g, 0.13 mmol) in CH_2Cl_2 (20 mL) was added PPh_3 (0.07 g, 0.27 mmol) and the resulting solution was stirred at room temperature for 5 h. The solution was evaporated to dryness and the residue was stirred with MeOH (10 mL), giving **3** as a white solid that was filtered and air dried. Obtained: 0.11 g (36% yield). A second fraction of pure **3** was obtained after evaporation of the filtrate and Et_2O addition (25 mL). Obtained: 0.07 g. Total yield of **3**: 58%.

Anal. calcd. for $C_{57}H_{47}Cl_2O_5P_3Pt$: C, 58.47; H, 4.04. Found: C, 58.57; H, 3.94, IR (cm^{-1}): 1643 (ν_{CO}), 283 ($\nu_{Pt\text{-}Cl}$). FAB-MS [m/z, (%)]: 1071 (27%) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ 8.00–7.00 (m, 44 H, Ph), 5.73 (dd, 1H, CH_2P, $^2J_{H\text{-}H} = 17.1$ Hz, $^2J_{P\text{-}H} = 10.8$ Hz), 4.95 (dd, 1H, CH_2P, $^2J_{P\text{-}H} = 13.5$ Hz), 4.84 (ddd, 1H, PtCH, $^2J_{P\text{-}H} = 8.7$ Hz, $^3J_{P\text{-}H} = 3.6$ Hz, $^4J_{P\text{-}H} = 2.1$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.10 (d, 1P, Pt–PPh_3, $^3J_{P\text{-}P} = 18.8$ Hz, $^1J_{P\text{-}Pt} = 3623$ Hz), 21.90 (dd, 1P, *P*Ph_2 in ring, $^4J_{P\text{-}P} = 7.28$ Hz), 20.17 (d, CH_2PPh_3).

[Pt{C_6H_4-2-PPh_2C(H)COCH_2PPh_3}($NCCH_3$)$_2$]-(ClO_4)$_2$, 4. To a solution of **2** (0.25 g, 0.13 mmol) in NCMe at room temperature (20 mL) $AgClO_4$ (0.057 g, 0.27 mmol) was added, resulting in the immediate precipitation of AgCl. The resulting suspension was stirred for 1 h with exclusion of light, then filtered, and the filtrate was evaporated to dryness. The white residue was treated with *n*-hexane (10 mL), giving **4** as a white solid that was filtered, washed with *n*-hexane (10 mL) and air dried. Obtained: 0.22 g (77.60% yield).

Anal. calcd. for $C_{43}H_{38}Cl_2N_2O_9P_2Pt$: C, 48.96; H, 3.63; N, 2.65. Found: C, 49.60; H, 3.52; N, 2.27. IR (cm^{-1}): 2322 (ν_{CN}), 1670 (ν_{CO}). FAB-MS [m/z, (%)]: 872 (100%) $[M - 2\ NCMe - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ 8.00–7.00 (m, 29 H, Ph), 5.33 (d, CHPt, 1H, $^2J_{P\text{-}H} = 1.2$ Hz), 5.13 (d, CH_2P, 2H, $^2J_{P\text{-}H} = 12.3$ Hz), 2.46 (s, 3H, NCMe), 2.41 (s, 3H, NCMe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.03 (d, *P*Ph_2 in ring, $^4J_{P\text{-}P} = 8$ Hz), 21.06 (d, CH_2PPh_3).

[Pt{C_6H_4-2-PPh_2C(H)COCH_2PPh_3}(acac-O,O′)](ClO_4) 5. To a CH_2Cl_2 solution (20 mL) of **2** (0.25 g, 0.13 mmol) Tl(acac) (0.08 g, 0.27 mmol) was added. The resulting suspension was stirred at room temperature for 5 h, then filtered. The solvent was evaporated from the filtrate to dryness and the residue was treated with *n*-hexane (20 mL), giving **5** as a white solid, which was filtered, washed with *n*-hexane and air dried. Obtained: 0.16 g (60.2% yield).

Anal. calcd. for $C_{44}H_{39}ClO_7P_2Pt$: C, 54.20; H, 4.03. Found: C, 54.26; H, 4.46. IR (cm^{-1}): 1656 (ν_{CO}, ylide), 1558, 1520 (ν_{CO}, acac). FAB-MS [m/z, (%)]: 872 (13%) $[M - ClO_4]^-$. ^1H NMR ($CDCl_3$): δ 8.04–6.66 (m, 29 H, Ph), 5.24 (s, 1H, CH-acac), 5.25 (br AB spin system, CH_2P, 2H, $^2J_{H\text{-}H} = 13.8$ Hz), 4.71 (s, 1H, CHPt), 1.89 (s, 3H, CH_3-acac), 1.58 (s, 3H, CH_3-acac). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.36 (d, 1P, *P*Ph_2 in ring, $^4J_{P\text{-}P} = 7.7$ Hz), 21.12 (d, CH_2PPh_3).

[Pt{C_6H_4-2-PPh_2C(H)COCH_2PPh_3}(dppe)](ClO_4)$_2$, 6. To a THF solution (30 mL) of **2** (0.25 g, 0.13 mmol) $AgClO_4$ (0.05 g, 0.27 mmol) was added. The resulting suspension was stirred at room temperature with exclusion of light for 30 min, then filtered. Dppe (0.10 g, 0.27 mmol) was added to the filtrate and this solution was stirred for 1 h. Evaporation of the solvent and *n*-hexane addition (20 mL) gave **6** as a white solid, which was filtered and air dried. Obtained: 0.22 g (61% yield). Complex **6** was recrystallized from a CH_2Cl_2–Et_2O (1 : 10) mixture to gave **6** · 0.25 CH_2Cl_2 as white crystals, which were used for analytical and spectroscopic purposes. The amount of CH_2Cl_2 was determined by ^1H NMR.

Anal. calcd. for $C_{65}H_{56}Cl_2O_9P_4Pt \cdot 0.25\ CH_2Cl_2$: C, 56.13; H, 4.04. Found: C, 55.47; H, 3.52. IR (cm^{-1}): 1657 (ν_{CO}). FAB-MS [*m/z*, (%)]: 1271 (8%) $[M - ClO_4]^+$. ^1H NMR ($CDCl_3$): δ 7.94–6.75 (m, 49 H, Ph), 5.36 (t, CHPt, 1H, $^2J_{P\text{-}H} = {}^3J_{Ptrans\text{-}H} = 6.30$ Hz, $^2J_{Pt\text{-}H} = 80$ Hz), 4.29 (dd, CH_2P, 1H, $^2J_{H\text{-}H} = 16.5$ Hz, $^2J_{P\text{-}H} = 9.90$ Hz), 3.78 (dd, CH_2P, 1H, $^2J_{P\text{-}H} = 12$ Hz), 2.88–1.80 (m, 4 H, CH_2-dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.61 (d, 1P, PPh_2-*trans*-C_{ylide}, $^3J_{P\text{-}P} = 17.6$ Hz, $^1J_{P\text{-}Pt} = 3050$ Hz), 43.46 (d, 1P, PPh_2-*trans*-C_{aryl}, $^3J_{P\text{-}P} = 32.9$ Hz, $^1J_{P\text{-}Pt} = 1786$ Hz), 28.73 (ddd, 1P, PPh_2 in ring, $^4J_{P\text{-}P} = 8.5$ Hz), 21.13 (d, 1P, CH_2PPh_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 194.57 (dd, CO, $^2J_{P\text{-}C} = 10.56$ Hz, $^2J_{P\text{-}C} = 5.1$ Hz), 165.62 (ddd, C_1, C_6H_4, $^2J_{Ptrans\text{-}C} = 109.6$ Hz, $^2J_{Pcis\text{-}C} = 28.8$ Hz, $^2J_{P\text{-}C} = 5.9$ Hz), 135–128 (m, Ph + C_6H_4), 44.82 (td, CH_{ylide}, $^1J_{P\text{-}C} = {}^2J_{Ptrans\text{-}C} = 75.9$ Hz, $^2J_{Pcis\text{-}C} = 7.6$ Hz), 38.81 (dd, CH_2P, $^1J_{P\text{-}C} = 60.2$ Hz, $^3J_{P\text{-}C} = 9.7$ Hz), 28.76 (m, CH_2-dppe).

[Pt{C_6H_4-2-$PPh_2C(H)COCH_2PPh_3$}(phen)](ClO_4)$_2$, 7. In a similar way to that described for **6**, **2** (0.21 g, 0.11 mmol) reacts with $AgClO_4$ (0.05 g, 0.23 mmol) and phen (0.04 g, 0.23 mmol) to give **7** as a white solid. Obtained: 0.23 g (85% yield). Complex **7** was recrystallized from a CH_2Cl_2–Et_2O (1 : 10) mixture, which gave **7** · CH_2Cl_2 as white crystals, which were used for analytical and spectroscopic purposes. The amount of CH_2Cl_2 was determined by ^1H NMR.

Anal. calcd. for $C_{50}H_{40}Cl_2N_2O_9P_2Pt \cdot CH_2Cl_2$: C, 50.46; H, 3.42; N, 2.26. Found: C, 50.61; H, 3.54; N, 2.58. IR (cm^{-1}): 1657 (ν_{CO}). FAB-MS [*m/z*, (%)]: 1053 (13%) $[M - ClO_4]^+$, 952 (100%) $[M - 2\ ClO_4 - H]^+$. ^1H NMR ($CDCl_3$): δ 10.09 (d, 1H, H_α, phen, $^3J_{\alpha\beta} = 4.5$ Hz), 9.24 (d, 1H, $H_{\alpha'}$, phen, $^3J_{\alpha'\beta'} = 5.1$ Hz), 8.70 (d, 1H, H_γ, phen, $^3J_{\gamma\beta} = 8.4$ Hz), 8.56 (d, 1H, $H_{\gamma'}$, phen, $^3J_{\gamma'\beta'} = 8.4$ Hz), 8.15 (dd, 1H, $H_{\beta'}$, phen), 8.01 (d, 1H, H_δ, phen, $^3J_{\delta\delta'} = 9$ Hz), 7.99 (dd, 1H, H_β, phen), 7.95 (d, 1H, $H_{\delta'}$), 7.88–7.26 (m, 29 H, Ph), 5.80 (s, 1H, CHPt), 5.47 (dd, 1H, CH_2P, $^2J_{H\text{-}H} = 18.00$ Hz, $^2J_{P\text{-}H} = 12.30$ Hz), 5.15 (dd, 1H, CH_2P, $^2J_{P\text{-}H} = 12$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.55 (d, PPh_2 in ring, $^4J_{P\text{-}P} = 10$ Hz), 20.79 (d, CH_2PPh_3).

[Pt{C_6H_4-2-$PPh_2C(H)COC(H)2PPh_3$}(dppe)](ClO_4), 8. To a suspension of **6** (0.20 g, 0.14 mmol) in THF (20 mL) was added an excess of NaH (0.10 g, 4.16 mmol). This mixture was stirred at room temperature for 10 h. During this time, a slow evolution of gas (H_2) was observed, and the color of the suspension changed gradually from white to yellow. After the reaction time, the suspension was filtered and the solution was evaporated to dryness, extracted with CH_2Cl_2 (20 mL) and filtered again. The resulting solution was evaporated to dryness and the oily residue was treated with Et_2O (15 mL), giving **8** as a yellow solid. Obtained: 0.11 g (63.9% yield). Due to the presence of traces of the bis-oxide $P(O)Ph_2CH_2CH_2P(O)Ph_2$, complex **8** was recrystallized from CH_2Cl_2–*n*-hexane to give **8** · 2 CH_2Cl_2 as yellow crystals, which were used for analytical and spectroscopic purposes.

Anal. calcd. for $C_{65}H_{55}ClO_5P_4Pt \cdot 2\ CH_2Cl_2$: C, 55.86; H, 4.13. Found: C, 56.16; H, 4.84. IR (cm^{-1}): 1529 (ν_{CO}). FAB-MS [*m/z*, (%)]: 1170 (85%) $[M - ClO_4]^+$. ^1H NMR (CD_2Cl_2): δ 7.91–6.88 (m, 49 H, Ph), 4.15 (t, CHPt, 1H, $^2J_{P\text{-}H} = {}^3J_{P\text{-}H} = 7.8$ Hz, $^2J_{Pt\text{-}H} = 69$ Hz), 3.09 [d, –C(H)=P, 1H, $^2J_{P\text{-}H} = 25.2$ Hz], 2.47–1.82 (m, 4 H, CH_2-dppe). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 45.28 (d, 1P, PPh_2-trans C_{ylide}, $^3J_{P\text{-}P} = 17.7$ Hz, $^1J_{P\text{-}Pt} = 2688$ Hz), 44.41 (d, 1P, PPh_2-*trans*-C_{aryl}, $^3J_{P\text{-}P} = 36.3$ Hz, $^1J_{P\text{-}Pt} = 1856$ Hz), 30.87 (ddd, 1P, PPh_2 in ring, $^4J_{P\text{-}P} = 7.2$ Hz), 13.60 (d, 1P, CH=PPh_3).

[Pt{C_6H_4-2-$PPh_2C(H)COC(H)2PPh_3$}(PPh_3)$_2$](ClO_4), 9. To a THF suspension (20 mL) of **4** (0.174 g, 0.16 mmol) was added excess of PPh_3 (0.130 g, 0.49 mmol). The suspension gradually dissolved and to the resulting solution NaH (0.10 g, excess) was added. This mixture was stirred at room temperature overnight and then filtered. The filtrate was evaporated to dryness, extracted with CH_2Cl_2 (15 mL), filtered again and the resulting solution evaporated to dryness to give **9** as a white solid, which was collected with Et_2O (20 mL) and air dried. Obtained: 0.130 g (58% yield).

Anal. calcd. for $C_{75}H_{61}ClO_5P_4Pt$: C, 64.49; H, 4.40. Found: C, 64.86; H, 4.37. IR (cm^{-1}): 1531 (ν_{CO}). FAB-MS [*m/z*, (%)]: 1297 (10%) $[M - ClO_4]^+$, 1035 (100%) $[M - ClO_4 - PPh_3]^+$. ^1H NMR ($CDCl_3$): δ 7.94–6.70 (m, 59 H, Ph + C_6H_4), 3.89 [d, –C(H)=P, 1H, $^2J_{P\text{-}H} = 26.1$ Hz], 3.62 (m, CHPt, 1H, $^2J_{Pt\text{-}H} = 64$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 30.70 (dd, 1P, PPh_2 in ring, $^3J_{P\text{-}P} = 32.7$ Hz, $^3J_{P\text{-}P} = 17.5$ Hz), 26.86 (t, 1P, PPh_3-*trans*-C_{ylide}, $^3J_{P\text{-}P} = {}^2J_{P\text{-}P} = 17.5$ Hz, $^1J_{P\text{-}Pt} = 2576$ Hz), 22.90 (dd, 1P, PPh_3-*trans*-C_{aryl}, $^1J_{P\text{-}Pt} = 1698$ Hz), 14.37 (s, 1P, CH=PPh_3).

[Pt{C_6H_4-2-$PPh_2C(H)COC(H)(AuCl)PPh_3$}(dppe)]-($ClO_4$), 10. To a CH_2Cl_2 solution (15 mL) of complex **8** (0.074 g, 0.058 mmol) ClAu(tht) (0.018 g, 0.058 mmol) was added and the resulting solution was stirred at room temperature for 15 min. Evaporation of the solvent to dryness and treatment of the white residue with Et_2O (10 mL) gave **10** as a white solid. Obtained: 0.059 g (68% yield). Due to a small amount of decomposition products, complex **10** was recrystallized from CH_2Cl_2–*n*-hexane to give white crystals of **10** · 2CH_2Cl_2, which were used for analytical and spectroscopic purposes.

Anal. calcd. for $C_{65}H_{55}AuCl_2O_5P_4Pt \cdot 2\ CH_2Cl_2$: C, 48.10, H, 3.55. Found: C, 48.04; H, 3.87. IR (cm^{-1}): 1621 (ν_{CO}), 340 ($\nu_{Au\text{-}Cl}$). FAB-MS [*m/z*, (%)]: 1403 (35%) $[M - ClO_4]^+$ 1170 (15%) $[M - ClO_4 - AuCl]^+$. ^1H NMR ($CDCl_3$): δ 7.90–6.64 (m, 49 H, Ph + C_6H_4), 5.18 (td, CHPt, 1H, $^2J_{P\text{-}H} = {}^3J_{P\text{-}H} = 8$ Hz, $^3J_{P\text{-}H} = 1.5$ Hz, $^2J_{Pt\text{-}H} = 55$ Hz), 2.77 (s, br, 1H, CHAu), 2.52–1.99 (m, 4 H, CH_2-dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 45.63 (d, 1P, PPh_2-*trans*-C_{ylide}, $^3J_{P\text{-}P} = 17.9$ Hz, $^1J_{P\text{-}Pt} = 2933$ Hz), 41.02 (d, 1P, PPh_2-*trans*-C_{aryl}, $^3J_{P\text{-}P} = 30.5$ Hz, $^1J_{P\text{-}Pt} = 1856$ Hz), 27.98 (ddd, 1P, PPh_2 in ring, $^4J_{P\text{-}P} = 13.4$ Hz), 25.49 [d, 1P, CH(AuCl)PPh_3].

[Pt{C_6H_4-2-$PPh_2C(H)COC(H)(AuCl)PPh_3$}($PPh_3$)$_2$]-($ClO_4$), 11. Complex **11** was obtained following the same method as that described for **10**: complex **9** (0.108 g, 0.077 mmol) and ClAu(tht) (0.025 g, 0.077 mmol) reacted in CH_2Cl_2 (10 mL) to give **11** as a white solid. Obtained: 0.086 g (69% yield). Complex **11** was recrystallized from CH_2Cl_2–*n*-hexane, giving white crystals of **11** · 0.5 CH_2Cl_2, which were used for analytical and spectroscopic purposes.

Anal. calcd. for $C_{75}H_{61}AuClO_5P_4Pt \cdot 0.5\ CH_2Cl_2$: C, 54.25; H, 3.74. Found: C, 54.19; H, 3.86. IR (cm^{-1}): 1631 (ν_{CO}), 329 ($\nu_{Au\text{-}Cl}$). FAB-MS [*m/z*, (%)]: 1529 (5%) $[M - ClO_4]^+$, 1267 (20%) $[M - ClO_4 - PPh_3]^+$, 1035 (20%) $[M - ClO_4 - PPh_3 - AuCl]^+$. ^1H NMR ($CDCl_3$): δ 7.79–6.47 (m, 59 H, Ph + C_6H_4), 4.55 (t, CHPt, 1H, $^3J_{P\text{-}H} = {}^2J_{P\text{-}H} = 9.3$ Hz, $^2J_{Pt\text{-}H} = 88$ Hz), 2.88 (s, br, 1H, CHAu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 29.61 (ddd, 1P, PPh_2 in ring, $^3J_{P\text{-}P} = 32.2$ Hz, $^3J_{P\text{-}P} = 17.7$ Hz, $^4J_{P\text{-}P} = 10$ Hz), 27.12 [d, 1P, CH(AuCl)PPh_3], 22.51 (t, 1P, PPh_3-*trans*-C_{ylide}, $^3J_{P\text{-}P} = {}^2J_{P\text{-}P} = 17.5$ Hz, $^1J_{P\text{-}Pt} = 2615$ Hz), 19.14 (dd, 1P, PPh_3-*trans*-C_{aryl}, $^1J_{P\text{-}Pt} = 1644$ Hz).

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