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Synthesis and Structure of Pd and Pt Complexes with Doubly Stabilized Phosphorus Ylides

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The doubly stabilized P-ylide ligands $Ph_3P{=}C(CO_2Me)$-$C(=S)N(H)Ph$ (**L1**), $Ph_3P{=}C(CN)C(=S)N(H)Ph$ (**L2**), and $Ph_3P{=}C(CN)$–[(*E*)-$C(CO_2Me){=}CH(CO_2Me)$] (**L3**) have been prepared and fully characterized. The X-ray structures of **L1** and **L2** are reported. The reactivity of **L1**, **L2**, and **L3** towards cationic Pd^{II} and Pt^{II} precursors with two vacant coordination sites has been studied. Adducts of general formula $[M(C\hat{}X)$-$(\mathbf{L}n)]ClO_4$, $[M(C\hat{}X)(\mathbf{L}n)_2]ClO_4$, and $[M(\mu\text{-}\mathbf{L}n)(C\hat{}X)]_2(ClO_4)_2$ ($C\hat{}X$ = ancillary ligands) were obtained. The ylides **L*n*** coordinate to the metal center through their heteroatoms (O, N, S), while the C bonding of **L*n*** has not been observed in any of the cases studied.

Introduction

We have recently shown that the α-stabilized P-ylides $Ph_3P{=}C(H)R$ [R = CN, C(O)R′; R′ = Me, Ph, OMe, NMe_2] behave as versatile ligands towards Pd^{II} and Pt^{II} precursors, and several coordination modes of these ylides have been characterized. Thus, the ylide can coordinate to the metal center through the C_α atom, the carbonyl oxygen, or the N atom of the cyano group. We have even characterized situations in which the same ylide shows a combination of bonding modes.[1] An interesting fact is that, in spite of the presence of several potential donor atoms on the same ylide, they always behave as ambidentate ligands,[1] that is, using only one donor atom each time. Further replacement of the ylidic H atom by other functional groups increases the functionality of the ylides and should expand their bonding capabilities. In this context, we have now focused our attention on doubly stabilized P-ylides. The introduction of an additional stabilizing functional group can be achieved through several simple synthetic procedures: acylation,[2] reactivity towards alkynes or other unsaturated compounds,[3] reactivity of iminophosphoranes with alkynes,[4] retro-Wittig reactions,[5] and other less common processes.[6]

While the chemistry of P-ylide compounds with two stabilizing groups, and their organic applications, has been the subject of intensive research, their coordination chemistry and bonding properties towards transition metals are scarcely represented.[7] Representative examples are the reaction of Hg^{II} halides HgX_2 (X = Cl, Br, I) or different U^{VI} salts with $Ph_3P{=}C[C(O)Me][C(O)Ph]$ (ABPPY), which results in the formation of mono- and dinuclear complexes with the *O*(acetyl)-bonded ABPPY ylide.[7a,7d] It is remarkable that the reactivity of the same HgX_2 precursors towards $Ph_3P{=}C(H)C(O)Ph$ (BPPY) results in *C*-bonded mono- and polynuclear complexes.[8] On the other hand, the reaction of $[PtCl_2(NCC_6F_5)_2]$ with $Ph_3P{=}C(H)CO_2Me$ gives the imine-ylide complex $[PtCl_2\{NH{=}C(C_6F_5)$-$C(=PPh_3)C(O)Me\}_2]$,[7b] in which the generated doubly stabilized ylide remains bonded to the Pt center through the imine N atom. As can be observed, all complexes with doubly stabilized ylides share a common feature, namely their bonding to the metal through the heteroatoms. Aiming to expand the knowledge on the bonding properties of doubly stabilized P-ylides, we have studied the reactivity of $Ph_3P{=}C(CO_2Me)C(=S)N(H)Ph]$ (**L1**),[3a] $Ph_3P{=}C(CN)C$-$(=S)N(H)Ph$ (**L2**),[3a] and $Ph_3P{=}C(CN)$–[(*E*)-$C(CO_2$-$Me){=}CH(CO_2Me)]$ (**L3**)[3b] towards orthometalated bis-solvato derivatives of Pd^{II} and Pt^{II}. We have found different stoichiometries and different bonding modes for each ylide (monodentate, didentate, chelating, bridging), and we have also found that in none of the cases studied does the ylide bond to the metal center through the ylidic C_α atom.

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Results and Discussion

Synthesis and Reactivity of L1

The ylide $Ph_3P{=}C(CO_2Me)C(=S)N(H)Ph$ (**L1**) was prepared following reported methods[3a] by treatment of

$Ph_3P{=}C(H)CO_2Me$[9b] with phenyl isothiocyanate (PhNCS). Since in the original work this compound was poorly characterized, and also for comparative purposes, a complete characterization of **L1** was performed. The IR spectrum of **L1** shows an intense absorption at 1629 cm^{-1}, attributed to the C=O stretch, and two very intense absorptions at 1526 and 1107 cm^{-1}, assigned to the stretch of the C=N and C=S bonds of the thioamide group, respectively.[10] The N–H stretch was not observed in the IR spectrum. The ^1H NMR spectrum of **L1** shows a very broad singlet at δ = 12.25 ppm due to the NH proton. This strongly deshielded position can be easily explained by taking into account the formation of an intramolecular hydrogen bond between the NH group and the carbonyl oxygen, as depicted in Figure 1. The formation of this hydrogen bond could also account for the lack of observation of the ν_{NH} band in the IR spectrum, which is shifted to lower energies with respect to its expected position (about 3400 cm^{-1})[10] and is probably hidden under the polyethylene absorptions (2800–3000 cm^{-1}). A similar intramolecular H bond has been found in the related N-ylide $H_5C_5NC[C(O)Ph]C(S)N(H)Ph$.[11] The $^{31}P\{^1H\}$ NMR spectrum of **L1** shows the presence of a single signal at δ = 11.33 ppm, and the $^{13}C\{^1H\}$ NMR spectrum also shows a good agreement with the proposed structure. Key features are the signal due to the P=C carbon at δ = 71.48 ppm (d, $^1J_{P,C}$ = 143.1 Hz), and that due to the C=S carbon at δ = 189.01 ppm (d, J = 16.6 Hz).[12] These observations agree with the structures depicted in Figure 1 for **L1**. The X-ray structure of **L1** has also been determined.

A molecular drawing of **L1** is shown in Figure 2, the most relevant parameters concerning data collection and structure solution and refinement are given in the Experimental Section, and selected bond lengths and angles are collected in Table 1. The molecular skeleton of **L1** is very similar to that reported previously for the closely related ylide $H_5C_5NC[C(O)Ph]C(S)N(H)Ph$.[11] Key features are the cisoid arrangement of the P=C and C=S bonds, also observed in other thiocarbonyl stabilized ylides,[13] and the transoid arrangement of the P=C and C=O bonds, as usually observed in ester-stabilized ylides.[2f,14] The atoms P(1), C(19), C(20), O(1), C(22), S(1), and N(1) are nearly coplanar, since the maximum deviation of the best least-squares plane is 0.13 Å (C20). The P=C_α bond length is elongated [P(1)–C(19) 1.751(2) Å] and both C_α–C bond lengths are identical [C(19)–C(22) 1.436(3), C(19)–C(20) 1.437(3) Å]. These values are shorter than the standard value for a $C(sp^2)$–$C(sp^2)$ single bond (1.478 Å),[15] but are longer than those found in free[2f,16] or *O*-bonded[9a,17] ylides [range: 1.366–1.394 Å] containing a single functional group. The C(22)–S(1) bond length [1.690(2) Å] is identical to that found in related ylides [1.693(2) Å],[11] and is slightly longer than usual values for C=S double bonds [1.671 Å].[15] All these facts also show an extensive delocalization of the ylidic charge density through the chain of atoms O(1)–C(20)–C(19)–C(22)–S(1), probably due to the simultaneous presence of two delocalizing groups. In good agreement with the NMR spectroscopic data, an intramolecular hydrogen bond between the NH proton and the carbonyl oxygen can be established and characterized with the following param-

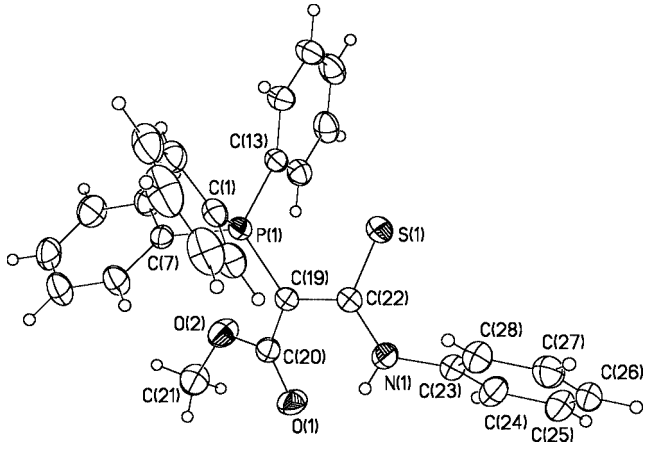


Figure 2. Thermal ellipsoid plot of **L1**. Non-hydrogen atoms are drawn at the 50% probability level.

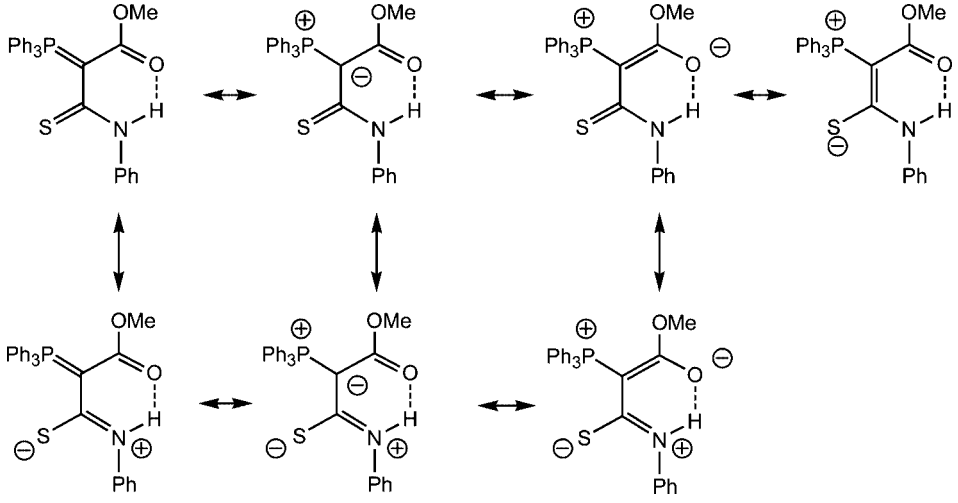


Figure 1. Resonance forms for ligand **L1**.

eters: H(1A)···O(1) 1.939(3) and N(1)···O(1) 2.642(3) Å; N(1)–H(1A)···O(1) 138.14(15)°. The intramolecular P(1)–S(1) distance is 3.034 Å, which is shorter than those found in other ylides[13] and is much shorter than the sum of the van der Waals radii (3.60 Å).[18] The P(1)–C(19)–C(22)–S(1) torsion angle is –8.9° and the P(1)–C(19)–C(22) bond angle is 115.19(15)°, a value smaller than expected for an sp^2-hybridised carbon.

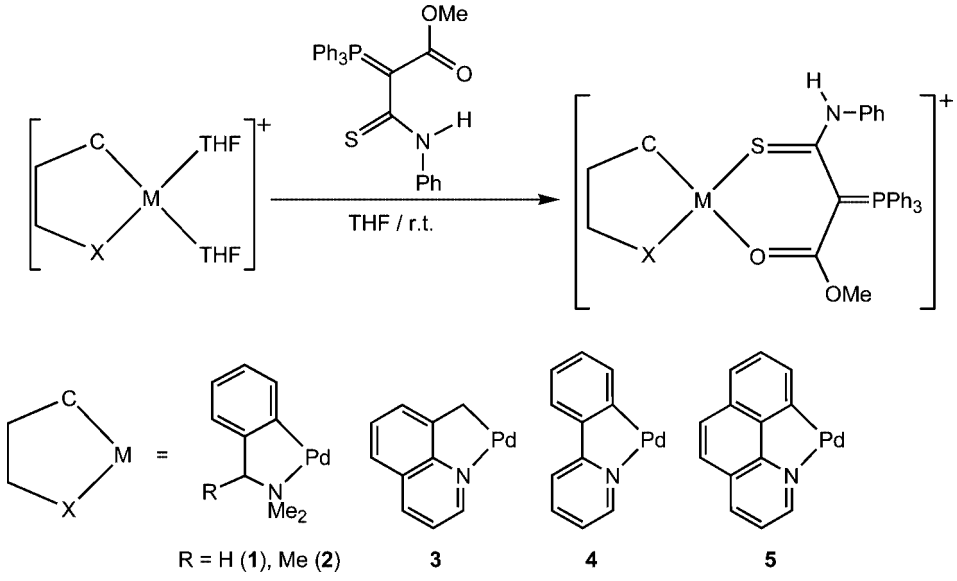
Table 1. Selected bond lengths [Å] and angles [°] for **L1**.

P(1)–C(19)	1.751(2)	P(1)–C(13)	1.801(2)
P(1)–C(1)	1.805(2)	P(1)–C(7)	1.817(2)
C(19)–C(22)	1.436(3)	C(19)–C(20)	1.437(3)
C(20)–O(1)	1.216(3)	C(20)–O(2)	1.334(3)
O(2)–C(21)	1.438(3)	C(22)–N(1)	1.340(3)
C(22)–S(1)	1.690(2)	N(1)–C(23)	1.420(3)
O(1)–C(20)–O(2)	120.4(2)	O(1)–C(20)–C(19)	126.2(2)
O(2)–C(20)–C(19)	113.3(2)	C(20)–O(2)–C(21)	118.6(2)
N(1)–C(22)–C(19)	117.89(19)	N(1)–C(22)–S(1)	122.22(17)
C(19)–C(22)–S(1)	119.85(17)	C(22)–N(1)–C(23)	127.9(2)

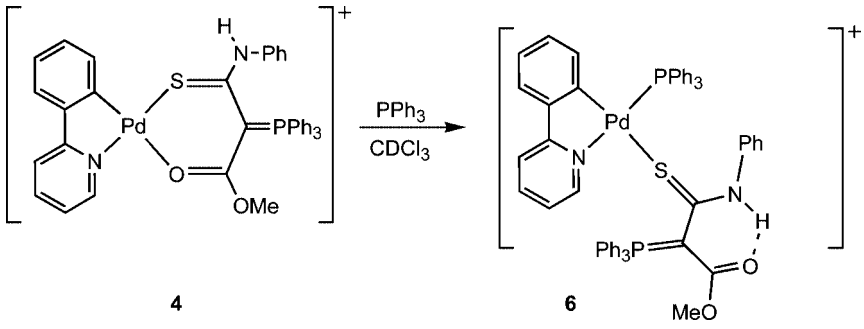
The resonance forms shown in Figure 1 suggest that there are at least four potential donor atoms for **L1** (two O atoms, one S, and the C_α). We thus explored the reactivity of **L1** towards the bis-solvate complexes $[Pd(C^X)(thf)_2]ClO_4$ (see Scheme 1), prepared as usual by reaction of the corresponding dinuclear chlorido-bridged derivatives with $AgClO_4$ (1:2 molar ratio) in thf. Treatment of freshly prepared solutions of $[M(C^X)(thf)_2]ClO_4$ with **L1** (1:1 molar ratio) in thf at 25 °C resulted in the formation of the cationic derivatives $[Pd(C^X)(\mathbf{L1})]ClO_4$ (**1**–**5**), which show elemental analyses and mass spectra (FAB+) in good agreement with the proposed stoichiometry. The IR spectra of **1**–**5** show several remarkable features: (i) a notable decrease in the position of the ν_{CO} absorption with respect to free **L1**; (ii) a shift of the ν_{CN} absorption to high energies with respect to free **L1**, while the ν_{CS} band is found shifted to lower energies; and (iii) a weak band due to the NH group. All these facts suggest strongly that ligand **L1** is bonded to the Pd atom through the S atom of the thioamide unit and through the carbonyl oxygen of the resonance-stabilized CO_2Me group, and that the ylidic C_α atom is not involved in bonding with the metal atom. This bonding mode also implies that the NH···O hydrogen bond is broken, and hence explains the increase in the NH stretch, since the ylide must rotate around the C_α–C(S) bond to adopt the final bonding mode.

The NMR spectra of **1**–**5** give additional structural information. The ^1H NMR spectra show that the molecular plane behaves as a symmetry plane, excluding the C coordination of **L1**, and also show a broad signal (δ = 7.20–7.50 ppm) due to the NH proton. This shift can be explained by the cleavage of the H bond after coordination of **L1**. The $^{13}C\{^1H\}$ NMR spectra of **1**–**5** show a doublet at δ = 72 ppm ($^1J_{P,C}$ = 104 Hz) due to the ylidic C atom, and the $^{31}P\{^1H\}$ NMR spectra show the presence of a peak at δ = 19–20 ppm. All these data confirm the absence of an interaction between the C_α atom and the Pd center,[9a] and therefore the S,O bonding mode of **L1**. This should, in principle, give two geometric isomers but, according to the NMR spectroscopic data, only one of them is obtained. A tentative structure, depicted in Scheme 1, can be proposed taking into account the hard/soft nature of the donor atoms bonded directly to the Pd atom and the antisymbiotic effect[19] shown by the Pd center. This reasoning has been successfully applied in the coordination chemistry of α-stabilized ylides.[1a] In agreement with this, it is sensible to suppose that *trans* to the aryl C atom (soft donor) the oxygen atom of **L1** (hard donor) would be more stabilized than the S atom (soft donor).[20]

The S,O-chelating bonding mode can be transformed into an S-monodentate mode by simple addition of L ligands. Thus, complex **4** reacts with PPh_3 (1:1 molar ratio) in $CDCl_3$ to give **6** (see Scheme 2). The NMR spectroscopic data of **6** show that the intramolecular H bond has been restored, since the signal attributed to the NH proton ap-



Scheme 1.



4 6

Scheme 2.

pears at δ = 11.61 ppm, a position close to that found in free **L1** (δ = 12.25 ppm). A plausible structure for **6** is shown in Scheme 2, taking into account the known reluctance of PPh_3 ligands to coordinate *trans* to metalated C_{aryl} atoms.

Synthesis and Reactivity of L2

The exchange of the CO_2Me group for the CN group promotes notable differences of reactivity. The ylide $Ph_3P{=}C(CN)C(=S)N(H)Ph$ (**L2**) was prepared following reported methods[3a] by reaction of $Ph_3P{=}C(H)CN$[3d] with PhNCS. The IR spectrum of **L2** shows intense absorptions at 3262 (NH), 2159 (CN), and 1524 and 1108 cm^{-1} (thioamide).[21] The shifts of the CN[22] and thioamide bands suggest an extensive delocalization of the charge density, and this fact agrees with the presence of the resonance forms shown in Figure 3. The ^1H NMR spectrum of **L2** shows a singlet at δ = 8.49 ppm due to the NH proton. This signal is shifted upfield when compared with **L1** meaning, probably, that a similar hydrogen bond is not present in solution. The ylidic C_α atom appears in the $^{13}C\{^1H\}$ NMR spectrum as a doublet at δ = 49.62 ppm ($^1J_{P,C}$ = 162 Hz), while the CS atom (δ = 189.68 ppm) appears at higher field than expected (usually about δ = 205 ppm).[12,21] The X-ray structure of **L2** has also been determined.

The molecular skeleton of **L2** (Figure 4 and Table 2) is very similar to that reported for **L1**, and the geometrical parameters of the P–C_α–C(S)–N–C unit are nearly the same as those found in **L1**. For instance, the P–C_α [1.7401(17) Å], C_α–C_β(S) [1.432(2) Å], and C_β–S [1.6831(17) Å] bond lengths are identical, within experimental error, to the corresponding values found in **L1** [1.751(2), 1.436(3), and 1.690(2) Å, respectively], and similar conclusions can be derived from a comparison of the bond angles. Thus, ligand **L2** also shows an extensive delocalization of the charge density, as can be deduced from the spectroscopic data. The C(1)–N(1) bond length [1.152(2) Å] is slightly longer than those reported for typical C≡N bonds (1.136 Å),[15] but is similar to those found in other cyano-stabilized ylides which contain additional stabilizing groups.[22] This elongation can be related to the presence of an intermolecular hydrogen bond between the N(2)–H(2) dipole of one molecule and the N(1)–C(1) group of another molecule. As a result of this, **L2** forms dimers in the crystal. This H bond is characterized by the following parameters: N(1)···N(2) 3.009(3), N(1)···H(2) 2.251(3) Å; N(1)···H(2)–N(2) 152.23(2)°. The intramolecular P(1)–S(1) distance is 3.090 Å, slightly longer than that found in **L1**, but is shorter

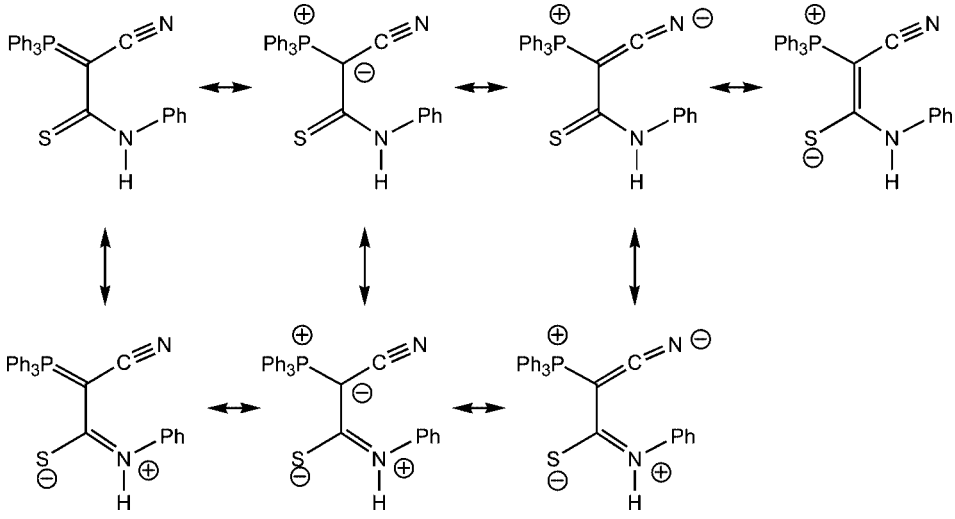


Figure 3. Resonance forms for ligand **L2**.

than the sum of the van der Waals radii (3.60 Å),[18] while the torsion angle P(1)–C(2)–C(3)–S(1) is –10.29°.

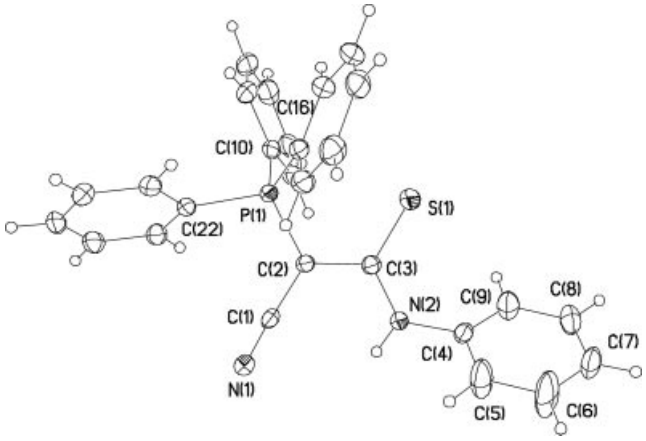


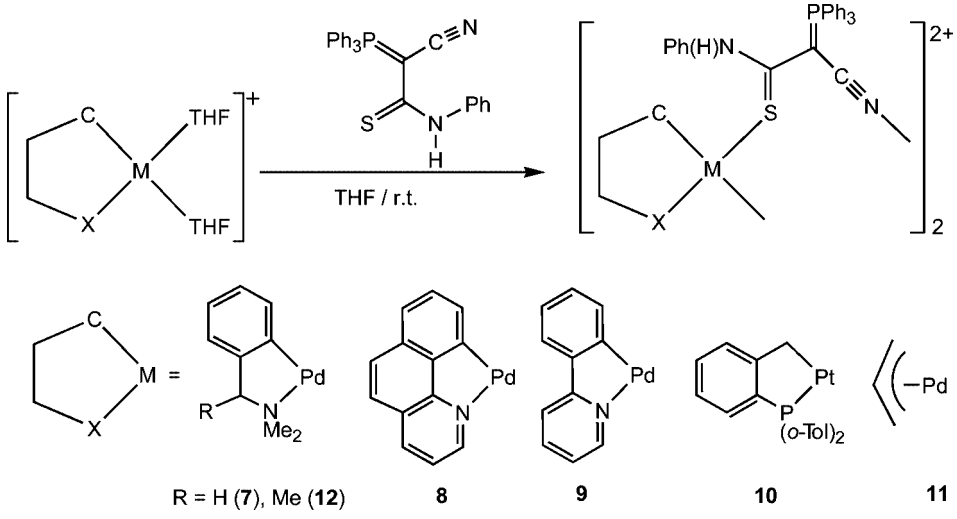
Figure 4. Thermal ellipsoid plot of **L2**. Non-hydrogen atoms are drawn at the 50% probability level.

Table 2. Selected bond lengths [Å] and angles [°] for **L2**.

P(1)–C(2)	1.7401(17)	P(1)–C(10)	1.7945(18)
P(1)–C(16)	1.8036(17)	P(1)–C(22)	1.8047(17)
C(1)–N(1)	1.152(2)	C(1)–C(2)	1.409(2)
C(2)–C(3)	1.432(2)	S(1)–C(3)	1.6831(17)
C(3)–N(2)	1.356(2)	N(2)–C(4)	1.421(2)
N(1)–C(1)–C(2)	176.82(18)	C(1)–C(2)–C(3)	121.22(15)
C(1)–C(2)–P(1)	119.83(12)	C(3)–C(2)–P(1)	118.16(12)
N(2)–C(3)–C(2)	117.30(15)	N(2)–C(3)–S(1)	123.35(13)
C(2)–C(3)–S(1)	119.34(13)	C(3)–N(2)–C(4)	126.39(15)
C(3)–N(2)–H(2)	117.3(14)	C(4)–N(2)–H(2)	114.1(14)

The reaction of $[M(C\hat{}X)(thf)_2]ClO_4$ with **L2** (1:1 molar ratio, thf, room temp.) gives complexes of stoichiometry $[M(C\hat{}X)(\mathbf{L2})](ClO_4)$ (**7**–**12**, Scheme 3). Their mass spectra (FAB+) show intense peaks due to a mononuclear stoichiometry, and those of **10** and **12** show additional peaks at 1968 and 1480 amu, respectively, with the correct isotopic distribution for an $[M_2(C\hat{}X)_2(\mathbf{L2})_2(ClO_4)]^+$ stoichiometry, and suggesting that **7**–**12** are dinuclear in nature. The IR spectra of **7**–**12** show the ν_{CN} stretch in the 2195–2206 cm^{-1} region, and the ν_{CS} stretch in the 1027–1064 cm^{-1} range. With these data, two structures can be envisaged: a mononuclear one with **L2** as a C_α,S-chelate,[23] and a binuclear compound with the ylide acting as an N,S- or C_α,S-bridging ligand. In this case, chelation through the N-cyano and S atoms is discarded because of the constraint imposed by the nitrile group. The measurement of Λ_M in solution could be a convenient tool to determine the nuclearity of complexes **7**–**12**, through the determination of the slope of the Onsager equation.[24] However, **7**–**12** are extremely insoluble in the usual noncoordinating solvents and they only show a moderate solubility in strongly coordinating solvents such as dmso or acetonitrile. This means that in solution the solvent could be incorporated into the coordination sphere of the metal, with concomitant changes of nuclearity or bonding modes of the ylide. The IR spectrum of **11** in MeCN shows the absorption of the ν_{CS} stretch at 1102 cm^{-1}, virtually at the same position as in free **L2** (1108 cm^{-1}), while the ν_{CN} stretch appears at 2181 cm^{-1} and two new bands at 2293 and 2248 cm^{-1} are also seen. These facts suggest that MeCN is bonded to the Pd atom replacing the S atom, which is no longer bonded, and that the environment of the C(H)–CN group is the same in solution and in the solid state.

The NMR spectra of **7**–**12** provide additional valuable information. Key features of the NMR spectra are: (i) the behavior of the molecular plane as a symmetry plane; (ii) the low-field shift of δ(P) in the $^{31}P\{^1H\}$ NMR spectrum with respect to **L2**; (iii) the similarity of $\delta(C_\alpha)$ and $^1J_{P,C}$ values in **7**–**12** and in free **L2**.[23] According to our previous experience,[23] all these observations exclude the C coordination of the ylide and strongly suggest the N-cyano bonding of **L2** to the Pd atom. In conclusion, we propose a dinuclear structure with an N,S-bridging ylide ligand for complexes **7**–**12**, as depicted in Scheme 3. Finally, and as explained for **L1**, the absence of symmetry in **L2** should also result in two geometric isomers after coordination. For similar reasons to those reported for complexes **1**–**5**, and also



Scheme 3.

due to the previously described coordinating behavior of cyano ylides,[23] we propose the bonding of the N atom of the ylide *trans* to the orthometalated C atom.

Synthesis and Reactivity of L3

The ylide $Ph_3P{=}C(CN)C(CO_2Me){=}C(H)CO_2Me$ (**L3**) was prepared following the procedure reported by Trippett et al.[3b] by reaction of $Ph_3P{=}C(H)CN$[3d] with DMAD (dimethylacetylenedicarboxylate) in refluxing MeOH, as a yellow solid stable to the air and to moisture. The yield for **L3** has been improved with respect to methods reported previously (65% of analytic and spectroscopically pure product vs. 43%). In addition, **L3** has been fully characterized spectroscopically because very few details were given in the original report.[3b] The IR spectrum of **L3** shows absorptions of all expected functional groups, at 2169 (ν_{CN}), 1744, 1689 (ν_{COO}), and 1531 (ν_{CC}) cm^{-1}. The NMR parameters of **L3** follow a close relationship with those reported for **L1** and **L2**. For instance, the $^{13}C\{^1H\}$ NMR spectrum shows the signal due to C_α at δ = 32.27 ppm as a doublet ($^1J_{P,C}$ = 130 Hz) that is strongly downfield shifted with respect to the starting ylide. The ^1H NMR spectrum shows the expected signals, although the (*E*)- or (*Z*)-configuration of the C=C double bond is not defined. A 1D-NOESY experiment performed for **L3** shows a small, but detectable, NOE in the signals of the OMe groups when the signal due to the =CH proton (δ = 4.81 ppm) is irradiated, which clearly agrees with an (*E*) configuration.

The ligand **L3** is multidentate, as is evident from the resonance forms shown in Figure 5. Plausible donor atoms are the C_α atom, the cyano N atom, the carbonyl oxygens, and even the C=C double bond. The reactivity of **L3** towards bis-solvate derivatives of Pd^{II} and Pt^{II} has been studied. The reaction of $[M(C\hat{}X)(thf)_2]ClO_4$ with **L3** (1:1 molar ratio, thf, room temp.) gives solids of stoichiometry $[M(C\hat{}X)(\mathbf{L3})](ClO_4)$ (**13**–**18**), as derived from their elemental analyses (Scheme 4). The mass spectra (FAB+) of **13**–**18** show the presence of peaks due to the stoichiometry $[M(C\hat{}X)(\mathbf{L3})]^+$, with the correct isotopic distribution. We have not observed peaks due to species of higher nuclearity, as observed for **L2**. The use of the ESI-MS as an identification tool of the nuclearity of the species in solution is a well established fact.[25] In the case of complexes **13**–**18**, the analysis of their NCMe solutions only showed, once again, peaks due to the $[M(C\hat{}X)(\mathbf{L3})]^+$ stoichiometry. This fact suggests that these complexes are mononuclear in nature. Additional proof can be derived from molar conductivity measurements[24] and from NMR diffusion experiments.[26]

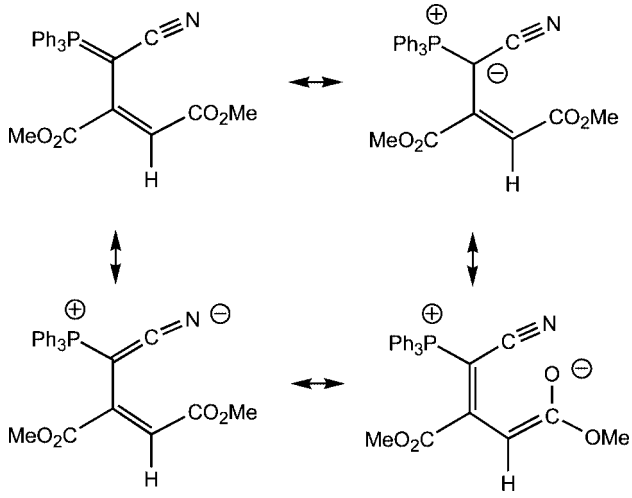
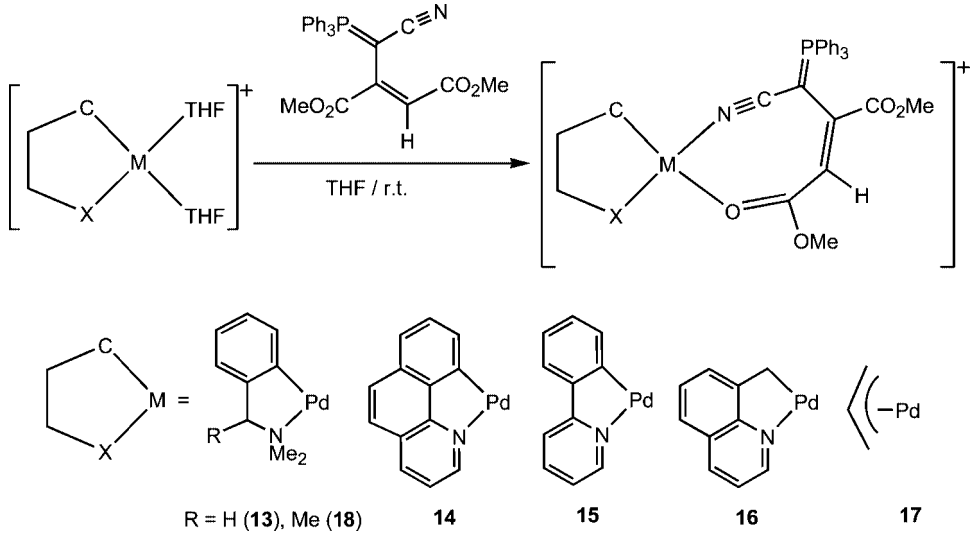


Figure 5. Resonance forms for ligand **L3**.

Since these complexes are adequately soluble in the usual organic solvents, the value of the molar conductivity can be determined. For complex **13**, the values determined for Λ_M are 114.0 (acetone, $c = 2\times10^{-4}$ M) and 81.7 $\Omega^{-1}cm^2mol^{-1}$ ($MeNO_2$, $c = 1\times10^{-3}$ M). These values are typical of 1:1 electrolytes[3b] and mean that **13**–**18** could be mononuclear with **L3** acting as a chelating ligand. The IR spectra of **13**–**18** show two relevant features: (i) an increase of the ν_{CN} stretch; and (ii) a slight decrease of one of the ν_{CO} stretches,



Scheme 4.

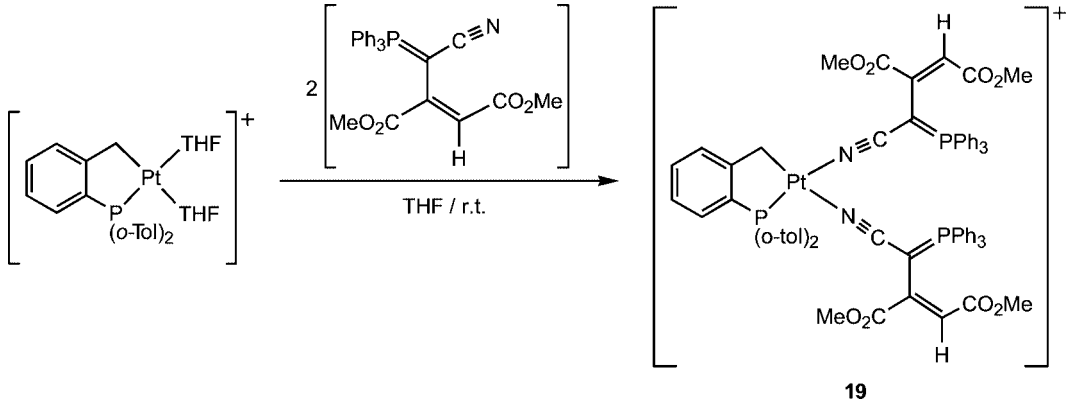
both with respect to **L3**. As we have seen, the increase of the ν_{CN} stretch could be due either to the C(ylide) or the N(cyano) bonding to the metal, while the decrease of the ν_{CO} indicates the coordination of the oxygen of one carbonyl group. Interestingly, the IR spectra of **13**–**18** in solution are virtually the same as in the solid state, thereby suggesting that the bonding mode of the ylide remains the same in solution. The NMR spectra of **13**–**18**, measured in nonbonding solvents ($CDCl_3$) and compared with **L3**, show similar features to those described for **L1** and **L2**. The small variations of δ(P), $\delta(C_\alpha)$, and $^1J_{P,C}$ mean that the P=C moiety in coordinated **L3** is not involved in bonding with the Pd atom. According to the IR and NMR spectroscopic data, the ylide **L3** coordinates to the metal center in **13**–**18** through the N atom of the cyano group and through one oxygen atom of one carbonyl group. The mass spectra and the conductivity measurements suggest, in addition, that the complexes are mononuclear and that **L3** acts as a chelating ligand. The pulsed gradient spin-echo (PGSE) NMR diffusion methods (DOSY) have proved to be a valuable tool for the determination of relative molecular sizes in solution.[26] We have compared the diffusion coefficients of one representative of **13**–**18** with those obtained for other mononuclear complexes with the same ligands. We have shown that complexes **1**–**5** behave as mononuclear in solution. The determination of the value of *D* for **3** [8-mq as ancillary ligand, see Equation (1)] gives a value of 5.93×10^{-10} m^2s^{-1} (2 mM, $CDCl_3$, 300 K, δ = 1.7 ms, Δ = 100 ms). This value fits very well with that determined for complex **16** (8-mq as ancillary ligand, *D* = 5.92×10^{-10} m^2s^{-1}) under the same experimental conditions (2 mM, $CDCl_3$, 300 K, δ = 1.8 ms, Δ = 100 ms). Thus, it is sensible to suppose that **13**–**18** are also mononuclear (Scheme 4), even taking into account the geometric constraint imposed by the cyano group. Two factors could contribute to the stabilization of the chelating mode of **L3**. The first one could be the formation of a highly flexible eight-membered ring, and the second one is the possible bent coordination of the CN group, as has been shown previously.[27]

The behavior of the cyclometalated complex [Pt{*o*-$CH_2C_6H_4P(o\text{-tol})_2$}$(S)_2$]$ClO_4$ (S = solvent) towards **L3** is slightly different. In this case, when the reaction is carried out in a 1:1 molar ratio, a low yield of **19** is obtained together with some decomposition to Pt^0. The yield of **19** improves up to 80% when the reaction is performed with a 1:2 (Pt/**L3**) molar ratio (see Scheme 5). Even when a substoichiometrict amount of **L3** is employed, complex **19** is the only species isolated. The characterization of **19** is straightforward. The ^{1}H NMR spectrum shows the incorporation of two **L3** ligands per cyclometalated unit since only one peak is observed for the Me of the tolyl groups while the peaks due to the ligand appear duplicated. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of three singlets with relative intensities 1:1:1 at δ = 19.97 (**L3**), 19.69 (**L3**), and 18.09 ppm.

The reluctance of C_α to bond to the metal center is a recurrent fact throughout the bonding modes of **L1**–**L3**. A plausible explanation for this lack of reactivity could be centered on the fact that the charge density of C_α is delocalized throughout the molecular skeleton, including the two stabilizing groups. This should lead to a decrease of the formal charge of C_α, which becomes a poor donor and which cannot compete against the heteroatoms present in the same molecule (N, S, O, ...).

Conclusions

The ylides **L1**, **L2**, and **L3**, all of which contain two stabilizing groups at the ylidic C_α atom, have been prepared and characterized. The X-ray crystal structures of **L1** and **L2** have been determined; they show extensive delocalization of the ylidic charge density. Ligands **L1**–**L3** coordinate to Pd^{II} and Pt^{II} solvates in a variety of forms. Ligand **L1** bonds as a chelate through the S atom and the resonance-stabilized C=O group; ligand **L2** coordinates as a bridging ligand through the S atom and the cyano N atom; and ligand **L3** can coordinate as a chelate, through the cyano N atom and one oxygen of a C=O group, or as a monodentate ligand through the cyano N atom. In spite of the presumed nucleophilic properties of C_α, this atom does not coordinate to the metal center in any of the cases studied due to delocalization of its charge density.



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Scheme 5.

Experimental Section

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 *J. Chem. Educ.* **1973**, *50*, A335–A337.

General Methods: Solvents were dried and distilled under argon using standard procedures before use. Elemental analyses were carried out with a Perkin–Elmer 2400-B microanalyser. IR spectra (4000–400 cm^{-1}) were recorded with a Perkin–Elmer Spectrum One IR spectrophotometer from nujol mulls between polyethylene sheets. ^1H (300.13, 400.13 MHz), $^{13}C\{^1H\}$ (75.47, 100.61 MHz), and $^{31}P\{^1H\}$ (121.49, 161.97 MHz) NMR spectra were recorded in $CDCl_3$, CD_2Cl_2, or [D$_6$]DMSO solutions at 25 °C (other temperatures are specified) with Bruker ARX300 and Avance400 spectrometers (δ in ppm, J in Hz). The ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced using the solvent signal as internal standard whereas $^{31}P\{^1H\}$ NMR spectra were externally referenced to H_3PO_4 (85%). The ^1H SELNO-1D and SELRO-1D NMR experiments were performed with optimized mixing times (D8, P15) depending on the irradiated signal. ESI/APCI mass spectra were recorded using an Esquire 3000 ion-trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a standard ESI/APCI source. Samples were introduced by direct infusion with a syringe pump. Nitrogen served both as the nebulizer gas and the dry gas. Helium served as cooling gas for the ion trap and collision gas for MS^n experiments. Other mass spectra (positive ion FAB) were recorded from CH_2Cl_2 solutions on a V. G. Autospec spectrometer. The starting materials $Ph_3P{=}C(H)CO_2Me$,[9b] $Ph_3P{=}C(H)CN$,[3d] [Pd(μ-Cl)($C_6H_4CH_2NMe_2$-C^2,N)]$_2$,[28] [Pd(μ-Cl){$SC_6H_4C(H)MeNMe_2$-C^2,N}]$_2$,[28] [Pd(μ-Cl)($NC_{13}H_8$-C^{10},N)]$_2$,[29] [Pd(μ-Cl)($CH_2NC_9H_6$-C^8,N)]$_2$,[30] [Pd(μ-Cl)(C_6H_4-2-NC_5H_4-C^2,N)],[31] [M(μ-Cl)(*o*-$CH_2C_6H_4$)P(*o*-tol)$_2$]$_2$ (M = Pd,[32] Pt[33]), and [Pd(μ-Br)(η^3-C_3H_5)]$_2$,[34] were prepared following reported methods. Other reagents such as DMAD (MeO_2C-C≡C-CO_2Me) or PhN=C=S were purchased from commercial sources (Aldrich) and used without further purification.

$Ph_3P{=}C(CO_2Me)C(=S)N(H)Ph$ (L1): The ylide **L1** was prepared following the method described in the literature by Bestmann and Pfohl[3a] by reaction of $Ph_3P{=}C(H)CO_2Me$ with PhNCS in toluene (66% yield). The characterization of **L1** is reported here since no data were given in the original paper. $C_{28}H_{24}NO_2PS$ (469.54): calcd. C 71.62, H 5.15, N 2.98, S 6.83; found C 71.45, H 5.11, N 2.84, S 6.77. MS (FAB+): *m*/*z* (%) 469 (18) [M$^+$]. IR: $\tilde{\nu}$ = 1107 (ν_{CS}), 1526 (ν_{CN}), 1584 (Ph), 1629 (ν_{CO}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 3.00 (s, 3 H, OMe), 7.03 (tt, $^3J_{H,H}$ = 7.2, $^4J_{H,H}$ = 0.9, 1 H, H_p, NPh), 7.24 (t, $^3J_{H,H}$ = 7.2, 2 H, H_m, NPh), 7.32–7.51 (m, 9 H, PPh_3), 7.69 (dd, 2 H, H_o, NPh), 7.73–7.82 (m, 6 H, H_o, PPh_3), 12.25 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 49.67 (OMe), 71.47 (d, $^1J_{P,C}$ = 143.1, P=C), 123.71 (C_{meta}, NPh), 124.31 (C_{para}, NPh), 128.20 (C_{ortho}, NPh), 128.36 (d, $^3J_{P,C}$ = 12.7, C_{meta}, PPh_3), 128.50 (d, $^1J_{P,C}$ = 97, C_{ipso}, PPh_3), 131.12 (d, $^4J_{P,C}$ = 2.6, C_{para}, PPh_3), 132.94 (d, $^2J_{P,C}$ = 9.3, C_{ortho}, PPh_3), 140.38 (C_{ipso}, NPh), 168.93 (d, $^2J_{P,C}$ = 16.4, C=O), 189.01 (d, $^2J_{P,C}$ = 16.6, C=S) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 11.33 ppm.

Synthesis of 1: $AgClO_4$ (0.045 g, 0.217 mmol) was added to a suspension of [Pd(μ-Cl)($C_6H_4CH_2NMe_2$-C^2,N)]$_2$ (0.060 g, 0.108 mmol) in dry thf (20 mL) under an Ar atmosphere. The resulting suspension was stirred for 20 min at room temperature with exclusion of light, and then filtered through a Celite pad in order to remove the AgCl. The ylide **L1** (0.102 g, 0.217 mmol) was added to this freshly prepared solution of the solvate derivative. The resulting solution was stirred for 30 min and then the solvent evaporated to dryness. Treatment of the residue with Et_2O (25 mL) and vigorous stirring gave **1** as a yellow solid, which was filtered, washed with additional Et_2O (10 mL), and air dried. Yield: 0.060 g (34.1%). Complex **1** was recrystallized from CH_2Cl_2/Et_2O to give yellow crystals of **1**·0.5CH_2Cl_2, which were used for analytic and spectroscopic purposes. The amount of CH_2Cl_2 was determined by integration of the signal in the ^1H NMR spectrum. $C_{37}H_{36}ClN_2O_6PPdS$·0.5CH_2Cl_2 (852.06): calcd. C 52.86, H 4.38, N 3.29, S 3.76; found C 52.93, H 4.31, N 3.12, S 3.83. MS (FAB+): *m*/*z* (%) 709 (15) [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1066 (ν_{CS}), 1575 (ν_{CN}), 1596 (ν_{CO}), 3260 (ν_{NH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 2.81 (s, 6 H, NMe_2), 3.08 (s, 3 H, OMe), 4.03 (s, 2 H, CH_2N), 6.58–6.61 (m, 2 H, H_o, NPh), 6.77–6.82 (m, 2 H, C_6H_4), 6.98–7.00 (m, 2 H, C_6H_4), 7.21 (m, 3 H, H_m, H_p, NPh), 7.27 (br. s, 1 H, NH), 7.67–7.96 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 51.16 (NMe_2), 52.80 (OMe), 71.53 (d, $^1J_{P,C}$ = 103.6, P=C), 71.81 (CH_2N), 122.42 (d, $^1J_{P,C}$ = 91.3, C_{ipso}, PPh_3), 123.17, 125.33, 126.00, 133.49, 137.83, 142.57 (C_6H_4), 126.06 (C_{meta}), 128.20 (C_{para}), 129.40 (C_{ortho}), 148.65 (C_{ipso}) (NPh), 130.69 (d, $^2J_{P,C}$ = 12.5, C_{ortho}), 133.67 (d, $^3J_{P,C}$ = 9.9, C_{meta}), 134.71 (C_{para}) (PPh_3), 172.49 (d, $^2J_{P,C}$ = 10.2, C=O), 186.70 (d, $^2J_{P,C}$ = 4.1, CS) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.29 ppm.

Synthesis of 2: Complex **2** was obtained following the same synthetic procedure as reported for **1**. [Pd(μ-Cl){(*S*)-$C_6H_4CH(Me)NMe_2$-C^2,N}]$_2$ (0.060 g, 0.103 mmol) was treated with $AgClO_4$ (0.043 g, 0.207 mmol) and **L1** (0.097 g, 0.207 mmol) in thf to give **2** as an orange solid. Yield: 0.113 g (66.3%). Complex **2** was recrystallized from CH_2Cl_2/Et_2O to give orange crystals of **2**·0.5CH_2Cl_2, which were used for analytic and spectroscopic purposes. The amount of CH_2Cl_2 was determined by integration of the signal in the ^1H NMR spectrum. $C_{38}H_{38}ClN_2O_6PPdS$·0.5CH_2Cl_2 (866.09): calcd. C 53.39, H 4.54, N 3.23, S 3.70; found C 53.28, H 4.34, N 3.39, S 3.88. MS (FAB+): *m*/*z* (%) 723 (30) [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1080 (ν_{CS}), 1575 (ν_{CN}), 1600 (ν_{CO}), 3220 (ν_{NH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.63 (d, $^3J_{H,H}$ = 6.3, 3 H, Me), 2.63 (s, 3 H, NMe_2), 2.87 (s, 3 H, NMe_2), 3.08 (s, 3 H, OMe), 4.03 (q, 1 H, CH), 6.59 (m, 2 H, H_o, NPh), 6.83 (m, 2 H, C_6H_4), 6.92–7.03 (m, 2 H, C_6H_4), 7.22 (m, 3 H, H_m, H_p, NPh), 7.25 (br. s, 1 H, NH), 7.65–7.96 (m, 15 H, PPh_3) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.25 ppm.

Synthesis of 3: Complex **3** was obtained following the same synthetic procedure as reported for **1**. [Pd(μ-Cl)($CH_2NC_9H_6$-C^8,N)]$_2$ (0.061 g, 0.107 mmol) was treated with $AgClO_4$ (0.044 g, 0.212 mmol) and **L1** (0.101 g, 0.215 mmol) in thf to give **3** as a yellow solid. Yield: 0.122 g (69.5%). $C_{38}H_{32}ClN_2O_6PPdS$ (817.57): calcd. C 55.83, H 3.94, N 3.42, S 3.92; found C 56.26, H 3.74, N 3.14, S 4.10. MS (FAB+): *m*/*z* (%) 717 (27) [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1065 (ν_{CS}), 1564 (ν_{CN}), 1599 (ν_{CO}), 3216 (ν_{NH}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.21 (s, 3 H, OMe), 3.36 (s, 2 H, CH_2Pd), 6.57 (br., 2 H, H_o, NPh), 7.21 (br. s, 3 H, NH, NC_9H_6), 7.51–7.60 [m, 4 H, H_m, H_p (NPh), NC_9H_6], 7.66–7.80 [m, 10 H, H_m, H_p (PPh_3) + NC_9H_6], 7.90–7.97 (m, 6 H, H_o, PPh_3), 8.41 (d, $^3J_{H,H}$ = 8.1, 1 H, NC_9H_6), 8.66 (br. s, 1 H, NC_9H_6) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 21.60 ($PdCH_2$), 52.69 (OMe), 70.63 (d, $^1J_{P,C}$ = 106.1, P=C), 125.08 (d, $^1J_{P,C}$ = 93, C_{ipso}, PPh_3), 121.98, 124.56, 126.87, 128.25, 137.92, 138.88, 147.42, 149.08, 152.21 (NC_9H_6), 126.21 (C_{meta}), 128.93 (C_{para}), 129.42 (C_{ortho}), 148.99 (C_{ipso}) (NPh), 130.65 (d, $^2J_{P,C}$ = 11.1, C_{ortho}), 133.60 (d, $^3J_{P,C}$ = 9.5, C_{meta}), 134.59 (C_{para}) (PPh_3) ppm; the CO and CS signals were not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.69 ppm.

Synthesis of 4: Complex **4** was obtained following the same synthetic procedure as reported for **1**. [Pd(μ-Cl)(C_6H_4-2-NC_5H_4-C^2,N)]$_2$ (0.062 g, 0.105 mmol) was treated with $AgClO_4$ (0.044 g, 0.212 mmol) and **L1** (0.101 g, 0.215 mmol) to give **4** as a yellow

solid. Yield: 0.088 g (50.3%). $C_{39}H_{32}ClN_2O_6PPdS$ (829.58): calcd. C 56.47, H 3.89, N 3.38, S 3.86; found C 56.46, H 3.76, N 3.33, S 4.21. MS (FAB+): *m/z* (%) 729 (30) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1080 (ν_{CS}), 1578 (ν_{CN}), 1600 (ν_{CO}), 3259 (ν_{NH}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.21 (s, 3 H, OMe), 6.64 (dd, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1.6, 2 H, H_o, NPh), 7.02 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.2, 1 H, Phpy), 7.04 (s, 1 H, NH), 7.14 (td, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 1.8, 1 H, Phpy), 7.24–7.27 [m, 4 H, H_m+H_p (NPh) + Phpy], 7.32 (td, $^3J_{H,H}$ = 6.6, $^4J_{H,H}$ = 0.9, 1 H, Phpy), 7.55 (d, $^3J_{H,H}$ = 7.5, 1 H, Phpy), 7.68–7.99 (m, 17 H, PPh_3 + Phpy), 8.45 (d, $^3J_{H,H}$ = 5.0, 1 H, Phpy) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 53.09 (OMe), 71.67 (d, $^1J_{P,C}$ = 102.8, P=C), 119.59, 123.32, 124.74, 125.77, 130.06, 134.20, 137.82, 140.10, 146.47, 147.07, 164.27 (Phpy), 122.18 (d, $^1J_{P,C}$ = 91, C_{ipso}, PPh_3), 126.16 (C_{meta}), 128.44 (C_{para}), 129.50 (C_{ortho}), 149.73 (C_{ipso}) (NPh), 130.77 (d, $^2J_{P,C}$ = 12.4, C_{ortho}), 133.68 (d, $^3J_{P,C}$ = 9.7, C_{meta}), 134.78 (C_{para}) (PPh_3), 186.47 (d, $^2J_{P,C}$ = 4.4, C=S) ppm; the CO signal was not observed. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.27 ppm.

Reaction of 4 with PPh_3: PPh_3 was added in small portions to a suspension of **4** in CD_2Cl_2 (0.6 mL) in an NMR tube. NMR spectra were measured each time, until complete transformation of **4**. At this point, complete dissolution had occurred. The amount of PPh_3 required matched a 1:1 molar ratio (**4**:PPh_3), and gave complex **6** as a single isomer in 100% spectroscopic yield. Selected NMR spectroscopic data of **6**: ^1H NMR (CD_2Cl_2): δ = 3.00 (s, 3 H, OMe), 6.31 (t, $^3J_{H,H}$ = 6.9, 1 H, Phpy), 6.46–6.59 (m, 6 H, NPh + Phpy), 6.91 (t, $^3J_{H,H}$ = 7.2, 1 H, Phpy), 7.24–7.74 (m, 33 H, PPh_3 + Phpy), 7.89 (br. s, 1 H, Phpy), 7.96 (td, $^3J_{H,H}$ = 7.5, $^4J_{H,H}$ = 1.5, 1 H, Phpy), 11.61 (s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 17.65 (P=C), 38.09 ppm (Pd–PPh_3).

Synthesis of 5: Complex **5** was obtained following the same synthetic procedure as reported for **1**. $[Pd(\mu\text{-}Cl)(bhq\text{-}C,N)]_2$ (bhq = $NC_{13}H_8$; 0.066 g, 0.102 mmol) was treated with $AgClO_4$ (0.042 g, 0.205 mmol) and **L1** (0.096 g, 0.205 mmol) to give **5** as a yellow solid. Yield: 0.115 g (65.7%). Complex **5** was recrystallized from CH_2Cl_2/Et_2O to give crystals of **5**·$0.5CH_2Cl_2$ (determined by NMR), which were used for analytic and spectroscopic purposes. $C_{41}H_{32}ClN_2O_6PPdS{\cdot}0.5CH_2Cl_2$ (896.07): calcd. C 55.62, H 3.71, N 3.13, S 3.58; found C 55.36, H 3.88, N 2.87, S 3.74. MS (FAB+): *m/z* (%) 753 (10) $[M - ClO_4]^+$. IR: $\tilde{\nu}$ = 1060 (ν_{CS}), 1586 (br., ν_{CN} + ν_{CO}), 3225 (ν_{NH}) cm^{-1}. ^1H NMR (CD_2Cl_2): δ = 3.28 (s, 3 H, OMe), 6.68 (dd, $^3J_{H,H}$ = 5.7, $^4J_{H,H}$ = 1.8, 2 H, H_o, NPh), 7.19 (d, $^3J_{H,H}$ = 7.2, 1 H, $NC_{13}H_8$), 7.28 (m, 3 H, H_m+H_p, NPh), 7.34 (t, $^3J_{H,H}$ = 7.5, 1 H, $NC_{13}H_8$), 7.38 (s, 1 H, NH), 7.63 (m, 2 H, $NC_{13}H_8$), 7.67–7.73 [m, 7 H, H_m (PPh_3) + $NC_{13}H_8$], 7.76–7.82 [m, 4 H, H_p (PPh_3) + $NC_{13}H_8$], 7.90–7.98 (m, 6 H, H_o, PPh_3), 8.42 (dd, $^3J_{H,H}$ = 8.1, $^4J_{H,H}$ = 1.2, 1 H, H_4, $NC_{13}H_8$), 8.66 (dd, $^3J_{H,H}$ = 5.1, 1 H, H_2, $NC_{13}H_8$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 53.12 (OMe), 72.07 (d, $^1J_{P,C}$ = 103.0, P=C), 122.31 (d, $^1J_{P,C}$ = 91.2, C_{ipso}, PPh_3), 122.40, 122.46, 124.01, 124.06, 127.49, 128.96, 131.22, 134.44, 137.89, 138.31, 141.93, 146.27, 153.71 ($NC_{13}H_8$), 126.09 (C_{meta}), 128.30 (C_{para}), 129.45 (C_{ortho}), 147.33 (C_{ipso}) (NPh), 130.71 (d, $^2J_{P,C}$ = 12.5, C_{ortho}), 133.74 (d, $^3J_{P,C}$ = 9.4, C_{meta}), 134.69 (C_{para}) (PPh_3), 172.82 (d, $^2J_{P,C}$ = 10.0, C=O), 186.38 (d, $^2J_{P,C}$ = 4.7, C=S) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 19.62 ppm.

Ph_3P=C(CN)C(S)N(H)Ph (L2): PhN=C=S (0.543 mL, 0.614 g, 4.55 mmol) was added to a suspension of Ph_3P=C(H)CN (1.370 g, 4.55 mmol) in freshly distilled toluene (50 mL). The resulting mixture was refluxed for 1 h and then stirred for 72 h at 25 °C to give a yellow suspension. This suspension was evaporated to dryness and the residue treated with Et_2O (50 mL) to give **L2** as a white solid. Yield: 1.122 g (56.5%). $C_{27}H_{21}N_2PS$ (436.52): calcd. C 74.29, H 4.85, N 6.41, S 7.34; found C 74.78, H 4.84, N 7.11, S 7.63. MS (FAB+): *m/z* (%) 437 (100) $[M + H]^+$. IR: $\tilde{\nu}$ = 1108 (ν_{CS}), 1524 ($\nu_{C=N}$), 2159 (ν_{CN}), 3262 (ν_{NH}) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 7.09 (t, 1 H, H_{para}, Ph), 7.28 (t, $^3J_{HmHp}$ = $^3J_{HmHo}$ = 7.5, 2 H, H_{meta}, Ph), 7.41–7.52 [m, 8 H, H_{meta}(PPh_3) + H_{ortho}(Ph)], 7.56–7.60 (m, 3 H, H_{para}, PPh_3), 7.71–7.80 (m, 6 H, H_{ortho}, PPh_3), 8.49 (br. s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 49.62 (d, $^1J_{P,C}$ = 162, P=C), 120.99 (d, $^1J_{P,C}$ = 20.7, C_{ipso}, PPh_3), 124.02 (C_{meta}, Ph), 125.16 (C_{para}, Ph), 125.29 (CN), 128.47 (C_{ortho}, Ph), 128.96 (d, $^3J_{P,C}$ = 13, C_{meta}, PPh_3), 132.65 (d, $^4J_{P,C}$ = 2.8, C_{para}, PPh_3), 133.75 (d, $^2J_{P,C}$ = 9.8, C_{ortho}, PPh_3), 139.47 (d, $^4J_{P,C}$ = 1.5, C_{ipso}, Ph), 189.68 (d, $^2J_{P,C}$ = 15.4, C=S) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 14.80 (s, C=PPh_3) ppm.

Synthesis of 7: $AgClO_4$ (0.053 g, 0.257 mmol) was added to a suspension of $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NMe_2\text{-}C^2,N)]_2$ (0.071 g, 0.128 mmol) in 20 mL of freshly distilled thf under argon. The resulting mixture was stirred at room temperature with exclusion of light for 30 min, then filtered through a Celite pad. This freshly prepared solution was treated with a stoichiometric amount of **L2** (0.112 g, 0.257 mmol) giving, after a few seconds, a deep yellow precipitate of **7**. This suspension was stirred at room temperature for an additional 20 min, then the yellow solid was filtered, washed with thf (5 mL) and Et_2O (20 mL), dried by suction, and subsequently identified as **7**. Yield: 0.141 g (70.5%). $C_{36}H_{33}ClN_3O_4PPdS$ (776.57): calcd. C 55.68, H 4.28, N 5.41, S 4.13; found C 55.81, H 4.50, N 5.11, S 4.03. MS (FAB+): *m/z* (%) 676 (100) $[M/2 - ClO_4]^+$. IR: $\tilde{\nu}$ = 1060 (ν_{CS}), 1558 ($\nu_{C=N}$), 2196 (ν_{CN}), 3203 (ν_{NH}) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 2.24 (s, 6 H, NMe_2), 3.53 (s, 2 H, CH_2N), 6.26 (d, $^3J_{H,H}$ = 7.5, 1 H, C_6H_4), 6.64 (m, 1 H, C_6H_4), 6.76 (d, $^3J_{H,H}$ = 6.6, 1 H, C_6H_4), 6.84 (t, $^3J_{H,H}$ = 6.9, 1 H, C_6H_4), 7.13–7.19 (m, 3 H, H_o+H_p, Ph), 7.28 (t, $^3J_{H,H}$ = 7.2, 2 H, H_m, Ph), 7.73–7.93 (m, 15 H, PPh_3), 10.33 (s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR ([D_6]DMSO): δ = 20.22 (s, C=PPh_3) ppm.

Synthesis of 8: Complex **8** was prepared following a synthetic procedure similar to that reported for **7**. Thus, $[Pd(\mu\text{-}Cl)(bhq\text{-}C,N)]_2$ (bhq = $C_{13}H_8N$, 0.078 g, 0.122 mmol) was treated with $AgClO_4$ (0.050 g, 0.244 mmol) and **L2** (0.110 g, 0.244 mmol), in thf (20 mL), to give **8** as a yellow solid. Yield: 0.110 g (55%). $C_{40}H_{29}ClN_3O_4PPdS$ (820.58): calcd. C 58.55, H 3.56, N 5.12, S 3.91; found C 58.85, H 3.41, N 4.76, S 3.82. MS (FAB+): *m/z* (%) 720 (27) $[M/2 - ClO_4]^+$. IR: $\tilde{\nu}$ = 1056 (ν_{CS}), 1568 ($\nu_{C=N}$), 2195 (ν_{CN}), 3188 (ν_{NH}) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 6.66 (d, $^3J_{H,H}$ = 9, 1 H, bhq), 6.79 (t, $^3J_{H,H}$ = 9, 1 H, bhq), 7.00–7.24 (m, 5 H, Ph), 7.57 (d, $^3J_{H,H}$ = 6, 1 H, bhq), 7.65–7.69 (m, 2 H, bhq), 7.76–8.01 (m, 16 H, PPh_3 + 1 H bhq), 8.54 (br. d, $^3J_{H,H}$ = 9, 2 H, bhq), 10.58 (br. s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR ([D_6]DMSO), δ = 21.08 (s, C=PPh_3) ppm.

Synthesis of 9: Complex **9** was prepared following a synthetic procedure similar to that reported for **7**. Thus, $[Pd(\mu\text{-}Cl)(NC_5H_5\text{-}2\text{-}C_6H_4\text{-}C,N)]_2$ (0.080 g, 0.134 mmol) was treated with $AgClO_4$ (0.056 g, 0.269 mmol) and **L2** (0.117 g, 0.269 mmol), in thf (20 mL), to give **9** as a yellow solid. Yield: 0.140 g (70%). $C_{38}H_{29}ClN_3O_4PPdS$ (796.56): calcd. C 57.30, H 3.67, N 5.27, S 4.02; found C 57.09, H 3.20, N 5.08, S 3.65. MS (FAB+): *m/z* (%) 696 (100) $[M/2 - ClO_4]^+$. IR: $\tilde{\nu}$ = 1059 (ν_{CS}), 1538 ($\nu_{C=N}$), 2197 (ν_{CN}), 3196 (ν_{NH}) cm^{-1}. ^1H NMR ([D_6]DMSO): δ = 6.48 (d, $^3J_{H,H}$ = 6, 1 H, Phpy), 6.84 (t, $^3J_{H,H}$ = 6, 1 H, Phpy), 6.88 (t, $^3J_{H,H}$ = 6, 1 H, Phpy), 7.00 (t, $^3J_{H,H}$ = 9, 1 H, Phpy), 7.15 (m, 4 H, H_o+H_m, Ph), 7.33 (t, $^3J_{H,H}$ = 6, 1 H, H_p, Ph), 7.50 (d, $^3J_{H,H}$ = 9, 1 H, Phpy), 8.08–7.56 (m, 17 H, PPh_3 + Phpy), 8.19 (s, 1 H, Phpy), 10.53 (s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ([D_6]DMSO): δ = 50.80 (d, $^1J_{P,C}$ = 137.7, P=C), 117.65 (d, $^2J_{P,C}$ = 14.7, CN), 119.03 (NPh, C_{meta}), 121.60 (d, $^1J_{P,C}$ = 93.9, C_{ipso}, PPh_3), 122.75, 124.14, 124.48, 125.65,

133.36, 136.46, 140.05, 145.39, 147.35, 149.56, 163.04 (Phpy), 125.37 (NPh, C_{ortho}), 128.37 (C_{para}, PPh_3), 129.23 (NPh, C_{para}), 129.69 (d, $^3J_{P,C}$ = 12.7, C_{meta}, PPh_3), 134.05 (d, $^2J_{P,C}$ = 10.0, C_{ortho}, PPh_3), 139.23 (C_{ipso}, NPh), 183.27 (d, $^2J_{P,C}$ = 14.5, C=S) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 20.92 (C=PPh_3) ppm.

Synthesis of 10: Complex **10** was prepared following a synthetic procedure similar to that reported for **7**. Thus, [Pt(μ-Cl)[*o*-$CH_2C_6H_4P$(*o*-$MeC_6H_4)_2$]]$_2$ (0.103 g, 0.096 mmol) was treated with $AgClO_4$ (0.040 g, 0.193 mmol) and **L2** (0.084 g, 0.193 mmol), in thf (20 mL), to give **10** as a yellow solid. Yield: 0.0461 g (23%). $C_{48}H_{41}ClN_2O_4P_2PtS$ (1034.42): calcd. C 55.73, H 4.00, N 2.71, S 3.10; found C 55.47, H 3.71, N 2.94, S 2.61. MS (FAB+): *m*/*z* (%) 934 (37) [M/2 – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1027 (ν_{CS}), 1530 ($\nu_{C=N}$), 2199 (ν_{CN}), 3180 (ν_{NH}) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 2.11 (s, 6 H, Me), 2.78 (s, 2 H, $PtCH_2$), 7.95–6.87 (m, 32 H, PPh_3 + C_6H_4), 10.90 (br. s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 20.25 (C=PPh_3), 32.09 ($^1J_{PtP}$ = 3843, C^P–Pt) ppm.

Synthesis of 11: Complex **11** was prepared following a synthetic procedure similar to that reported for **7**. Thus, [Pd(μ-Br)(η^3-C_3H_5)]$_2$ (0.0664 g, 0.146 mmol) was treated with $AgClO_4$ (0.061 g, 0.292 mmol) and **L2** (0.127 g, 0.292 mmol), in thf (20 mL), to give **11** as a green-yellow solid. Yield: 0.159 g (79.4%). $C_{30}H_{26}ClN_2O_4PPdS$ (683.44): calcd. C 52.72, H 3.83, N 4.10, S 4.69; found C 51.95, H 4.15, N 3.72, S 4.53. MS (FAB+): *m*/*z* (%) 583 (47) [M/2 – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1027 (ν_{CS}), 1530 ($\nu_{C=N}$), 2181 (ν_{CN}), 3240 (ν_{NH}) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 2.98 (br. s, 2 H, CH_2), 4.17 (br. s, 2 H, CH_2), 5.37 (m, 1 H, CH), 6.91 (m, 2 H, Ph), 7.12–7.18 (m, 3 H, Ph), 7.39–7.87 (m, 15 H, PPh_3), 10.70 (br. s, 1 H, NH) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 20.13 (s, C=PPh_3) ppm.

Synthesis of 12: Complex **12** was prepared following a synthetic procedure similar to that reported for **7**. Thus, [Pd(μ-Cl)-{(*S*)-$C_6H_4CH(Me)NMe_2$-C^2,*N*}]$_2$ (0.0731 g, 0.126 mmol) was treated with $AgClO_4$ (0.052 g, 0.252 mmol) and **L2** (0.110 g, 0.252 mmol), in thf (20 mL), to give **12** as a yellow solid. Yield: 0.120 g (60%). $C_{37}H_{35}ClN_3O_4PPdS$ (790.59): calcd. C 56.21, H 4.46, N 5.31, S 4.05; found C 56.28, H 4.15, N 4.86, S 4.81. MS (FAB+): *m*/*z* (%) 690 (40) [M/2 – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1064 (ν_{CS}), 1542 ($\nu_{C=N}$), 2206 (ν_{CN}), 3232 (ν_{NH}) cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): δ = 1.18 (d, $^3J_{H,H}$ = 6, 3 H, Me), 2.09 (s, 3 H, NMe_2), 2.34 (s, 3 H, NMe_2), 3.72 (d, $^3J_{H,H}$ = 6, 1 H, CH), 6.30 (d, $^3J_{H,H}$ = 6.9, 1 H, C_6H_4), 6.66 (m, 2 H, C_6H_4), 6.85 (t, $^3J_{H,H}$ = 7.5, 1 H, C_6H_4), 7.13–7.36 (m, 5 H, Ph), 7.73–7.92 (m, 15 H, PPh_3), 10.23 (br. s, 1 H, NH) ppm. $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 15.13 (Me), 43.91 (NMe_2), 48.63 (NMe_2), 51.29 (d, $^1J_{P,C}$ = 134.7, P=C), 71.92 (CH), 118.05 (d, $^2J_{P,C}$ = 15.9, CN), 121.55 (d, $^1J_{P,C}$ = 24.5, C_{ipso}, PPh_3), 122.50 (s, C_{para}, NPh), 124.02, 125.46, 128.98, 135.06, 142.98, 152.54 (C_6H_4), 124.95 (C_{meta}, NPh), 128.48 (C_{ortho}, NPh), 129.68 (d, $^3J_{P,C}$ = 12.7, C_{meta}, PPh_3), 133.97 (d, $^2J_{P,C}$ = 10.2, C_{ortho}, PPh_3), 133.98 (C_{para}, PPh_3) 139.44 (C_{ipso}, NPh), 183.71 (d, $^2J_{P,C}$ = 13.7, C–S) ppm. $^{31}P\{^1H\}$ NMR ([D$_6$]DMSO): δ = 20.40 (s, C=PPh_3) ppm.

Ph_3P=C(CN)-[(*E*)-C(CO_2Me)=CH(CO_2Me)] (L3): A suspension of Ph_3P=C(H)CN (1.000 g, 3.32 mmol) and DMAD (MeO_2C–C≡C–CO_2Me) (0.41 mL, 0.472 g, 3.32 mmol) in MeOH (20 mL) was refluxed for 20 min under argon. Once cooled, the reaction mixture was further stirred at room temperature for 18 h to give a yellow suspension. The precipitated solid of **L3** was filtered, washed with MeOH (10 mL) and Et_2O (20 mL), and dried by suction. Yield: 0.951 g (64.6%). IR: $\tilde{\nu}$ = 1531 (ν_{CC}), 1689 (ν_{COO}), 1744 (ν_{COO}), 2169 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.46 (s, 3 H, OMe), 3.54 (br. s, 3 H, OMe), 4.81 (s, 1 H, =CH), 7.51–7.70 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 32.27 (d, $^1J_{P,C}$ = 129.9, P=C), 49.36 (OMe), 51.01 (OMe), 97.74 (d, $^3J_{P,C}$ = 6.6, =CH), 120.26 (d, $^1J_{P,C}$ = 91.8, C_{ipso}, PPh_3), 120.44 (d, $^2J_{P,C}$ = 15.4, CN), 128.04 (d, $^3J_{P,C}$ = 12.8, C_{meta}, PPh_3), 132.37 (d, $^4J_{P,C}$ = 2.8, C_{para}, PPh_3), 132.58 (d, $^2J_{P,C}$ = 10.3, C_{ortho}, PPh_3), 150.90 (d, $^2J_{P,C}$ = 8.8, =C), 165.15 (COO), 167.35 (COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 19.95 ppm.

Synthesis of 13: $AgClO_4$ (0.0935 g, 0.451 mmol) was added to a suspension of [Pd(μ-Cl)($C_6H_4CH_2NMe_2$-C^2,*N*)]$_2$ (0.124 g, 0.225 mmol) in thf (20 mL) under Ar. The resultant mixture was stirred at room temperature for 20 min with exclusion of light, then filtered through a Celite pad. The freshly prepared solution of the bis(solvate) was treated with **L3** (0.200 g, 0.451 mmol) to give a yellow solution, which was stirred for an additional 30 min. The yellow solution was then evaporated to dryness and the yellow residue was treated with Et_2O (30 mL) and stirred continuously to give **13** as a yellow solid. Yield: 0.316 g (89.5%). $C_{35}H_{34}ClN_2O_8PPd$ (783.49): calcd. C 53.65, H 4.37, N 3.57; found C 53.50, H 4.59, N 3.24. MS (FAB+): *m*/*z* (%) 683 (100) [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1557 (ν_{CC}), 1698 (ν_{COO}), 1732 (ν_{COO}), 2192 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$, 213 K): δ = 2.26 (s, 3 H, NMe_2), 2.70 (s, 3 H, NMe_2), 3.60 (br., 2 H, CH_2N), 3.63 (s, 3 H, OMe), 3.76 (br. s, 3 H, OMe), 4.81 (s, 1 H, =CH), 6.38 (d, $^3J_{H,H}$ = 7.2, 1 H, C_6H_4), 6.68 (t, $^3J_{H,H}$ = 7.8, 1 H, C_6H_4), 6.80 (d, $^3J_{H,H}$ = 7.2, 1 H, C_6H_4), 6.91 (t, $^3J_{H,H}$ = 7.2, 1 H, C_6H_4), 7.59–7.77 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.66 (d, $^1J_{P,C}$ = 127.8, P=C), 51.13 (OMe), 52.88 (OMe), 52.20 (NMe_2), 72.93 (CH_2N), 102.62 (d, $^3J_{P,C}$ = 5.1, =CH), 120.54 (d, $^1J_{P,C}$ = 92, C_{ipso}, PPh_3), 121.88, 125.19, 130.17, 134.62, 150.12 (C_6H_4, one of the quaternary C atoms was not observed), 125.79 (d, $^2J_{P,C}$ = 15.37, CN), 129.96 (d, $^3J_{P,C}$ = 12.7, C_{meta}, PPh_3), 133.96 (d, $^2J_{P,C}$ = 10.4, C_{oho}, PPh_3), 134.44 (s, C_{para}, PPh_3), 149.86 (d, $^2J_{P,C}$ = 7.4, =C), 165.90 (COO), 168.20 (d, $^3J_{P,C}$ = 11.1, COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.18 (C=PPh_3) ppm.

Synthesis of 14: Complex **14** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pd(μ-Cl)(bhq-*C*,*N*)]$_2$ (bhq = $C_{13}H_8N$, 0.144 g, 0.225 mmol) was treated with $AgClO_4$ (0.0932 g, 0.45 mmol) and **L3** (0.200 g, 0.45 mmol), in thf (20 mL), to give **14** as a yellow solid. Yield: 0.167 g (45%). $C_{39}H_{30}ClN_2O_8PPd$ (827.50): calcd. C 56.61, H 3.65, N 3.38; found C 56.26, H 3.98, N 2.96. MS (ESI, positive ions): *m*/*z* = 726.9 [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1557 (ν_{CC}), 1698 (ν_{COO}), 1733 (ν_{COO}), 2212 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.51 (s, 3 H, OMe), 3.71 (br. s, 3 H, OMe), 4.85 (s, 1 H, =CH), 6.94 (d, $^3J_{H,H}$ = 6.3, 1 H, bhq), 7.25 (t, $^3J_{H,H}$ = 7.8, 1 H, bhq), 7.47 (m, 1 H, bhq), 7.53 (d, $^3J_{H,H}$ = 8.1, 1 H, bhq), 7.57–7.82 [m, 17 H, PPh_3 + 2 H(bhq)], 8.23 (d, $^3J_{H,H}$ = 7.8, 1 H, bhq), 8.74 (br. s, 1 H, bhq) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 34.84 (d, $^1J_{P,C}$ = 127.7, P=C), 51.20 (OMe), 53.22 (OMe), 102.81 (d, $^3J_{P,C}$ = 4.6, =CH), 120.37 (d, $^1J_{P,C}$ = 91.8, C_{ipso}, PPh_3), 121.93, 123.48, 126.69, 128.35, 128.63, 129.54, 131.85, 133.43, 137.69, 140.29, 143.19, 148.97, 153.55 (bhq), 126.49 (d, $^2J_{P,C}$ = 15.37, CN), 130.08 (d, $^3J_{P,C}$ = 13.0, C_{meta}, PPh_3), 134.05 (d, $^2J_{P,C}$ = 10.4, C_{ortho}, PPh_3), 134.47 (s, C_{para}, PPh_3), 149.86 (d, $^2J_{P,C}$ = 7.4, =C), 165.68 (COO), 168.68 (COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.28 (C=PPh_3) ppm.

Synthesis of 15: Complex **15** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pd(μ-Cl)(NC_5H_5-2-C_6H_4-*C*,*N*)]$_2$ (0.074 g, 0.124 mmol) was treated with $AgClO_4$ (0.052 g, 0.25 mmol) and **L3** (0.110 g, 0.25 mmol), in thf (20 mL), to give **15** as a pale-yellow solid. Yield: 0.190 g (95%). $C_{37}H_{30}ClN_2O_8PPd$ (803.48): calcd. C 55.31, H 3.76, N 3.49; found C 55.26, H 3.98, N 3.17. MS (ESI, positive ions): *m*/*z* 702.9 [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1558 (ν_{CC}), 1698 (ν_{COO}), 1732 (ν_{COO}), 2192 (ν_{CN})

cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.49 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 4.84 (s, 1 H, =CH), 6.63 (d, $^3J_{H,H}$ = 7.8, 1 H, Phpy), 6.87 (t, $^3J_{H,H}$ = 7.2, 1 H, Phpy), 7.05 (t, $^3J_{H,H}$ = 7.2, 1 H, Phpy), 7.13 (t, $^3J_{H,H}$ = 6.6, 1 H, Phpy), 7.29 (d, $^3J_{H,H}$ = 7.5, 1 H, Phpy), 7.56 – 7.78 [m, 17 H, PPh_3 + 2 H (Phpy)], 7.85 (m, 1 H, Phpy) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 34.79 (d, $^1J_{P,C}$ = 126.8, P=C), 51.18 (OMe), 52.85 (OMe), 102.77 (d, $^3J_{P,C}$ = 4.9, =CH), 118.97, 123.10, 123.71, 125.68, 129.48, 133.63, 140.04, 149.93, 145.12, 149.77, 150.06 (Phpy), 120.33 (d, $^1J_{P,C}$ = 92, C_{ipso}, PPh_3), 126.25 (d, $^2J_{P,C}$ = 15.8, CN), 130.07 (d, $^3J_{P,C}$ = 13.0, C_{meta}, PPh_3), 133.92 (d, $^2J_{P,C}$ = 10.3, C_{ortho}, PPh_3), 134.72 (s, C_{para}, PPh_3), 149.72 (d, $^2J_{P,C}$ = 7.4, =C), 165.89 (d, $^2J_{P,C}$ = 5.1, COO), 168.38 (d, $^3J_{P,C}$ = 11.6, COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.24 (C=PPh_3) ppm.

Synthesis of 16: Complex **16** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pd(μ-Cl)($NC_9H_6CH_2$-C,N)]$_2$ (0.0718 g, 0.126 mmol) was treated with $AgClO_4$ (0.0524 g, 0.253 mmol) and **L3** (0.112 g, 0.253 mmol), in thf (20 mL), to give **16** as a yellow solid. Yield: 0.189 g (94%). $C_{36}H_{30}ClN_2O_8PPd$ (791.47): calcd. C 54.63, H 3.82, N 3.53; found C 54.37, H 3.92, N 3.18. MS (ESI, positive ions): *m*/*z* = 690.9 [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1557 (ν_{CC}), 1698 (ν_{COO}), 1731 (ν_{COO}), 2200 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.46 (br. s, 2 H, CH_2Pd), 3.49 (s, 3 H, OMe), 3.69 (br. s, 3 H, OMe), 4.81 (s, 1 H, =CH), 7.40 (m, 2 H, 8-mq), 7.66 (m, 17 H, PPh_3 + 8-mq), 8.22 (br. s, 2 H, 8-mq) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 25.58 ($PdCH_2$), 34.50 (d, $^1J_{P,C}$ = 127.5, P=C), 51.16 (OMe), 52.97 (OMe), 102.41 (d, $^3J_{P,C}$ = 2.9, =CH), 120.41 (d, $^1J_{P,C}$ = 91.9, C_{ipso}, PPh_3), 121.87, 124.30, 126.60, 128.20, 128.47, 129.31, 138.50, 150.51, 150.27 (8-mq), 130.05 (d, $^3J_{P,C}$ = 12.9, C_{meta}, PPh_3), 133.97 (d, $^2J_{P,C}$ = 10.3, C_{ortho}, PPh_3), 134.89 (C_{para}, PPh_3), 145.99 (d, $^2J_{P,C}$ = 4.8, =C), 166.01 (COO), 168.60 (d, $^3J_{P,C}$ = 10.4, COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.12 (C=PPh_3) ppm.

Synthesis of 17: Complex **17** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pd(μ-Br)(η^3-C_3H_5)]$_2$ (0.066 g, 0.145 mmol) was treated with $AgClO_4$ (0.060 g, 0.290 mmol) and **L3** (0.120 g, 0.29 mmol), in thf (20 mL), to give **17** as an orange solid. Yield: 0.154 g (77%). $C_{29}H_{27}ClNO_8PPd$ (690.36): calcd. C 50.45, H 3.94, N 2.03; found C 50.23, H 3.91, N 1.98. MS (FAB+): *m*/*z* (%) 590 (47) [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1557 (ν_{CC}), 1695 (ν_{COO}), 1732 (ν_{COO}), 2192 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.22 (br., 2 H, CH_2, allyl), 2.73 (d, $^3J_{H,H}$ = 10.5, 2 H, CH_2, allyl), 3.48 (s, 3 H, OMe), 3.71 (br. s, 3 H, OMe), 4.76 (s, 1 H, =CH), 5.33 (q, 1 H, CH, allyl), 7.50 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 33.99 (d, $^1J_{P,C}$ = 127.2, P=C), 51.14 (OMe), 52.74 (OMe), 62.89 (CH_2 allyl), 102.33 (d, $^3J_{P,C}$ = 4.6, =CH), 115.67 (CH allyl), 120.40 (d, $^1J_{P,C}$ = 92, C_{ipso}, PPh_3), 127.63 (d, $^2J_{P,C}$ = 12.4, CN), 130.20 (d, $^3J_{P,C}$ = 12.9, C_{meta}, PPh_3), 133.90 (d, $^2J_{P,C}$ = 10.4, C_{ortho}, PPh_3), 134.35 (d, $^4J_{P,C}$ = 5.5, C_{para}, PPh_3), 150.00 (d, $^2J_{P,C}$ = 7.6, =C), 165.92 (COO), 168.21 (d, $^3J_{P,C}$ = 11.3, COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.27 (C=PPh_3) ppm.

Synthesis of 18: Complex **18** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pd(μ-Cl){(*S*)-$C_6H_4CH(Me)NMe_2$-C^2,*N*}]$_2$ (0.0725 g, 0.125 mmol) was treated with $AgClO_4$ (0.052 g, 0.250 mmol) and **L3** (0.111 g, 0.25 mmol), in thf (20 mL), to give **18** as a yellow solid. Yield: 0.1964 g (98.2%). $C_{36}H_{36}ClN_2O_8PPd$ (797.52): calcd. C 54.22, H 4.55, N 3.51; found C 54.20, H 4.47, N 3.30. MS (ESI, positive ions): *m*/*z* = 696.9 [M – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1558 (ν_{CC}), 1698 (ν_{COO}), 1732 (ν_{COO}), 2199 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 1.45 (d, $^3J_{H,H}$ = 6.0, 3 H, CMe), 2.52 (s, 3 H, NMe_2), 2.70 (s, 3 H, NMe_2), 3.48 (s, 3 H, OMe), 3.67–3.74 (br. s, 4 H, OMe+CH), 4.81 (s, 1 H, =CH), 6.37 (d, $^3J_{H,H}$ = 7.8, 1 H, C_6H_4), 6.67–6.73 (m, 2 H, C_6H_4), 6.92 (t, $^3J_{H,H}$ = 7.8, 1 H, C_6H_4), 7.24–7.75 (m, 15 H, PPh_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 18.91 (Me), 34.45 (d, $^1J_{P,C}$ = 127.3, P=C), 46.15 (NMe_2), 51.16 (OMe), 51.49 (NMe_2), 53.16 (OMe), 74.85 (CHN), 102.70 (d, $^4J_{P,C}$ = 4.9, =CH), 119.85 (d, $^1J_{P,C}$ = 91.9, C_{ipso}, PPh_3), 122.15, 122.92, 125.10, 125.34, 152.21 (C_6H_4; C_2 was not observed), 125.95 (d, $^2J_{P,C}$ = 16.2, CN), 130.03 (d, $^3J_{P,C}$ = 12.9, C_{meta}, PPh_3), 133.99 (d, $^2J_{P,C}$ = 10.4, C_{ortho}, PPh_3), 134.42 (d, $^4J_{P,C}$ = 2.3, C_{para}, PPh_3), 149.78 (d, $^2J_{P,C}$ = 7.6, =C), 165.82 (CO_2), 168.04 (d, $^3J_{P,C}$ = 10.8, CO_2) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 20.17 (s, C=PPh_3) ppm.

Synthesis of 19: Complex **19** was prepared following a synthetic procedure similar to that reported for **13**. Thus, [Pt(μ-Cl){*o*-$CH_2C_6H_4P$(*o*-$MeC_6H_4)_2$}]$_2$ (0.103 g, 0.096 mmol) was treated with $AgClO_4$ (0.040 g, 0.192 mmol) and **L3** (0.170 g, 0.384 mmol), in thf (20 mL), to give **19** as a yellow solid. Yield: 0.161 g (80.2%). $C_{71}H_{64}ClN_2O_{12}P_3Pt$ (1460.76): calcd. C 58.38, H 4.42, N 1.92; found C 59.05, H 4.29, N 1.65. MS (FAB+): *m*/*z* (%) 941 (100) [M – ylide – ClO_4]$^+$. IR: $\tilde{\nu}$ = 1564 (ν_{CC}), 1699 (ν_{COO}), 1733 (ν_{COO}), 2198 (ν_{CN}) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 2.26 (s, 6 H, Me), 3.19 (s, 3 H, OMe), 3.48 (s, 2 H, $PtCH_2$), 3.50 (s, 6 H, 2 OMe), 3.69 (s, 3 H, OMe), 4.80 (s, 1 H, =CH), 4.85 (s, 1 H, =CH), 6.85–7.76 (m, 42 H, PPh_3 + C_6H_4) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 12.19 ($PtCH_2$), 23.08 (d, $^3J_{P,C}$ = 7.0, Me), 33.94 (d, $^1J_{P,C}$ = 127.7, P=C), 34.31 (d, $^1J_{P,C}$ = 128.3, P=C), 51.10 (OMe), 51.20 (OMe), 52.21 (OMe), 52.78 (OMe), 102.44 (d, $^4J_{P,C}$ = 6.5, =CH), 103.25 (d, $^4J_{P,C}$ = 5.2, =CH), 120.29 (d, $^1J_{P,C}$ = 92.1, C_{ipso}, PPh_3), 120.62 (d, $^1J_{P,C}$ = 92.1, C_{ipso}, PPh_3), 124.04 (d, $^2J_{P,C}$ = 15.9, CN), 125.07 (d, $^2J_{P,C}$ = 16.2, CN), 126.04 (d, $J_{P,C}$ = 10.8, C_6H_4), 129.77 (d, $^3J_{P,C}$ = 12.9, C_{meta}, PPh_3), 130.13 (d, $^3J_{P,C}$ = 12.9, C_{meta}, PPh_3), 131.30 (d, $J_{P,C}$ = 8.9, C_6H_4), 131.71 (d, $J_{P,C}$ = 11.6, C_6H_4), 133.33 (d, $J_{P,C}$ = 5.0, C_6H_4), 133.34 (d, $J_{P,C}$ = 25.5, C_6H_4), 133.88 (d, $^2J_{P,C}$ = 10.4, C_{ortho}, PPh_3), 134.40 (d, $^4J_{P,C}$ = 2.6, C_{para}, PPh_3), 134.74 (d, $^4J_{P,C}$ = 1.9, C_{para}, PPh_3), 141.59 (d, $J_{P,C}$ = 10.7, C_6H_4), 149.18 (d, $^2J_{P,C}$ = 30.9, =C), 149.29 (d, $^2J_{P,C}$ = 30.3, =C), 157.26 (d, $^1J_{P,C}$ = 27.0, C_6H_4), 165.83 (COO), 165.99 (COO), 167.68 (d, $^3J_{P,C}$ = 13.9, COO), 167.82 (d, $^3J_{P,C}$ = 15.9, COO) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = 18.09 ($^1J_{Pt,P}$ = 4605, C^P–Pt), 19.69 (C=PPh_3), 19.97 (C=PPh_3) ppm.

Crystallography. Data Collection: X-ray quality crystals were grown by slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of the corresponding crude compound. A single crystal of dimensions 0.25×0.18×0.16 mm^3 (**L1**) or 0.30×0.24×0.06 mm^3 (**L2**) was mounted at the end of a quartz fiber in a random orientation and covered with epoxy. Data collection was performed on a Bruker Smart CCD diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). A hemisphere of data was collected in each case based on three ω-scan runs (starting ω = –30°) at values φ = 0°, 90° and 180° with the detector at 2θ = 30°. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 10 s per frame. The diffraction frames were integrated using the program SAINT[35] and the integrated intensities were corrected for absorption with SADABS.[36]

Structure Solution and Refinement: The structures were solved and developed by Patterson and Fourier methods.[37] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2-times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[38]

Crystallographic Data for L1: $C_{28}H_{24}NO_2PS$, M = 469.51, T = 291(2) K, monoclinic $C2/c$, a = 26.710(3), b = 9.5585(1), c =

20.620(2) Å, β = 114.396(2)°, V = 4794.4(9) Å^3, Z = 8, $D_{calcd.}$ = 1.301 Mg m^{-3}, μ = 0.228 mm^{-1}, a total of 15869 reflections were collected, of which 5764 [R_{int} = 0.0366] independent reflections were used in the refinement of 299 parameters and 0 restraints. The final R factors were R_1 = 0.0516, wR_2 = 0.1129 for $I > 2\sigma(I)$ and R_1 = 0.0940, wR_2 = 0.1303 for all reflections, Goof = 1.022.

Crystallographic Data for L2: $C_{27}H_{21}N_2PS$, M = 436.49, T = 100(1) K, monoclinic $P2_1/c$, a = 11.1040(2), b = 12.2318(2), c = 16.2397(2) Å, β = 94.980(1)°, V = 2197.38(6) Å^3, Z = 4, $D_{calcd.}$ = 1.319 Mg m^{-3}, μ = 0.238 mm^{-1}, a total of 37050 reflections were collected, of which 5033 [R_{int} = 0.0546] independent reflections were used in the refinement of 284 parameters and 0 restraints. The final R factors were R_1 = 0.0433, wR_2 = 0.1048 for $I > 2\sigma(I)$ and R_1 = 0.0548, wR_2 = 0.1095 for all reflections, Goof = 1.061.

CCDC-612165 (for **L1**) and -612166 (for **L2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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