# Aroylphosphanes: base-free synthesis and their coordination chemistry with platinum-group metals

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# Aroylphosphanes: Base-free synthesis and their coordination chemistry with platinum group metals.

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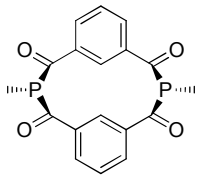
A series of aroylphosphanes have been prepared in good yield *via* the base-free condensation of the respective aroyl chloride and $HPPh_2$. Alongside the cyclophane *m*-{-C(O)-$C_6H_4$(C(O)PMe)}$_2$ (**1**), the IR spectroscopic signatures of $C_6H_4R\{C(O)PPh_2\}$ (R = 3-Me **2**, 3-$CH_2Cl$ **3**, 4-$CO_2Me$ **4**, 4-CN **5**) and the bis-aroylphosphanes $C_6H_4\{2,6\text{-}C(O)PPh_2\}_2$ (**6**) and $C_6H_3N\{2,6\text{-}C(O)PPh_2\}_2$ (**7**) are consistent with manifestation of 'phosphomide' character; however, weight of evidence suggests negligible contribution from this canonical form. Comparison is drawn to the structurally characterised $O=P(C_6H_5Me\text{-}2)_3$ (**8**) in which the lone-pair is sequestered. The coordination of **2** – **5** to rhodium(I), palladium(II) and platinum(II) is described, affording rare examples of aroylphosphane complexes of the platinum group metals.

## Introduction

Phosphorus ligands are a ubiquitous feature of modern organometallic and coordination chemistry. The facility with which their steric profiles and electronic properties (σ-basicity/π-acidity) can be varied renders them a versatile means of controlling metal reactivity, whether through the imposition of spectator bulk, or direct modification of metal electron density. Consequently, prolific levels of activity surround the synthesis and development of phosphanes bearing a variety of functionalities (alkyl, aryl, alkenyl, alkynyl, OR).[1] However, somewhat less studied are acylphosphanes, in which one or more carbonyl moieties is directly bonded to phosphorus. This relative neglect has been attributed to inherent weakness of the P–C(O) linkage,[2] which renders them prone to hydrolytic and/or oxidative cleavage. Computational studies have suggested this weakness to be the result of hyperconjugative interactions between the *n*(O) and σ*(P–C) orbitals,[3] while simultaneously dismissing any appreciable delocalisation of the phosphorus lone-pair into the carbonyl (*cf.* amides) that might mitigate the 'weakening' effect, while earlier work invoked $p_\pi$-$d_\pi$ interactions in a similar context.[4] Notwithstanding, the conceptual analogy to amides, first defined by Issleib,[5] persists, being invoked for systems with low-energy acyl stretches (< 1700 $cm^{-1}$), lying in the region typical of amides. This notion has been further evidenced by observed increase in $\nu_{C=O}$ upon *P*-coordination of these molecules, attributed to sequestration of the lone-pair and thus loss of delocalisation.[6]

The coordination chemistry of such "phosphomide" ligands is, nonetheless, scant and largely restricted to groups 6 – 8 (Cr,[7] Mo,[7,8] W,[9] Mn,[10] Re,[11] Fe,[12] Ru[13]) with an emphasis on the first-row metals. A limited range of group 9 complexes has been described with 'Cp'$RhCl_2$' (Cp' = Cp, Cp*)[6] and 'Cp*$IrCl_2$'[14] fragments, however, *trans*-$Rh(CO)(L)_2Cl$ (L = $PH_2\{C(O)Me\}$, $PPh_2\{C(O)C_7F_{15}\}$, $PPh_2\{C(O)p\text{-}An\}$[6]) and [Rh{$\kappa^2$-*P,P*-$C_6H_3N\{PC(O)PPh_2\}_2$-2,6}Cl][13a] are the only low-valent group 9 complexes known. Similarly, until recently only $[Ni(CO)_3(PAd\{C(O)^tBu\}_2)]$,[12h] *cis*-$[Pt(PPh_2\{C(O)C_6H_5\})_2Cl_2]$ and *cis*-$[Pd(PPh_2\{C(O)C_6H_5\}_2\text{-}(SnCl_3)Cl]$[15] were known from group 10, though complexes of the bis(phosphomides) $C_6H_4\{PC(O)PPh_2\}_2$-1,3 (Ni, Pd)[13b] and $C_6H_3N\{PC(O)PPh_2\}_2$-2,6 (Ni, Pd, Pt)[13a] have since been described. Moreover, we have recently communicated the, formally related, cyclophane **1**, along with its platinum complexes $[Pt(\kappa^1\text{-}\mathbf{1})_2Cl_2]$ and $[\{Pt(PEt_3)Cl_2\}_2\{\mu\text{-}\mathbf{1}\}]$.[16]



**1**

Herein, we describe the facile synthesis of a series of aroylphosphane derivatives and their coordination chemistry with representative platinum group metals. The synthesis and coordination chemistry of **1** has previously been reported in preliminary form.[16]

## Results and Discussion

### Synthesis of aroylphosphane ligands

The aroylphosphanes **2** to **5** are obtained in good yield (> 70 %) from reaction of the respective aroyl chloride and $HPPh_2$ (Scheme 1) and isolated upon removal of volatiles. We have similarly prepared the bisphosphomides $C_6H_4\{C(O)PPh_2\}_2$-1,3 (**6**)[13a] and $C_5H_3N\{C(O)PPh_2\}_2$-2,6 (**7**),[13b] which were independently reported during the course of our works. We note that while condensation reactions are commonly employed for such syntheses,

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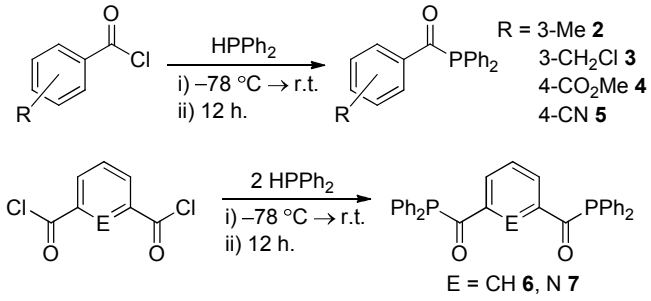
there is typically need for either extraneous base (to sequester HCl) or pre-metallation of the secondary phosphane, neither of which have we found to be necessary. While the participation of the phosphane itself as base in these reactions cannot be fully excluded, there is no evidence for generation of $[Ph_2PH_2]Cl$; moreover, the presence of traces of $HPPh_2$ in the crude products, taken alongside the high isolated (pure) yields of **2** – **7** are also inconsistent with the former serving as stoichiometric base. Indeed, the reactions require careful control of the equimolar reagent stoichiometries, the presence of excess $HPPh_2$ leading to significant contamination (*ca* 50 % by NMR) with intractable by-products.




Scheme 1. Synthesis of aroylphosphanes **2** to **7**.

The identities of **2** – **7** follow from NMR spectroscopic data, those for **4** – **7** being consistent with previous reports, against which the novel **2** and **3** compare well, their bulk purity being confirmed by microanalytical data. It is noteworthy that for this series of compounds (and indeed **1**) the strong infrared absorbances associated with the carbonyl moiety all fall in the region 1630 – 1650 $cm^{-1}$. This region has been previously considered indicative of appreciable delocalisation of the phosphorus lone-pair into the carbonyl, *viz.* true 'phosphomide' character. On this basis, compounds **2** – **7** would seem to be among the most pronounced examples of this behaviour, as compared with the archetypal $Ph_2PC(O)Me$ (1670 $cm^{-1}$),[5] and $CF_3(CF_2)_6C(O)PPh_2$ (1686 $cm^{-1}$)[6] for which partial delocalisation was invoked. Notwithstanding, the contribution of any such canonical form is clearly minimal, NMR spectroscopic features (*viz.* $\delta_P$, $\delta_C$ $^1J_{PC}$) being wholly consistent with fully saturated phosphorus and classical ketone moieties, with no evidence for multiple-bonding in the P–C linkage. Indeed, this situation is reflected in the structurally characterised cyclophane **1**,[16] which exhibits carbonyl stretches of 1657 and 1639 $cm^{-1}$,[17] but no geometric deviations to imply delocalisation, either in the solid state, or as computed for the gas phase.[18]

Indeed, key geometric parameters for **1** are comparable to those of $O=P(C(O)C_6H_4Me\text{-}2)_3$ (**8**,[19,20] Figure 1, Table 1) in which the lone-pair is sequestered. Moreover, upon formation of $[Pt(\mathbf{1})_2Cl_2]$[16] the acyl linkages adjacent to the coordination site ($d_{C=O}$ 1.201(4), 1.208(4) Å) remain comparable to those distal ($d_{C=O}$ 1.215(4), 1.214(4) Å) and those within the free ligand ($d_{C=O}$ 1.211(3), 1.202(3), 1.220(3), 1.210(3) Å), while the P–C(O) linkages are similarly unperturbed (1.890(4) – 1.897(3) Å, *cf.* 1.886(3) – 1.894(3) Å for **1**). Though marginally distorted pyramidal geometries about phosphorus are apparent, the inter-substituent angles remain consistent with the general range recorded in the CCDC (98 – 102°) for tertiary phosphanes; the slightly more truncated angles in **1** corresponds to the intracyclic angles and can thus be attributed to the constrained geometry.

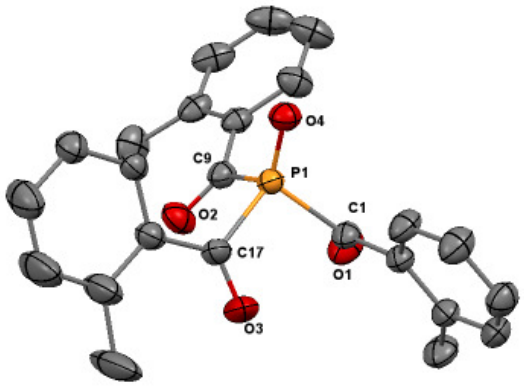



Figure 1. Molecular structure of **8** in crystals of the ether solvate with thermal ellipsoids at the 50 % probability level and hydrogen atoms omitted for clarity

Table 1. Selected, comparative geometric parameters (Å, deg) with standard uncertainties in parentheses, for **1**, $[Pt(\mathbf{1})_2Cl_2]$ and **8**.

| | **1**[16] | $[Pt(\mathbf{1})_2Cl_2]$[16] | **8** |
|---|---|---|---|
| C–O | 1.210(3) | 1.208(4)[a] | 1.213(3) |
| | 1.202(3) | 1.201(4)[a] | 1.213(3) |
| | 1.211(3) | 1.215(4)[b] | 1.216(3) |
| | 1.220(3) | 1.214(4)[b] | |
| P–C(O) | 1.892(3) | 1.896(3)[a] | 1.897(2) |
| | 1.890(3) | 1.897(3)[a] | 1.892(2) |
| | 1.894(3) | 1.890(4)[b] | 1.896(2) |
| | 1.866(3) | 1.895(4)[b] | |
| P–C–O | 120.7(2) | 115.6(3)[a] | 114.1(2) |
| | 120.0(2) | 115.7(3)[a] | 113.7(2) |
| | 120.4(2) | 119.1(3)[b] | 112.9(2) |
| | 120.6(2) | 119.2(3)[b] | |
| P–C–C | 117.5(2) | 121.5(2)[a] | 120.7(2) |
| | 118.2(2) | 121.9(2)[a] | 120.6(2) |
| | 117.1(2) | 119.1(2)[b] | 121.3(2) |
| | 117.3(2) | 119.0(2)[b] | |
| O–C–C | 121.8(3) | 122.8(3)[a] | 125.2(2) |
| | 121.8(3) | 122.3(3)[a] | 125.7(2) |
| | 122.5(3) | 121.9(3) | 125.8(2) |
| | 122.1(3) | 121.7(3) | |
| C–P–C | 95.7(1)[c] | 101.8(2)[a] | 97.9(1)[c] |
| | 98.7(2) | 102.0(2)[a] | 100.1(1)[c] |
| | 100.1(1) | 104.6(2)[a,c] | 99.4(1)[c] |
| | 95.1(1)[c] | 99.2(2)[b] | |
| | 99.6(1) | 98.7(2)[b] | |
| | 100.7(1) | 97.7(2)[b,c] | |

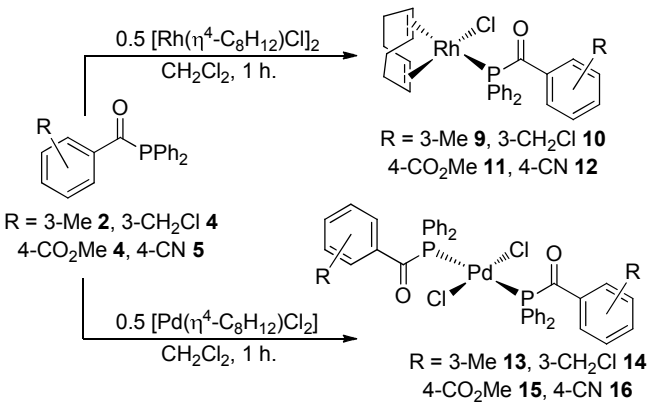
[a] Proximal to P→Pt. [b] Distal from P→Pt. [c] C(O)–P–C(O)

While structural data for **2** – **7** are not available, a comparable scenario would seem likely, given also the minimal changes in $\nu_{CO}$ noted upon coordination to transition metals (*vide infra*). It is also noteworthy that the greater variation in the magnitude of $\nu_{CO}$ results from its sensitivity to aryl substitution patterns, which correlate with Hammett parameters.[21] Taken together, these data imply negligible contributions from a 'phosphomide' canonical form within the free acylphosphanes, and may additionally raise questions as to the validity of using $\nu_{CO}$ as an indicator in this

context, or indeed for the manifestation of hyperconjugative or $p_\pi$-$d_\pi$ contributions.

### Coordination Chemistry

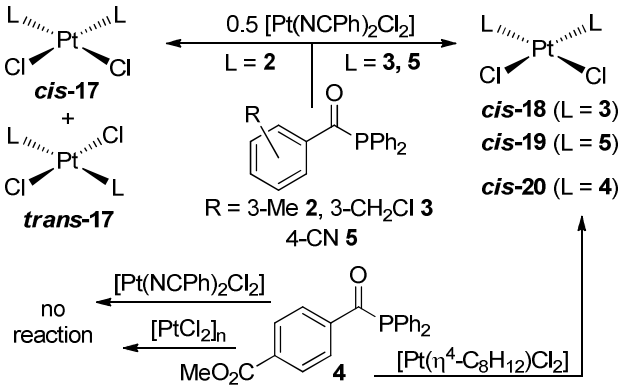
Compounds **2** – **5** each react readily with $[Rh(\eta^4\text{-}C_8H_{12})Cl]_2$, effecting dimer cleavage to afford $[Rh(\eta^4\text{-}C_8H_{12})(L)Cl]$ (L = **2** – **5**; scheme 2, complexes **9** – **12** respectively) as yellow or orange solids in high yield. In each case, a coordination shift of the phosphorus NMR resonance ($\Delta\delta_P$ ~ +25) is accompanied by appreciable coupling to rhodium ($^1J_{RhP}$ ~ 140 Hz), both comparable to those reported for $[Rh(CO)_2(L)Cl]$ (L = $Ph_2PC(O)R$; R = $C_6H_4OMe$-2, Me, $(CF_2)_6CF_3$),[6] the only precedent Rh(I) "phosphomide" complexes. Retention of the (symmetry broken) cyclooctadiene ligand is apparent from $^1H$ NMR data, while bulk purity was confirmed by microanalysis. Similarly, the palladium complexes $[Pd(L)_2Cl_2]$ (Scheme 2, **13** – **16** respectively) are readily obtained from the 2:1 reactions of **2** – **5** with $[Pd(\eta^4\text{-}C_8H_{12})Cl_2]$, and verified from NMR spectroscopic data ($\Delta\delta_P$ +12) and microanalysis. In each case, the exclusive product is assigned as the *trans* isomer, on the basis of the manifestation of virtual triplets for the $^{13}C\{^1H\}$ NMR resonances associated with the phosphorus substituents ($Ar^1$, C=O).[22]




Scheme 2. Coordination chemistry of **2** – **5** toward rhodium and palladium.

The chemistry of platinum, however, is somewhat more complex and highly dependent on the ligand (Scheme 3). Thus, **2** reacts with $[Pt(NCPh)_2Cl_2]$ (0.5 equiv.) to afford an approximately statistical mixture of *cis* and *trans*-$[Pt(\mathbf{2})_2Cl_2]$ (**17**; 55:45%), distinguished from the magnitude of $^1J_{PtP}$ ($J_{PtP}$-*cis* 3505 Hz; $J_{PtP}$-*trans* 2546 Hz) and the presence of virtual coupling for ***trans*-17**, discernible in the $^{13}C\{^1H\}$-NMR spectrum. In contrast, both **3** and **5** react under comparable conditions to afford exclusively ***cis*-18** and **19**.

The coordination chemistry of **4**, however, would appear somewhat more precocious, the free phosphomide being recovered unchanged from reaction with both $[Pt(NCPh)_2Cl_2]$ and $[PtCl_2]_n$, though its coordination was achieved through the 1:1 reaction with $[Pt(\eta^4\text{-}C_8H_{12})_2Cl_2]$, affording a 1:1 mixture of *cis*-$[Pt(\mathbf{4})_2Cl_2]$ (***cis*-20**; $\delta_P$ 16.1, $^1J_{PtP}$ 3504 Hz) and unreacted $[Pt(\eta^4\text{-}C_8H_{12})_2Cl_2]$, as determined on the basis of multinuclear NMR spectroscopy. Separation of this mixture has proven impracticable, while the stoichiometric reaction yields an entirely different species ($\delta_P$ 26.1, devoid of $^{195}Pt$–$^{31}P$ coupling), which remains unidentified. The chemistry of **4** in this context has not been further pursued.




Scheme 3. Coordination chemistry of **2** – **5** with platinum(II).

It is noteworthy that, as with previously reported phosphomide ligands, an increase in $\nu_{CO}$ (Table 2) is observed upon the coordination of **2** – **5**. Such change has been considered previously to imply a reduced contribution from the phosphomide canonical form (*i.e.* $^-O$–C=$PR_2$) due to sequestration of the lone pair.[6] However, this model would seem incompatible with recent computational studies[3] and our own observations (*vide supra*), which both imply limited, even negligible, levels of lone pair delocalisation within the free ligands. Indeed, while a superficial correlation between the metal oxidation state and magnitude of $\Delta\nu$ is apparent, which might be consistent with lone-pair sequestration arguments, correlation might also be drawn to metal basicity, given the established π-acid character of aroylphosphanes.[6] This might imply partial conjugation of the carbonyl π-system and C–P linkage, akin to Kostyanovsky's proposed, albeit outdated, $p_\pi \rightarrow d_\pi$ model, increases in $\nu_{CO}$ being indicative of competitive donation from the metal to P-based acceptor orbitals. However, we are not currently in a position to make decisive comment.

Table 2. Acyl stretching frequencies ($\nu_{CO}$)[a],[b] for **2** – **5** and their coordination complexes.

| L | Free | $Rh(C_8H_{12})(L)Cl$ | $Pd(L)_2Cl_2$ | $Pt(L)_2Cl_2$ |
|---|---|---|---|---|
| **2** | 1634 | 1657 | 1660 | 1659 |
| **3** | 1645 | 1656 | 1667 | 1669 |
| **4** | 1648 | 1663 | 1669 | 1670 |
| **5** | 1650 | 1660 | 1666 | 1666 |

[a] $cm^{-1}$ [b] As neat solids on ATR diamond cell.

## Conclusions

We have described the facile synthesis of a family of aroylphosphanes, including novel 3-alkyl deriviatives, *via* mild and base-free condensation protocols. The coordination chemistry of several of these ligands toward Rh, Pd and Pt salts has been described, affording the first systematic series of aroylphosphane complexes of the platinum group metals, thus significantly increasing the documented coordination compounds of such ligands.

Consideration of the structural features of the macrocyclic aroylphophane **1**, and the phosphine-oxide **8**, alongside spectroscopic data for the full series of ligands, lead us to conclude a negligible extent of *n*(P) delocalisation within the free ligands, raising question as to the validity of invoking $\nu_{CO}$ in assessment of "phosphomide" character – particularly given its sensitivity to

arene substitution patterns. Consequently, noted increases in $\nu_{CO}$ upon coordination cannot be attributed to loss of lone-pair delocalisation, though we cannot currently offer definitive comment on the origin of this effect.

## Experimental Section

### General Methods

All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under at atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å for DCM and THF) or potassium mirrors. Aroyl chlorides, $HPPh_2$ and $P(SiMe_3)_3$ were obtained from Sigma-Aldrich and used as supplied. Precious metal salts ($PtCl_2$, $PdCl_2$) were obtained from STREM and used as supplied; $[RhCl(1,5\text{-cod})]_2$ was previously prepared by literature methods. Deuterated solvents were supplied by Goss Scientific and purified by refluxing with potassium (hydrocarbon) or $CaH_2$ (chlorinated) for 3 days prior to use, being vacuum transferred and stored under inert atmosphere. NMR spectra were recorded on a Varian VNMRS 400 ($^1$H, 399.50 MHz; $^{13}$C, 100.46 MHz; $^{31}$P, 161.71 MHz; $^{195}$Pt, 85.53 MHz) or VNMRS 500 ($^1$H 499.91 MHz; $^{13}$C, 125.72 MHz) spectrometer. All spectra were referenced to $Me_4Si$, 85% $H_3PO_4$ or $K_2PtCl_6$ as appropriate. Carbon-13 NMR data were assigned with recourse to the 2D (HSQC, HMBC) spectra; detailed connectivity was assessed using $^1$H-$^{31}$P HMBC spectra. Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

### Synthesis

***m*-{-C(O)-C$_6$H$_4$(C(O)PMe)}$_2$ (1).** To an ethereal solution of $MeP(SiMe_3)_2$ (0.66 g, 2.27 mmol), cooled to −78°C, was added *m*-$C_6H_4\{C(O)Cl\}_2$ (0.46 g, 2.27 mmol) as solution in ether, leading to immediate formation of a yellow precipitate, suspended in a yellow supernatant solution. After stirring for 30 min. at −78°C, the mixture was allowed to attain ambient temperature and stirred for a further 12h. The solution was then removed by filtration and the precipitate washed with ether and dried *in vacuo*. Yield: 0.320 g, 79 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 1.58 (d, 6H, $^2J_{PH}$ = 3.1 Hz) 6.45 (t, 2H, $^3J_{HH}$ = 1.75 Hz), 7.15 (d, 4H, $^3J_{HH}$ = 1.67 Hz), 9.28 (br., 2H). $^{13}$C{$^1$H}-NMR: $\delta_C$ 1.7 (d, $^1J_{CP}$ 4.5 Hz, Me), 130.3 ($J_{CP}$ = 1.6 Hz, $C^m$), 130.6 (dd, $J_{CP}$ ~ 2 Hz, $C^{o,p}$), 134.0 (t, $^3J_{CP}$ = 13.9 Hz, $C^o$), 137.6 (d, $J_{CP}$ = 37.9 Hz, $C^i$), 205.9 (d, $J_{CP}$ = 46.0 Hz, C=O). $^{31}$P{$^1$H}-NMR: $\delta_P$ 32.7 (s). $\nu_{CO}$ = 1656, 1639 cm$^{-1}$. Anal. Found: C, 60.59 %; H, 3.82 %. Calcd for $C_{18}H_{14}O_4P_2$: C, 60.67 %; H, 3.93 %.

**C$_6$H$_4${C(O)PPh$_2$}(Me-3) (2).** To an ethereal solution of $HPPh_2$ (1.29 g, 6.95 mmol), cooled to −78°C, was added drop-wise $C_6H_4\{C(O)Cl\}$(Me-3) (1.07 g, 6.95 mmol) as solution in ether. The resulting colourless solution was stirred for 30 min. before being allowed to attain ambient temperature, whereupon a yellow colouration was assumed. The mixture was stirred for 1 h. Removal of the volatiles under reduced pressure afforded **1** as a crude yellow solid, which was washed with pentane and dried *in vacuo*. Yield: 1.41 g, 67 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 1.88 (s, 3 H, C$H_3$), 6.81 (d, 1 H, $^3J_{HH}$ 7.4 Hz, CH$^4$), 6.87 (t, 1 H, $^3J_{HH}$ 7.7 Hz, CH$^5$), 7.01 (m, 6 H, *m*-Ph, *p*-Ph), 7.50 (m, 4 H, *o*-Ph), 7.96 (s, 1 H, CH$^2$), 7.99 (d, 1H, $J_{HH}$ 7.7 Hz, CH$^6$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 21.0 (s, $\underline{C}H_3$), 126.3 (d, $^3J_{PC}$ = 11 Hz, $\underline{C}^6$H), 128.6 (s, $\underline{C}^5$H), 128.8 (s, $\underline{C}^2$H,), 128.9 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.5 (s, *p*-Ph), 133.9 (s, $\underline{C}^4$H), 135.3 (d, $^3J_{PC}$ = 20 Hz, *o*-Ph), 138.6 (s, $\underline{C}^3$Me), 140.2 (d, $^2J_{PC}$ 36 Hz, $\underline{C}^1$), 211.8 (d, $^1J_{PC}$ = 37 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 12.4. $\nu_{C=O}$ 1634 cm$^{-1}$. Anal. Found: C, 78.84; H, 5.47. Calcd. for $C_{20}H_{17}OP$: C, 78.93; H, 5.63.

**C$_6$H$_4${C(O)PPh$_2$}(CH$_2$Cl-3) (3).** As for **1** using $HPPh_2$ (0.701 g, 3.76 mmol) and $C_6H_4\{C(O)Cl\}(CH_2Cl\text{-}3)$ (0.712 g, 3.76 mmol). Yield: 1.13g, 89 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 3.83 (s, 2H, C$H_2$Cl), 6.77 (t, 1H, $^3J_{HH}$ = 7.6 Hz, CH$^5$), 6.88 (d, 1 H, $^3J_{HH}$ 7.5 Hz, CH$^4$), 7.01 (m, 6 H, *m*-Ph, *p*-Ph), 7.47 (m, 4 H, *o*-Ph), 7.96 (dq, 1 H, $J_{HH}$ 7.7 Hz, $J_{HH}$ 1.4 Hz CH$^6$), 8.03 (d, 1H, $J_{HH}$ 7.7 Hz, CH$^2$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 45.2 (s, $\underline{C}H_2$Cl), 128.3 (obscured, $\underline{C}^2$H), 128.5 (d, $J_{PC}$ 10Hz, $\underline{C}^6$H), 128.9 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.0 (d, $J_{PC}$ 1 Hz, $\underline{C}^5$H), 129.6 (s, *p*-Ph), 132.9 (d, $J_{PH}$ 1.5 Hz, $\underline{C}^4$H), 135.3 (d, $^3J_{PC}$ = 19 Hz, *o*-Ph), 138.4 (d, $J_{PC}$ 1 Hz, $\underline{C}^3$Me), 140.3 (d, $^2J_{PC}$ 36 Hz, $\underline{C}^1$), 211.4 (d, $^1J_{PC}$ = 38 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 12.9. $\nu_{C=O}$ 1645 cm$^{-1}$. Anal. Found: C, 70.90; H, 4.73. Calcd. for $C_{20}H_{16}OPCl$: C, 70.91; H, 4.76.

**C$_6$H$_4${C(O)PPh$_2$}(CO$_2$Me-4) (4).** As for **1** using $HPPh_2$ (0.572 g, 3.07 mmol) and $C_6H_4\{C(O)Cl\}(CO_2Me\text{-}4)$ (0.610 g, 3.07 mmol). Yield: 0.853 g, 80 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 3.35 (s, 3 H, C$H_3$), 7.00 (m, 6 H, *m*-Ph, *p*-Ph), 7.42 (m, 4 H, *o*-Ph), 7.84 (d, 2H, $^3J_{HH}$ 8.4 Hz, CH$^{3,5}$), 7.97 (dd, 2H, $^3J_{HH}$ 6.8 Hz, $^4J_{HH}$ 1.8 Hz, CH$^{2,6}$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 51.7 (s, $\underline{C}H_3$), 128.2 (obscured, $\underline{C}^{2,6}$H), 129.0 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.7 (s, $\underline{C}^{3,5}$H), 130.0 (s, *p*-Ph), 134.2 (s, $\underline{C}^4$), 135.3 (d, $^3J_{PC}$ = 19 Hz, *o*-Ph), 142.9 (d, $^2J_{PC}$ 35 Hz, $\underline{C}^1$), 165.6 (s, $CO_2$Me), 212.1 (d, $^1J_{PC}$ = 39 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 14.4. $\nu_{C=O}$ 1721 ($CO_2$Me), 1649 cm$^{-1}$. FAB-MS *m/z* 349 [MH]$^+$.

**C$_6$H$_4${C(O)PPh$_2$}(CN-4) (5).** As for **1** using $HPPh_2$ (0.741 g, 3.98 mmol) and $C_6H_4\{C(O)Cl\}$(CN-4) (0.659 g, 3.98 mmol). Yield: 1.00 g, 80 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ . 6.71 (d, 2H, $^3J_{HH}$ 8.4 Hz, CH$^{3,5}$), 7.01 (m, 6 H, *m*-Ph, *p*-Ph), 7.35 (m, 4 H, *o*-Ph), 7.63 (dd, 2H, $^3J_{HH}$ 8.5 Hz, CH$^{2,6}$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 116.5 (s, $\underline{C}^4$), 117.9 (s, $\underline{C}\equiv$N), 128.2 (obscured, $\underline{C}^{2,6}$H), 129.1 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.9 (s, *p*-Ph), 132.3 (s, $\underline{C}^{3,5}$H), 135.3 (d, $^3J_{PC}$ = 19 Hz, *o*-Ph), 141.9 (d, $^2J_{PC}$ 38 Hz, $\underline{C}^1$), 212.5 (d, $^1J_{PC}$ = 39 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 14.5. $\nu_{CN}$ 2229, $\nu_{C=O}$ 1650 cm$^{-1}$. FAB-MS *m/z* 349 [MH]$^+$.

**C$_6$H$_4${C(O)PPh$_2$}$_2$-1,3 (6).** In a manner analogous to that used for **1** using two equivalents of $HPPh_2$ (0.504 g, 2.71 mmol) and one of isophthaloyl chloride (0.275 g, 1.35 mmol) in THF. Yield: 0.574 g, 85 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $^1$H-NMR: $\delta_H$ 6.66 (t, 1H, $^3J_{HH}$ 7.9 Hz, CH$^5$), 6.99 (m, 8H, *m*-Ph), 7.01 (m, 4H, *p*-Ph), 7.40 (m, 8H, *o*-Ph), 7.90 (dt, 2H, $^3J_{PH}$ 7.8 Hz, $^3J_{HH}$ 1.5 Hz CH$^{4,6}$), 9.02 (m, 1H, C$^2$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 128.4 (obscured, $\underline{C}^2$H), 128.6 (obscured, $\underline{C}^5$), 129.0 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.7 (s, *p*-Ph), 132.1 (d, $^3J_{PC}$ = 9 Hz, $\underline{C}^{4,6}$H), 133.1 (d, $^1J_{PC}$ 6 Hz, *i*-Ph), 135.3 (d, $^2J_{PC}$ 18 Hz, *o*-Ph), 139.9 (d, $^2J_{PC}$ 38 Hz, $\underline{C}^{1,3}$), 211.2 (d, $^1J_{PC}$ = 38 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 12.9. $\nu_{CO}$ 1642, 1588 cm$^{-1}$. Anal. Found: C, 76.42; H, 4.80. Calcd. for $C_{32}H_{24}O_2P_2$: C, 76.49; H, 4.81.

**C$_5$H$_3$N{C(O)PPh$_2$}$_2$-2,6 (7).** As for **5**, using $HPPh_2$ (0.617 g, 3.32 mmol) and one of $C_5H_3N\{C(O)Cl\}_2$-2,6 (0.338 g, 1.67 mmol) in THF. Yield: 0.623 g, 74 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 6.71 (d, 1H, $^3J_{HH}$ 7.9 Hz, CH$^5$), 7.03 (m, 4H, *p*-Ph), 7.09 (m, 8H, *m*-Ph), 7.42 (d, 2H, $^3J_{HH}$ 7.4 Hz, CH$^{4,6}$), 7.63 (m, 8H, *o*-Ph). $^{13}$C{$^1$H}-NMR: $\delta_C$ 123.2 (t, $^3J_{PC}$ = 2 Hz, $\underline{C}^{4,6}$H), 128.7 (d, $^3J_{PC}$ = 8 Hz, *m*-Ph), 129.3 (s, *p*-Ph), 134.3 (d, $^1J_{PC}$ 6 Hz, *i*-Ph), 135.4 (d, $^3J_{PC}$ = 20 Hz, *o*-Ph), 153.4 (d, $^2J_{PC}$ 38 Hz, $\underline{C}^{1,3}$), 213.5 (d, $^1J_{PC}$ = 40 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 16.6. $\nu_{C=O}$ 1650 cm$^{-1}$. Anal. Found: C, 73.82; H, 4.55; N, 2.88. Calcd. for $C_{31}H_{23}NO_2P_2$: C, 73.95; H, 4.60; N, 2.78.

**O=P{C(O)C$_6$H$_4$Me-2)}$_3$ (8).** To an ethereal solution of $P(SiMe_3)_3$ (1.21 g, 4.84 mmol) held at −78°C was added $C_6H_4$(COCl)(Me-2) (2.24 g, 14.5 mmol) as solution in ether. After stirring for 30 min. at −78°C, the mixture was allowed to warm to ambient temperature and stirred for a further 48 h, whereupon a yellow precipitate was formed. Volatiles were removed under reduced pressure, then the solid washed with pentane and dried *in vacuo*. Yield: 1.66 g, 68 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 2.51 (s, 9H, $CH_3$) 6.84 (m, 3H, *p*-CH), 6.93 (m, 6H, *m*-CH), 8.04 (m, 3H, *o*-CH). $^{13}$C{$^1$H}-NMR: $\delta_C$ 21.1 (s, $\underline{C}H_3$), 125.7 (s, p-$\underline{C}$H), 131.5 (d, $^3J_{PC}$ = 15.8 Hz, *o*-$\underline{C}$H),

132.1 (d, $^4J_{PC}$ = 1.3 Hz, *m*-C̲H), 132.4 (d, $^4J_{CP}$ = 2.7 Hz, *m*-C̲H), 138.8 (d, $^3J_{PC}$ = 3.7 Hz, *o*-C̲), 140.8 (d, $^2J_{PC}$ = 33.3 Hz, *i*-C̲), 208.9 (d,$^1$ $J_{CP}$ = 34.8 Hz, C=O). $^{31}$P{$^1$H}-NMR: $\delta_P$ 67.2 (s). Anal. Found: C, 71.42 %; H, 5.19 %. Calcd for $C_{24}H_{21}O_4P_1$: C, 71.28 %; H, 5.23 %. ***Crystal data:*** $C_{24}H_{21}O_4P.(0.5Et_2O)$, $M_w$ = 441.46, triclinic, *P-1* (No. 2), *a* = 8.6469(4), *b* = 12.0839(5), *c* = 12.5443(4) Á, α = 106.344(2), *β* = 92.601, *γ* = 110.101(2) °, *V* = 1166.29(8) Á$^3$, *Z* = 2, $D_c$ = 1.257 Mg/m$^{-3}$, $\mu$(Mo-$K_\alpha$) = 0.149 mm$^{-1}$, *T* = 173(2) K, 5249 independent reflections, full-matrix $F^2$ refinement $R_1$ = 0.0599, $wR_2$ = 0.1765 on 5249 independent absorption corrected frelections [$I > 2\sigma(I)$; $2\theta_{max}$ = 55.08 °], 289 parameters. CCDC 1480086. These data can be obtained free of charge from The Cambridge Crystallogrpahic Data Centre via www.ccdc.ac.uk/data_request/cif.

**[Rh(η$^4$-$C_8H_{12}$){$PPh_2C(O)C_6H_4Me$-3}Cl] (9)**. To a solution of [Rh(η$^4$-$C_8H_{12}$)Cl]$_2$ (0.184 g, 0.37 mmol) in dichloromethane was added, at ambient temperature, **2** (0.227 g, 0.75 mmol) resulting in the immediate formation of an orange solution, stirring of which was continued overnight. After removal of the solvent under reduced pressure, the crude material was washed with pentane, then dried *in vacuo* to afford **9** as a yellow solid. Yield: 0.155 g, 76 %. NMR ($C_6D_6$, 30°C): $^1$H-NMR: $\delta_H$ 1.99 – 2.07 (br. m., 2 H, COD-C$H_{2\text{-exo}}$), 2.08 – 2.15 (br. m., 2 H, COD-C$H_{2\text{-exo}}$), 2.41 – 2.54 (br. m., 4 H, COD-C$H_{2\text{-endo}}$), 2.47 (s, 3H, C$H_3$), 3.42 (br. s, 2H COD-C*H*), 5.61 (br. s, 2H COD-C*H*), 7.32 – 7.37 (m., 4H, *m*-Ph), 7.39 – 7.45 (m., overlapped, 4H, CH$^4$, CH$^5$, *p*-Ph), 7.62 – 7.69 (m, 4H, *p*-Ph), 8.51 (br. s., 1H, CH$^2$), 8.71 (dd, $J_{HH}$ / $J_{PH}$ ca 4 Hz, 1 H, C*H*$^6$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 21.7 (s, C̲H$_3$), 29.2 (d, $J_{RhC}$ 1 Hz, COD-C̲H$_2$), 33.2 (d, $J_{RhC}$ 3 Hz, COD-C̲H$_2$), 71.0 (d, $J_{RhC}$ 14 Hz, COD-C̲H), 105.4 (dd, $J_{RhC}$ 12 Hz, $J_{PC}$ 7 Hz, COD-C̲H), 128.4 (d, $J_{PC}$ 10 Hz, *m*-Ph), 128.4 (s, C̲$^5$H), 128.6 (d, $J_{PC}$ 4 Hz, C̲$^6$H), 129.8 (d, $J_{PC}$ 40 Hz, *i*-Ph), 130.7 (d, $J_{PC}$ 2 Hz, *p*-Ph), 131.2 (d, $J_{PC}$ 4 Hz, C̲$^2$H), 134.9 (s, C̲$^4$H), 135.6 (d, $J_{PC}$ 11 Hz, *o*-Ph), 138.4 (s, C̲$^3$H), 138.6 (d, $J_{PC}$ 42 Hz, C̲$^1$), 202.2 (d, $J_{PC}$ 17 Hz, C̲(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 36.1 ($J_{RhP}$ 146 Hz), $\nu_{C=O}$ 1657 cm$^{-1}$. Anal. Found: C, 60.93 %; H, 5.18 %. Calcd for $C_{28}H_{29}OPRhCl$: C, 61.06 %; H, 5.31 %.

**[Rh(η$^4$-$C_8H_{12}$){$PPh_2C(O)C_6H_4CH_2Cl$-3}Cl] (10)**. As for **9** using [Rh(η$^4$-$C_8H_{12}$)Cl]$_2$ (0.138 g, 0.28 mmol) and **3** (0.189 g, 0.56 mmol). Yield: 0.124 g, 76 %. NMR ($CDCl_3$, 30°C): $^1$H-NMR: $\delta_H$ 2.00 – 2.10 (m. br., 2 H, COD-C$H_{2\text{exo}}$), 2.11 – 2.22 (m. br., 2 H, COD-C$H_{2\text{exo}}$), 2.43 – 2.56 (m. br., 4 H, COD-C$H_{2\text{endo}}$), 3.43 (s. br., 2H COD-C*H*), 4.68 (s, $CH_2Cl$), 5.63 (s. br., 2H COD-C*H*), 7.34 – 7.40 (m., 4H, *m*-Ph), 7.41 – 7.47 (m., 2H, *p*-Ph), 7.53 (t, $J_{HH}$ 7.7 Hz, 1H, CH$^5$), 7.64 (s., br., 2H, CH$^4$), 7.65 – 7.67 (m., 4H, *o*-Ph), 8.73 (d, br., $J_{HH}$ 7.5 Hz, 1H, CH$^6$), 8.81 (s., br., 1H, CH$^2$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 29.2 (s, COD-C̲H$_2$), 33.2 (s, COD-C̲H$_2$), 46.0 (s, C̲H$_2$Cl), 71.4 (d, $J_{RhC}$ 13 Hz, COD-C̲H), 105.8 (d, $J_{RhC}$ 11 Hz, $J_{PC}$ 7 Hz, COD-C̲H), 128.5 (d., $J_{PC}$ 10 Hz, *m*-Ph), 129.0 (s, C̲$^5$H), 130.9 (d., $J_{PC}$ 2 Hz, *p*-Ph), 130.8 (d, $J_{PC}$ 3 Hz, C̲$^6$H), 131.2 (d, $J_{PC}$ 4 Hz, C̲$^2$H), 133.9 (s., C̲$^4$H) 135.5 (d. $J_{PC}$ 10 Hz, *o*-Ph), 138.0 (s, C̲$^3$), 202.1 (br. C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 36.4 ($J_{RhP}$ 146 Hz). $\nu_{C=O}$ 1657 cm$^{-1}$. Anal. Found: C, 57.43 %; H, 4.75 %. Calcd for $C_{28}H_{28}OPRhCl_2$: C, 57.46 %; H, 4.82 %.

**[Rh(η$^4$-$C_8H_{12}$){$PPh_2C(O)C_6H_4CO_2Me$-4}Cl] (11)**. As for **9** using [Rh(η$^4$-$C_8H_{12}$)Cl]$_2$ (0.197 g, 0.40 mmol) and **4** (0.278 g, 0.80 mmol). Yield: 0.205 g, 86 %. NMR ($CDCl_6$, 30°C): $^1$H-NMR: $\delta_H$ 2.07 (m, br. 2 H, COD-C$H_{2\text{exo}}$), 2.16 (m, br. 2 H, COD-C$H_{2\text{exo}}$), 2.49 (br. 4 H, COD-C$H_{2\text{endo}}$), 3.43 (s. br., 2H COD-C*H*), 5.60 (s. br., 2H COD-C*H*), 3.97 (s, 3H, C$H_3$), 7.32 – 7.39 (m., 4H, *m*-Ph), 7.41 – 7.46 (m., 2H, 9-Ph), 7.58 – 7.65 (m., 4H, *o*-Ph), 8.18 (d, $^3J_{HH}$ 8 Hz, 2H, C*H*$^{3,5}$), 8.87 (d, $^3J_{HH}$ 8 Hz, 2H, C*H*$^{2,6}$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 29.2 (s, COD-C̲H$_2$), 38.9 (s, COD-C̲H$_2$), 52.7 (s, C̲H$_3$), 71.4 (d, $J_{RhC}$ 14 Hz, COD-C̲H), 106.0 (d, $J_{RhC}$ 11 Hz, $J_{RhC}$ 7 Hz, COD-C̲H), 128.6 (d, $J_{PC}$ 10 Hz, *m*-Ph), 129.8 (s, C̲$^{3,5}$H), 130.7 (d, $J_{PC}$ 4 Hz, C̲$^{2,6}$H), 131.0 (d, $J_{PC}$ 2 Hz, *p*-Ph), 135.4 (d, $J_{PC}$ 11 Hz, *o*-Ph), 141.7 (d, $J_{PC}$ 42 Hz, C̲$^1$), 166.3 (s, C̲O$_2$Me), 202.5 (d, $J_{PC}$ 18 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 36.9 ($J_{RhP}$ 146.9 Hz). $\nu_{C=O}$ 1718, 1663 cm$^{-1}$. Anal. Found: C, 58.42 %; H, 4.96 %. Calcd for $C_{29}H_{29}ClO_3PRh$: C, 58.55 %; H, 4.91 %.

**[Rh(η$^4$-$C_8H_{12}$){$PPh_2C(O)C_6H_4CN$-4}Cl] (12)**. As for **9** using [Rh(η$^4$-$C_8H_{12}$)Cl]$_2$ (0.072 g, 0.145 mmol) and **5** (0.091 g, 0.289 mmol). Yield: 0.070 g, 86 %. NMR ($CD_2Cl_2$, 30°C): $^1$H-NMR: $\delta_H$ 2.09 (m, br. 2 H, COD-C$H_{2\text{exo}}$), 2.20 (m, br. 2 H, COD-C$H_{2\text{exo}}$), 2.48 (br. 4 H, COD-C$H_{2\text{endo}}$), 3.45 (s. br., 2H COD-C*H*), 5.57 (s. br., 2H COD-C*H*), 7.36 – 7.42 (m, 4H *m*-Ph), 7.45 – 7.51 (m, 2H *p*-Ph), 7.55 – 7.62 (m, 4H *o*-Ph), 7.85 (d, $J_{HH}$ 8 Hz, 2H, CH$^{3,5}$), 8.86 (d, $J_{HH}$ 8 Hz, 2H, CH$^{2,6}$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 29.6 (s, COD-C̲H$_2$), 33.5 (s, COD-C̲H$_2$), 72.2 (d, $J_{RhC}$ 13 Hz, COD-C̲H), 107.0 (d, $J_{RhC}$ 12 Hz, $J_{RhC}$ 7 Hz, COD-C̲H), 117.3 (s, C̲$^4$), 118.6 (s,. C̲≡N), 129.1 (d, $J_{PC}$ 9 Hz, *m*-Ph), 131.6 (d, $J_{PC}$ 2 Hz, *p*-Ph), 131.3 (d, $J_{PC}$ 3 Hz, C̲$^{2,6}$H), 132.9 (s, C̲$^{3,5}$H), 135.8 (d, $J_{PC}$ 11 Hz, *o*-Ph), 141.9 (d, $J_{PC}$ 43 Hz, C̲$^1$), 203.0 (d, $J_{PC}$ 17 Hz, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 37.8 ($J_{RhP}$ 147.1 Hz). $\nu_{CN}$ 2229, $\nu_{C=O}$ 1660 cm$^{-1}$. Anal. Found: C, 59.85 %; H, 4.95 %; N, 2.57 %. Calcd for $C_{28}H_{26}ClNOPRh$: C, 59.86 %; H, 4.66 %; N, 2.85 %.

***trans*-[Pd{$PPh_2C(O)C_6H_4Me$-3}$_2$Cl$_2$] (13)**. To a solution of [Pd(η$^4$-$C_8H_{12}$)Cl$_2$] (0.085 g, 0.297 mmol) in dichloromethane was added, at ambient temperature, two equivalents of **2** (0.181 g, 0.595 mmol) resulting in the immediate formation of a yellow solution, stirring of which was continued overnight. After removal of the solvent under reduced pressure, the crude material was washed with pentane, then dried *in vacuo* to afford **13** as a yellow solid. Yield: 0.217 g, 93 %. NMR ($CDCl_3$, 30°C): $^1$H-NMR: $\delta_H$ 2.32 (s, 6H, C$H_3$), 7.26 (m, 2H, CH$^4$), 7.32 (m, 2H, CH$^5$), 7.36 (m, 8H, *m*-Ph), 7.45 (m, 4H, *p*-Ph), 7.75 (m, 8H, *o*-Ph), 8.09 (s, br. 2H, CH$^2$), 8.25 (d, $^3J_{HH}$ 7.8 Hz, 2 H, C*H*$^6$). $^{13}$C{$^1$H}-NMR: $\delta_C$ 21.5 (s, C̲H$_3$), 126.9 (t, $J_{PC}$ 22 Hz, C̲$^1$), 127.9 (t, $J_{PC}$ 2 Hz, C̲$^6$H), 128.5 (s, C̲$^4$H), 128.6 (t, $J_{PC}$ 4 Hz, *m*-Ph), 130.2 (t, $J_{PC}$ 2 Hz, C̲$^2$H), 131.3 (t, $J_{PC}$ 1 Hz, *p*-Ph), 134.9 (s, C̲$^5$H), 135.9 (t, $J_{PC}$ 6 Hz, *o*-Ph), 137.2 (t, $J_{PC}$ 23 Hz, *i*-Ph), 138.6 (s, C̲$^3$), 198.9 (br, C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 25.8 (s). $\nu_{C=O}$ 1660 cm$^{-1}$. Anal. Found: C, 61.02 %; H, 4.45 %. Calcd for $C_{40}H_{34}Cl_2O_2P_2Pd$: C, 61.13 %; H, 4.36 %.

***trans*-[Pd{$PPh_2C(O)C_6H_4CH_2Cl$-3}$_2$Cl$_2$] (14)**. As for **13** using [Pd(η$^4$-$C_8H_{12}$)Cl$_2$] (0.042 g, 0.147 mmol) and **3** (0.100 g, 0.295 mmol). Yield: 0.117 g, 93 %. NMR ($CDCl_3$, 30°C): $^1$H-NMR: $\delta_H$ 4.50 (s, 4 H, C$H_2$Cl), 7.34 (m, 2H C$^5$H), 7.38 (m, 8H, *m*-Ph), 7.47 (m, 4H, *p*-Ph), 7.54 (t, $^3J_{HH}$ 8.4 Hz, 2H, C$^4$H), 7.78 (dt, $^3J_{HH}$ 6.4 Hz, $J_{PH}$ 5.8 Hz, 8H, *o*-Ph), 8.23 (s. br., 2H, C$^2$H), 8.29 (d, $^3J_{HH}$ 7.7 Hz, 2H, C$^6$H). $^{13}$C{$^1$H}-NMR: $\delta_C$ 45.5 (s, C̲H$_2$Cl), 126.2 (t, $J_{PC}$ 23 Hz, *i*-Ph), 128.8 (t, $J_{PC}$ 5 Hz, *m*-Ph), 129.0 (s, C̲$^5$H), 129.6 (t, $J_{PC}$ 2 Hz, C̲$^2$H), 130.1 (t, $J_{PC}$ 2 Hz, C̲$^6$H), 131.5 (s, *p*-Ph), 133.8 (s, C̲$^4$H), 135.8 (t, $J_{PC}$ 6 Hz, *o*-Ph), 137.3 (t, $J_{PC}$ 21 Hz, C̲$^1$), 138.1 (s, C̲$^3$), 198.8 (br., C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 25.9 (s). $\nu_{C=O}$ 1657 cm$^{-1}$. Anal. Found: C, 56.24 %; H, 3.74 %. Calcd for $C_{40}H_{32}Cl_4O_2P_2Pd$: C, 56.20 %; H, 3.77 %.

***trans*-[Pd{$PPh_2C(O)C_6H_4(CO_2Me)$-4}$_2$Cl$_2$] (15)**. As for **13** using [Pd(η$^4$-$C_8H_{12}$)Cl$_2$] (0.162 g, 0.567 mmol) and **4** (0.395 g, 1.13 mmol). Yield: 0.452 g, 91 %. NMR ($CDCl_3$, 30°C): $^1$H-NMR: $\delta_H$ 3.95 (s, 6 H, C$H_3$), 7.39 (m, 8H, *m*-Ph), 7.48 (m, 4H, *p*-Ph), 7.78 (dt, $^3J_{HH}$ 6.9 Hz, $J_{PH}$ 5.6 Hz, 8H, *o*-Ph), 8.01 (d, $^3J_{HH}$ 8.5 Hz, 4H, C$^{3,5}$H), 8.31 (d, $^3J_{HH}$ 8.8 Hz, 4H, C$^{2,6}$H). $^{13}$C{$^1$H}-NMR: $\delta_C$ 52.7 (s, C̲H$_3$), 125.9 (t, $J_{PC}$ 23 Hz, *i*-Ph), 128.9 (t, $J_{PC}$ 5 Hz, *m*-Ph), 129.7 (t, $J_{PC}$ 2 Hz, C̲$^{2,6}$H), 129.8 (s, C̲$^{3,5}$H), 131.7 (s, *p*-Ph), 135.7 (t, $J_{PC}$ 6 Hz, *o*-Ph), 140.1 (t, $J_{PC}$ 23 Hz, C̲$^1$), 166.1 (s, C̲O$_2$) 199.2 (br., C(O)P). $^{31}$P{$^1$H}-NMR: $\delta_P$ 26.1 (s). $\nu_{C=O}$ 1720, 1670 cm$^{-1}$. Anal. Found: C, 57.63 %; H, 4.03 %. Calcd for $C_{42}H_{34}Cl_2O_6P_2Pd$: C, 57.72 %; H, 3.92 %.

***trans*-[Pd{$PPh_2C(O)C_6H_4CN$-4}$_2$Cl$_2$] (16)**. As for **13** using [Pd(η$^4$-$C_8H_{12}$)Cl$_2$] (0.053 g, 0.187 mmol) and **5** (0.118 g, 0.375 mmol). Yield: 0.139 g, 92 %. NMR ($CDCl_3$, 30°C): $^1$H-NMR: $\delta_H$ 7.42 (m, 8H, *m*-Ph), 7.54 (m, 4H, *p*-Ph), 7.74 (dt, $^3J_{HH}$ 7 Hz, $J_{PH}$ 6 Hz, 8H, *o*-Ph), 7.59 (d, $^3J_{HH}$ 8.5 Hz, 4H, C$^{3,5}$H), 8.26 (d, $^3J_{HH}$ 8.4 Hz, 4H, C$^{2,6}$H). $^{13}$C{$^1$H}-NMR: $\delta_C$ 117.0 (s, C$^4$), 117.8 (s, C̲≡N), 125.5 (t, $J_{PC}$ 24 Hz, *i*-Ph), 129.1 (t, $J_{PC}$ 5 Hz,

*m*-Ph), 129.9 (t, $J_{PC}$ 2 Hz, $\underline{C}^{2,6}$H), 131.1 (s, *p*-Ph), 132.3 (s, $\underline{C}^{3,5}$H), 135.6 (t, $J_{PC}$ 6 Hz, *o*-Ph), 139.8 (t, $J_{PC}$ 23 Hz, $\underline{C}^{1}$), 198.7 (t, $J_{PC}$ 12 Hz, C(O)P). $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 25.9 (s). $\nu_{CN}$ 2229, $\nu_{C=O}$ 1666 $cm^{-1}$ Anal. Found: C, 59.58 %; H, 3.52 %; N, 3.48%. Calcd for $C_{40}H_{28}Cl_2N_2O_2P_2Pd$: C, 59.46 %; H, 3.49 %; N, 3.47%.

***cis/trans*-[Pt{PPh$_2$C(O)C$_6$H$_4$Me-3}$_2$Cl$_2$] (17)**. To a solution of [Pt(NCPh)$_2$Cl$_2$] (0.143 g, 0.303 mmol) in dichloromethane was added, at ambient temperature, two equivalents of **2** (0.184 g, 0.605 mmol) resulting in the immediate formation of a pale yellow solution, stirring of which was continued overnight. After removal of the solvent under reduced pressure, the crude material was washed with Et$_2$O, then pentane and dried *in vacuo* to afford **17** as a yellow solid. Yield: 0.217 g, 93 %. $\nu_{C=O}$ 1661 $cm^{-1}$ (broad absorption due to mixture of isomers). Anal. Found: C, 54.86 %; H, 3.78 %. Calcd for $C_{40}H_{34}Cl_2O_2P_2Pt$: C, 54.93 %; H, 3.92 %.

***cis*-17 (55%):** NMR ($CDCl_3$, 30°C): $^{1}$H-NMR: $\delta_H$ 2.33 (s, 6H, C$H_3$), 7.18 (m, 8H, *m*-Ph), 7.28 (m, 2H, C$^4$H), 7.35 (m, 2H C$^5$H), 7.37 (m, 4H, *p*-Ph), 7.51 (m, 8H, *o*-Ph), 8.06 (s. br., 2H, C$^2$H), 8.17 (d, $^3J_{HH}$ 7.6 Hz, 2H, C$^6$H), $^{13}C\{^{1}H\}$-NMR: $\delta_C$ 21.5 (s, $\underline{C}H_3$), 125.4 (d, $J_{PC}$ 58 Hz, *i*-Ph), 127.4 (d, $J_{PC}$ 40 Hz, $\underline{C}^{1}$), 128.3 (s, $\underline{C}^{5}$H), 128.4 (d, $J_{PC}$ 10 Hz, *m*-Ph), 130.0 (s, $\underline{C}^{6}$H), 131.3 (s, $\underline{C}^{2}$H), 131.8 (s, *p*-Ph), 134.6 (s, $\underline{C}^{4}$H), 135.8 (d, $J_{PC}$ 10 Hz, $J_{PtC}$ 8 Hz *o*-Ph), 138.3 (s, $\underline{C}^{3}$), 195.1 (d, $J_{PC}$ 41 Hz, C(O)P). $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 14.8 (s, $J_{PtP}$ 3505 Hz). $^{195}Pt\{^{1}H\}$-NMR: $\delta_{Pt}$ –4351 (t, $^{1}J_{PtP}$ 3505 Hz).

***trans*-17 (45%):** NMR ($CDCl_3$, 30°C): $^{1}$H-NMR: $\delta_H$ 2.33 (s, 6H, C$H_3$), 7.27 (m, 2H C$^5$H), 7.36 (m, 8H, *m*-Ph), 7.36 (m, 2H, C$^4$H), 7.45 (m, 4H, *p*-Ph), 7.77 (dt, $^3J_{HH}$ 6.2 Hz, $J_{PH}$ 5.8 Hz, 8H, *o*-Ph), 8.16 (s. br., 2H, C$^2$H), 8.33 (d, $^3J_{HH}$ 7.7 Hz, 2H, C$^6$H). $^{13}C\{^{1}H\}$-NMR: $\delta_C$ 21.5 (s, $\underline{C}H_3$), 126.6 (t, $J_{PC}$ 27 Hz, *i*-Ph), 128.0 (br., $\underline{C}^{6}$H), 128.3 (s, $\underline{C}^{5}$H), 128.5 (t, $J_{PC}$ 6 Hz, *m*-Ph), 131.2 (br, $\underline{C}^{2}$H), 131.6 (s, *p*-Ph), 134.8 (s, $\underline{C}^{4}$H), 135.8 (t, $J_{PC}$ 6 Hz, *o*-Ph), 137.4 (t, $J_{PC}$ 23 Hz, $\underline{C}^{1}$), 138.4 (s, $\underline{C}^{3}$), 198.6 (br., C(O)P). $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 22.3 (s, $J_{PtP}$ 2546 Hz). $^{195}Pt\{^{1}H\}$-NMR: $\delta_{Pt}$ –3961 (t, $^{1}J_{PtP}$ 2546 Hz).

***cis*-[Pt{PPh$_2$C(O)C$_6$H$_4$CH$_2$Cl-3}$_2$Cl$_2$] (18)**. Prepared in comparable fashion to **17** using [Pt(NCPh)$_2$Cl$_2$] (0.211 g, 0.447 mmol) and **3** (0.303 g, 0.894 mmol). Yield: 0.217 g, 93 %. NMR ($C_6D_6$, 30°C): $^{1}$H-NMR: $\delta_H$ 4.58 (s, 4 H, C$H_2$Cl), 7.22 (m, 8H, *m*-Ph), 7.32 (m, 2H C$^5$H), 7.41 (m, 4H, *p*-Ph), 7.48 (m, 2H, C$^4$H), 7.50 (m, 8H, *o*-Ph), 8.21 (d, $^3J_{HH}$ 8.0 Hz, 2H, C$^6$H), 8.29 (s. br., 2H, C$^2$H), $^{13}C\{^{1}H\}$-NMR: $\delta_C$ 45.7 (s, $\underline{C}H_2$Cl), 124.8 (d, $J_{PC}$ 58 Hz, *i*-Ph), 128.6 (d, $J_{PC}$ 10 Hz, $J_{PtC}$ 8 Hz, *m*-Ph), 128.9 (s, $\underline{C}^{5}$H), 130.0 (s, $\underline{C}^{6}$H),130.1 (s, $\underline{C}^{2}$H), 132.0 (s, *p*-Ph), 133.6 (s, $\underline{C}^{4}$H), 135.8 (d, $J_{PC}$ 10 Hz, $J_{PtC}$ 8 Hz *o*-Ph), 136.7 (d, $J_{PC}$ 40 Hz, $\underline{C}^{1}$), 137.8 (s, $\underline{C}^{3}$), 194.6 (C(O)P). $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 15.3 (s, $^{1}J_{PtP}$ 3503 Hz). $^{195}Pt\{^{1}H\}$-NMR: $\delta_{Pt}$ –4354 (t, $^{1}J_{PtP}$ 3503). $\nu_{CN}$ 2229, $\nu_{C=O}$ 1668 $cm^{-1}$. Anal. Found: C, 50.88 %; H, 3.33 %. Calcd for $C_{40}H_{32}Cl_4O_2P_2Pt$: C, 50.92 %; H, 3.42 %.

***cis*-[Pt{PPh$_2$C(O)C$_6$H$_4$CN-4}$_2$Cl$_2$] (19)**. Prepared in comparable fashion to **17** using [Pt(NCPh)$_2$Cl$_2$] (0.211 g, 0.424 mmol) and **5** (0.267 g, 0.848 mmol). Yield: 0.320 g, 84 %. NMR ($CDCl_3$, 30°C): $^{1}$H-NMR: $\delta_H$ 7.25 (m, 8H, *m*-Ph), 7.40 (m, 4H, *p*-Ph), 7.45 (m, 8H, *o*-Ph), 7.60 (d, $^3J_{HH}$ 8 Hz, 4H, C$^{3,5}$H), 8.21 (d, $^3J_{HH}$ 8Hz, 4H, C$^{2,6}$H). $^{13}C\{^{1}H\}$-NMR: $\delta_C$ 116.6 (s, C$^4$), 117.8 (s, $\underline{C{\equiv}N}$), 124.2 (t, $J_{PC}$ 58 Hz, *i*-Ph), 128.8 (d, $J_{PC}$ 11 Hz, $J_{PtC}$ 10 Hz, *m*-Ph), 130.8 (s, $\underline{C}^{2,6}$H), 132.5 (s, *m*-Ph), 132.1 (s, $\underline{C}^{3,5}$H), 135.6 (d, $J_{PC}$ 9 Hz, $J_{PtC}$ 10 Hz, *o*-Ph), 139.5 (d, $J_{PC}$ 49 Hz, $\underline{C}^{1}$), 194.8 (d, $J_{PC}$ 44 Hz, C(O)P). $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 16.5 (s, $J_{PtP}$ 3493). $^{195}Pt\{^{1}H\}$-NMR: $\delta_{Pt}$ 4374 (t, $^{1}J_{PtP}$ 3493 Hz). $\nu_{CN}$ 2230, $\nu_{C=O}$ 1666 $cm^{-1}$. Anal. Found: C, 53.65 %; H, 3.15 %; N, 3.10 %. Calcd for $C_{40}H_{28}Cl_2N_2O_2P_2Pt$: C, 53.58 %; H, 3.15 %; N, 3.12 %.

***cis*-[Pt{PPh$_2$C(O)C$_6$H$_4$(CO$_2$Me)-4}$_2$Cl$_2$] (20)**. Prepared in a similar manner to **17**, but commencing from [Pt($\eta^4$-C$_8$H$_{14}$)Cl$_2$] (0.118 g, 0.316 mmol) and **4** (0.109 g, 0.316 mmol). Obtained as 1:1 mixture with [Pt($\eta^4$-C$_8$H$_{14}$)Cl$_2$]. Yield (crude): 0.216 g. NMR ($CDCl_3$, 30°C): $^{1}$H-NMR: $\delta_H$ 3.94 (s, 6 H, C$H_3$), 7.22 (m, 8H, *m*-Ph), 7.41 (m, 4H, *p*-Ph), 7.47 (m, 8H, *o*-Ph), 7.98 (d, $^3J_{HH}$ 8.9 Hz, 4H, C$^{3,5}$H), 8.26 (d, $^3J_{HH}$ 8.9 Hz, 4H, C$^{2,6}$H). [**Pt(C$_8$H$_{12}$)Cl$_2$:** 2.26 (m, 4H, COD-C$H_2$), 2.70 (m, 4H, COD-C$H_2$), 5.61 (m, $J_{PtH}$ 66.7 Hz, COD-C*H*)]. $^{13}C\{^{1}H\}$-NMR: $\delta_C$ 52.7 (s, $\underline{C}H_3$), 124.7 (d, $J_{PC}$ 58 Hz, *i*-Ph), 128.6 (t, $J_{PC}$ 11 Hz, $J_{PtC}$ 8 Hz, *m*-Ph), 129.5 (s, $\underline{C}^{3,5}$H), 130.5 (s, $\underline{C}^{2,6}$H), 132.2 (s, *p*-Ph), 135.7 (d, $J_{PC}$ 10 Hz, $J_{PtC}$ 8 Hz, *o*-Ph), 139.7 (d, $J_{PC}$ 49 Hz, $\underline{C}^{1}$), 166.1 (s, $\underline{C}O_2$) 195.1 (d, $J_{PC}$ 45 Hz, C(O)P). [**Pt(C$_8$H$_{12}$)Cl$_2$:** 31.1 (s, COD-$\underline{C}H_2$), 100.2 (s, $J_{PtC}$ 152 Hz, COD-$\underline{C}H$), 5.61 (m, $J_{PtH}$ 66.7 Hz)]. $^{31}P\{^{1}H\}$-NMR: $\delta_P$ 16.1 ($J_{PtP}$ 3504 Hz). $\nu_{CO}$(ester) 1721, $\nu_{CO}$ 1670 $cm^{-1}$.

**Supporting Information** (see footnote on the first page of this article): computational details for compound **1** (pdf and xyz) and crystallographic data for compound **8** in cif format.

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[17] The stretches are assigned to the anti-symmetric $B_1$ (1657 $cm^{-1}$) and $B_2$ (1639 $cm^{-1}$) modes on the basis of computed frequencies (corrected) at the B3LYP/6-311++G(3d,3p) level for **1** in $C_{2v}$ symmetry. The weak, symmetric, $A_1$ band (1654 $cm^{-1}$) is difficult to observe, while the $A_2$ mode is infrared silent.

[18] Geometry optimization of **1** was performed at the B3LYP/6-311+G(d,p) level commencing from the solid-state structure. The optimised state was characterised as a minimum on the basis of no imaginary frequencies. For full details see Supporting Information.

[19] Compound **8** was obtained in good yield (68 %) as the primary product from condensation of $P(SiMe_3)_3$ and 3 equiv. $C_6H_3Me\{C(O)Cl\}$-2. The source of oxygen is unclear, and might either be adventitious in nature (implying significant sensitivity for the phosphane) or the result of substrate (toluoyl chloride) degradation. It is notable that **8** has been previously claimed in the patent literature,[20] but with a significantly lower frequency $^{31}P\{^1H\}$ NMR signal than we observe ($\delta_P$ 26.9, *cf.* $\delta_P$ 67.2 for **8**). Given our more comprehensive and unequivocal supporting data, we reason the original report to be erroneous.

[20] D. G. Leppard, M. Köhler, G. Hug, **1996**, WO96/07662

[21] C. Hansch, A. Leo, R. W. Taft, *Chem. Rev.*, **1991**, *91*, 165 – 195 and references therein.

[22] 'Virtual coupling' is a commonly encountered higher-order effect in trans-square planar bis-phosphine complexes, resulting from the magnetic inequivalence of the (symmetrically equivalent) phosphorus centres, with respect to their α-substituents.[23] The effect is obviated in *cis* isomers by the significantly reduced magnitude of *cis* coupling interactions across a metal centre.

[23] R. V. Parish *in NMR, NQR, EPR and Mössbauer Spectroscopy in Inorganic Chemistry*, Ellis-Horwood, Chichester, **1990**, pp. 46 – 49.

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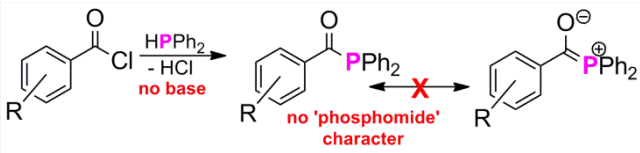


Text for Table of Contents.

The facile base-free synthesis of a range of aroylphosphanes is described. Consideration of their spectroscopic features, alongside structural data for related systems implies negligible 'phosphomide' character. Their coordination chemistry toward platinum group metals is described, providing rare examples of this type of complex.

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Aroylphosphanes: Base-free synthesis and their coordination chemistry with platinum group metals

**Keywords:** Phosphane ligands / Phosphanes / Transition Metals / Phosphomides / Coordination compounds