DALTON

Synthesis and reactivity of aryl- and alkyl-palladium(II) complexes with functional phosphines and phosphinoenolate ligands: first analogues of model nickel catalysts*

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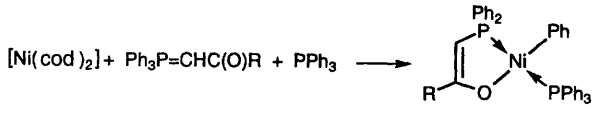
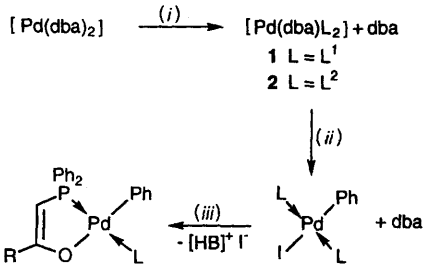
Phenyl- and methyl-palladium(II) complexes analogous to model nickel(II) catalysts were prepared from readily available precursors. The methods used allow different ligands to be introduced in the co-ordination sphere. For example, the chelating phosphinoenolate ligand in [PdPh{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}$L^2$] [$L^2$ = $Ph_2PCH_2C(O)NPh_2$] was displaced by 1 equivalent of $Ph_2PCH_2C(O)Ph$ (L^1) to give [PdPh{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$L^2$] whereas the terminal functional phosphine was displaced by $P(C_6H_{11})_3$ to give [PdPh{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}{$P(C_6H_{11})_3$}]. Owing to favourable ligand-redistribution reactions, treatment of a mixture of complexes *trans*-[PdMe(Cl)$L^2{}_2$], *trans*-[PdMe(Cl)$L^1{}_2$] and *trans*-[PdMe(Cl)L^1(L^2)] (which cannot be isolated pure) with an excess of NaOMe in toluene selectively afforded the phosphinoenolate complex [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$L^2$]. The enolate moiety of [PdPh{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}$L^2$] and of [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}$L^2$] reacted with R′N=C=O (R′ = Ph or *p*-tolyl) with formation of a carbon–carbon bond in a Michael-type addition and the products were shown to exist in the form of two isomers **a** and **b**, characterised by a N–H · · · O or a N–H · · · N hydrogen bond within the ligand system. Insertion of CO into the Pd–Me bond of [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}$L^2$] or [PdMe{$Ph_2C$[=C(O)NHPh]C(O)$NPh_2$}$L^2$] yielded the corresponding acyl complexes. Although [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}($PPh_3$)] inserted ethylene into its Pd–Me bond, as evidenced by quantitative formation of propylene, the palladium hydride that must be generated by the β-elimination reaction decomposes before further ethylene insertion can occur.

Phosphinoenolate nickel(II) complexes of the type [NiPh{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}($PPh_3$)] have served as models for the catalysts used in the Shell higher olefin process (SHOP) which converts ethylene into linear α-olefins.[1] Their synthesis is readily performed by oxidative addition of a functional phosphorane to the nickel(0) complex [Ni(cod)$_2$] (cod = cycloocta-1,5-diene) (Scheme 1). This reaction generates the Ni–Ph bond in which ethylene insertion will take place during the initiation step of the catalysis. The synthetic procedure allows one to vary the nature of the monodentate phosphine introduced and the R group on the ylide, which may lead to interesting selectivity effects in catalysis.[2] However, it does not allow a change of the metal since this oxidative-addition reaction is so far limited to nickel(0). We were interested in studying the chemistry of analogous d^8 metal complexes, particularly of palladium, in view of the numerous applications of this metal in homogeneous catalysis. To this end, we devised a synthetic approach based (*i*) on the co-ordination of functional phosphines to a palladium(0) complex, (*ii*) its conversion into an arylpalladium(II) complex by oxidative addition of PhI, and (*iii*) deprotonation of the functional phosphine by a base B to give the corresponding phosphinoenolate complexes (Scheme 2). The most convenient experimental procedure was found to involve preliminary formation of the arylpalladium(II) complex followed by co-ordination of the functional phosphine and deprotonation.[3] The functional phosphines investigated were $Ph_2PCH_2C(O)Ph$ (L^1)[4a] and $Ph_2PCH_2C(O)NPh_2$ (L^2)[5] which contains the more electron-donating NPh_2 group.



Scheme 1



Scheme 2 dba = Dibenzylideneacetone. (*i*) 2 L, L = Ph_2PCH_2-C(O)R, R = Ph (L^1) or NPh_2 (L^2); (*ii*) PhI; (*iii*) B (base)

Results and Discussion

Synthesis of arylpalladium(II) complexes

The reaction of [Pd(dba)$_2$] with 2 equivalents of Ph_2PCH_2-C(O)Ph (L^1) or $Ph_2PCH_2C(O)NPh_2$ (L^2) in toluene afforded the palladium(0) complexes [Pd(dba)$L^1{}_2$] **1** and [Pd(dba)$L^2{}_2$] **2**, respectively. Interestingly, an excess of functional phosphine does not displace dba from these complexes, in contrast to PPh_3 or $PMePh_2$ which lead to the formation of [Pd(PPh_3)$_n$] or [Pd($PMePh_2$)$_n$] (n = 3 or 4), respectively.[5] Complexes **1** and **2** are stable in solution for a few hours but could not be isolated pure in the solid state because their solubility properties are very similar to those of dba.

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Non-SI unit employed: atm = 101 325 Pa.

The oxidative-addition reaction of PhI to complex **1** or **2** (or to $[Pd(dba)_2]$ followed by the addition of 2 equivalents functional phosphine) yielded the expected products *trans*-$[PdPh(I)L_2]$ (L = L^1 **3** or L^2 **4**). However, their solubility was again very similar to that of the dba liberated. For this reason we modified the procedure and found that it should best involve the sequence of reactions shown in Scheme 3: first formation and isolation of [PdPh(I)(tmen)] (tmen = $Me_2NCH_2CH_2NMe_2$), which in contrast to dba is insoluble in diethyl ether, followed by addition of 2 equivalents of functional phosphine to give **3** and **4**, respectively.

Deprotonation of complex **4** by NaOMe in toluene afforded the desired aryl, phosphinoenolate complex $[\overline{PdPh\{Ph_2PCH{=}C(\overline{O})NPh_2\}}L^2]$ **5**. Its ^{31}P-$\{^1H\}$ NMR spectrum contains two doublets at δ 16.1 and 10.2 with a $^2J(PP)$ coupling of 393 Hz, typical for a *trans* arrangement of the phosphorus nuclei. The ^1H NMR spectrum contains two doublets at δ 3.78 [$^2J(PH)$ = 5.1] and 3.20 [$^2J(PH)$ = 7.9 Hz] for the PCH and PCH_2 protons, respectively. The formulation of **5** was confirmed by the observation of the molecular peak in the mass spectrum.[3]

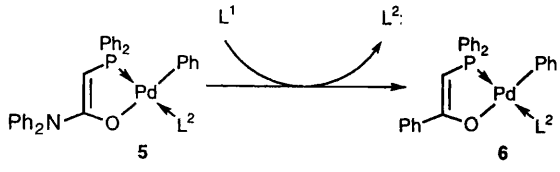
Somewhat surprisingly, the complex analogous to **5** but derived from the ketophosphine L^1, $[\overline{PdPh\{Ph_2PCH{=}C(\overline{O})Ph\}}L^1]$, could not be obtained by this method and only the known and stable complex *cis*-$[\overline{Pd\{Ph_2PCH{=}C(\overline{O})Ph\}_2}]$[4] was isolated. We believe that cleavage of the palladium–aryl bond was induced by catalytic amounts of MeOH which led to elimination of benzene and formation of a Pd^{II}–OMe bond.[6] The acidity of the PCH_2 hydrogen atoms of co-ordinated L^1 would lead to regeneration of methanol and formation of the second phosphinoenolate chelate (Scheme 4). This would be consistent with observations made on the reactions of the analogous alkyl complexes $[PdMe(Cl)L^1_2]$ with bases (see below) and explain the differences observed between related complexes of L^1 and L^2, the acidity of the PCH_2 protons of the latter being weaker than that of L^1 (see below).

It is interesting that the aryl complex $[\overline{PdPh\{Ph_2PCH{=}C(\overline{O})Ph\}}L^2]$ **6** could be obtained by reaction of **5** with 1 equivalent of L^1 (Scheme 5). *In situ* monitoring of this unusual reaction by ^{31}P-$\{^1H\}$ NMR spectroscopy showed complete conversion after 10 min with the appearance of a singlet at δ −14.2 for free L^2 and of a new AB-type pattern for **6** at δ 23.5 and 11.6 with a characteristic *trans* coupling $^2J(PP)$ of 385 Hz. The enolate proton resonates in the ^1H NMR spectrum at a typical value of δ 5.16. This ligand-replacement reaction is of the acid–base type, the PCH_2 protons of L^1 being more acidic than those of L^2. Although we have no direct evidence for a (probably short-lived) reaction intermediate, it is likely that the proton transfer from L^1 to the enolate carbon occurs after co-ordination of L^1 to palladium, which increases the acidity of the PCH_2 protons.

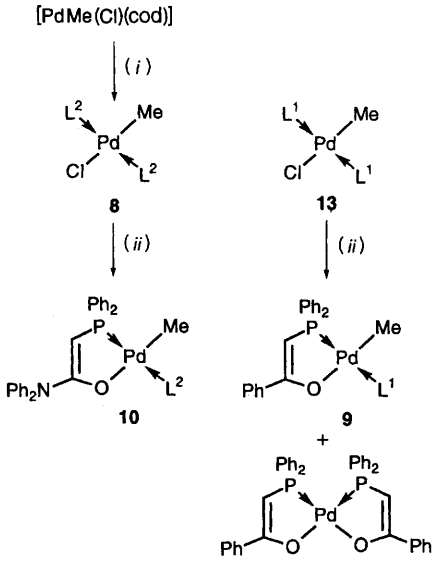
In situ ^{31}P-$\{^1H\}$ NMR experiments showed that $P(C_6H_{11})_3$ quantitatively displaces the L^2 ligand of **5** to give $[\overline{PdPh\{Ph_2PCH{=}C(\overline{O})NPh_2\}}\{P(C_6H_{11})_3\}]$ **7** [AB-type pattern at δ 25.7 and 12.7 with $^2J(PP)$ = 363 Hz]. This reaction and that of Scheme 5 allow a tuning of the stereoelectronic situation at the Pd by selective replacement of the monodentate phosphine or of the three-electron donor *P*,*O* chelate, respectively. Since complexes **6** and **7** could not be isolated pure owing to their solubility properties being too similar to those of L^2 liberated during their synthesis, we turned our attention toward the corresponding methyl complexes. We also hoped that the expected higher reactivity of the Pd–Me *vs.* the Pd–Ph bond would make these complexes better candidates for ethylene-insertion reactions.

Synthesis of phosphinoenolate methylpalladium(II) complexes

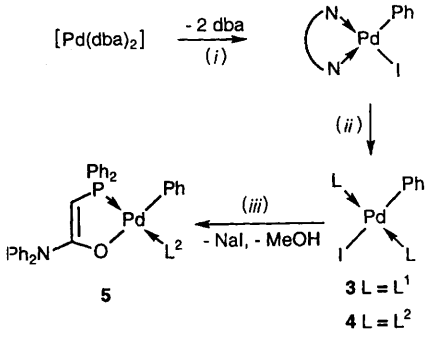
An extension of the reactions shown in Scheme 3 to the methyl compounds was not possible owing to the lack of a suitable reaction between MeI and $[Pd(dba)_2]$. Instead, we treated the methyl complex [PdMe(Cl)(cod)] with 2 equivalents of L^2 to form *trans*-$[PdMe(Cl)L^2_2]$ **8** in which the *trans* arrangement of the phosphines was indicated by the singlet at δ 23.6 in the ^{31}P-



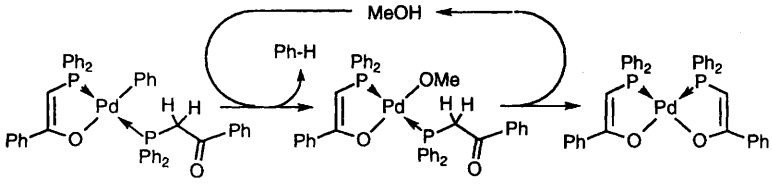
Scheme 5



Scheme 6 (*i*) $2L^2$, −cod, thf (tetrahydrofuran); (*ii*) excess of NaOMe, toluene, −NaCl, −MeOH

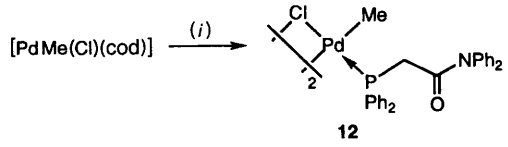


Scheme 3 (*i*) PhI, tmen; (*ii*) 2L, −tmen; (*iii*) NaOMe, toluene



Scheme 4

{^{1}H} NMR spectrum (see Experimental section). This complex was subsequently deprotonated by an excess of NaOMe in toluene to give [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}$L^2$] **10** (Scheme 6). Its formulation is fully consistent with the analytical and spectroscopic data (see Experimental section). Although **10** was isolated in *ca.* 80% yield based on [PdMe(Cl)(cod)], the analogous complex [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$L^1$] **9** was obtained by a similar route in only *ca.* 60% yield, owing to the formation of *cis*-[Pd{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$_2$] (Scheme 6). When the reaction mixture was stirred overnight no change was observed which indicated the thermodynamic stability of **9**. However, addition of an excess of NaOMe in toluene caused complete transformation of **9** into *cis*-[Pd{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$_2$]. In contrast, addition of an excess of NaH in thf did not affect the reaction mixture. These observations strongly suggest that a small amount of MeOH must have been present in the former case, which reacted with the Pd–Me bond in a manner analogous to that depicted in Scheme 4 for the Pd–Ph bond of [PdPh{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$L^1$]. It is interesting that the phenyl and methyl complexes **6** and [PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}$L^2$] **15** (see below), which contain the same phosphinoenolate ligand and the functional phosphine L^2, were stable under these conditions. This shows the stabilising (or protecting) role exerted by the ligand L^2 in these complexes.



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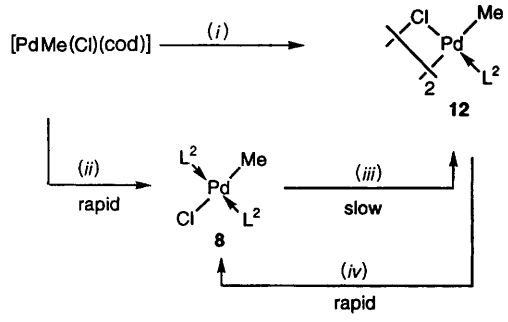
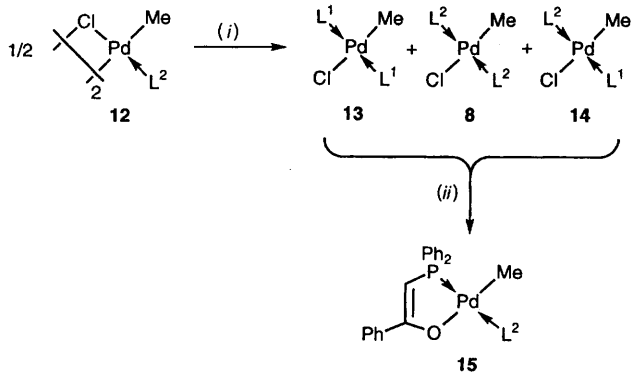
Scheme 7 (*i*) 1 equivalent L^2, Me_2CO, 4 d



Scheme 8 (*i*) 1 equivalent L^2, −cod Me_2CO, 4d; (*ii*) $2L^2$, −cod; (*iii*) [PdMe(Cl)(cod)], −cod; (*iv*) L^2

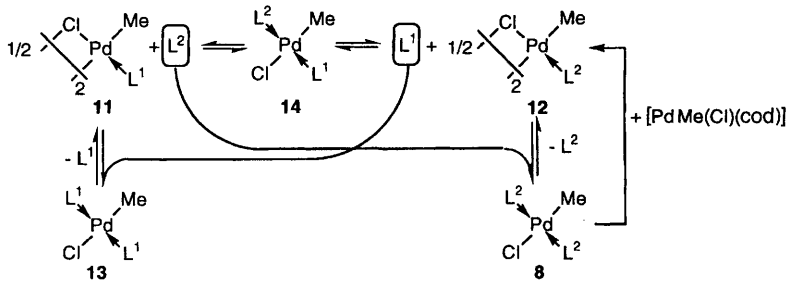


Scheme 9 (*i*) L^1, CH_2Cl_2; (*ii*) excess of NaOMe, toluene, −NaCl, −MeOH

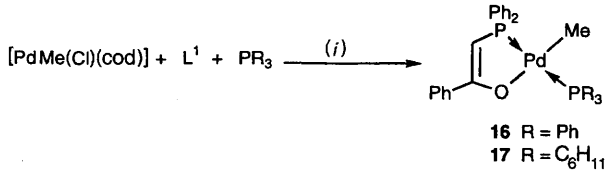
In order to develop a more general access to phosphinoenolate methylpalladium(II) complexes, our approach was to (*i*) co-ordinate two different functional phosphine ligands to the Pd and (*ii*) perform a deprotonation reaction that would lead to the desired products. Reaction of [PdMe(Cl)(cod)] with 1 equivalent of L^2 in acetone afforded the dinuclear complex [{Pd(μ-Cl)Me(L^2)}$_2$] **12** (Scheme 7). The IR spectrum of **12** contains a strong absorption at 1663 cm^{-1} for the amide function of L^2. This confirms the terminal bonding mode for this ligand and the dinuclear structure of the complex. The ^{1}H NMR spectrum contains two doublets at δ 3.55 [^2J(PH) = 9.6] and 0.57 [^3J(PH) = 2.1 Hz] for the PCH_2 and $PdCH_3$ protons, respectively. The presence of a singlet at δ 32.9 in the ^{31}P-{^{1}H} NMR spectrum is consistent with a *cis* or a *trans* arrangement of the phosphorus nuclei. Ladipo and Anderson [7] found two very close singlets at δ 32.5 and 32.0 for the *cis* and *trans* isomers of [{Pd(μ-Cl)Me(PEt_3)}$_2$].

Monitoring of the reaction in Scheme 7 by ^{31}P-{^{1}H} NMR spectroscopy showed that it proceeded by preliminary formation of *trans*-[PdMe(Cl)$L^2{}_2$] **8**. We then verified that **8** and [PdMe(Cl)(cod)] in a 1:1 ratio afforded complex **12**[3b] in quantitative yield after 2 d. Conversely, reaction of **12** with 1 equivalent of L^2 quantitatively afforded **8** after a few hours. From these experiments we conclude that the slow step in the formation of **12** according to Scheme 7 consists of the reaction of the intermediately formed **8** with [PdMe(Cl)(cod)] (Scheme 8).

In order to exploit the possibility of chloride bridge-splitting reactions of complex **12** to introduce a phosphine ligand different from L^2, we treated this complex with 2 molar equivalents of L^1. Three complexes were formed as a result of phosphine-redistribution reactions (Scheme 9). The presence of complexes **8** and *trans*-[PdMe(Cl)$L^1{}_2$] **13** was indicated by the ^{1}H NMR triplets for the PCH_2 protons at respectively δ 3.82 [^{2+4}J(PH) = 6.3] and 4.55 [^{2+4}J(PH) = 7.0 Hz] and comparison with data for authentic samples (see Experimental section). Complex *trans*-[PdMe(Cl)L^1(L^2)] **14** was always observed in the presence of **8** and **13** and could not be isolated pure. It was characterised by two triplets at δ 4.62 [^{2+4}J(PH) = 7.0] and 3.71 [^{2+4}J(PH) = 7.0 Hz] for the PCH_2 protons of L^1 and L^2, respectively. The easy set up of the equilibria between these square-planar complexes was independently verified by mixing **8** and **13** in equimolar amounts, which resulted in partial formation of **14**. This suggests the involvement of unsaturated, three-co-ordinated 14-electron intermediates or, alternatively, dimer **11** [which could not be isolated pure but was characterised in solution by ^{31}P-{^{1}H}



Scheme 10



Scheme 11 (*i*) (*a*) CH_2Cl_2, 3 h; (*b*) excess of NaOMe, 3 h

NMR ($CDCl_3$): δ 30.9] and **12**.[3b] These transformations are summarised in Scheme 10.

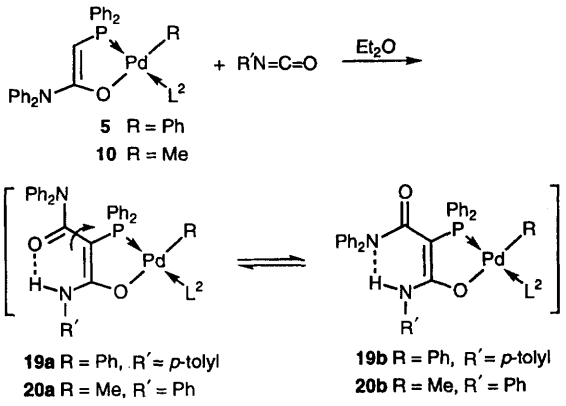
The necessary deprotonation step mentioned above was then applied to the functional phosphine complexes. Fortunately, when we treated the mixture of **8**, **13** and **14** with an excess of NaOMe in toluene the phosphinoenolate complex [PdMe{$Ph_2PCH{\cdots}C(\cdots O)Ph$}$L^2$] **15** was obtained as the sole product [Scheme 9 (*ii*)]. This selectivity results from the acidity of the PCH_2 protons of L^1 being greater than that of the PCH_2 protons of L^2, which progressively shifts the equilibria depicted in Scheme 10 towards the formation of **14**, the direct precursor to **15**. This is consistent with the synthesis described above of the phenylpalladium(II) complex **6** from **5** (Scheme 5). The reaction leading to **15** appears to be under kinetic control where formation and deprotonation of **14** is faster than deprotonation of **13** which would lead to some bis(phosphinoenolate) complex. The latter was not observed. Note however that mobility of a phosphinoenolate chelate from one metal centre to another cannot be ruled out and has been observed previously,[4b] although it is certainly thermodynamically less favourable than transfer of a neutral phosphine ligand. These observations led to the 'one-pot' synthesis of complexes [PdMe{$Ph_2PCH{\cdots}C(\cdots O)Ph$}($PR_3$)] (R = Ph **16** or C_6H_{11} **17**) from [PdMe(Cl)(cod)], L^1 and PR_3 (Scheme 11). The complex [PdMe{$Ph_2PCH{\cdots}C(\cdots O)NPh_2$}{$P(C_6H_{11})_3$}] **18** was obtained similarly from [PdMe(Cl)(cod)], L^2 and $P(C_6H_{11})_3$.

Reaction of complexes 5 and 10 with *p*-tolyl isocyanate

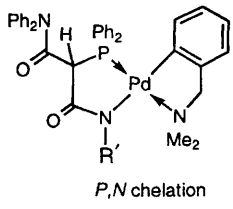
We have shown in previous studies that phosphinoenolate complexes react with organic isocyanates by formation of a carbon–carbon bond.[8] In order to probe the reactivity of the phosphinoenolate ligand in these complexes *p*-tolyl isocyanate was added to a solution of **5** in Et_2O. A white product was isolated which contained two isomers resulting from a Michael-type addition of the enolate C–H bond to the isocyanate (Scheme 12). Isomers **19a** and **19b** were identified by spectroscopic methods and comparison with the related product(s) obtained previously in the reactions of *cis*-[Pd{$Ph_2PCH{\cdots}C(\cdots O)Ph$}$_2$] with organic isocyanates.[8b] A molar ratio **19a**:**19b** of *ca.* 1:3 was determined by NMR spectroscopy. The singlets in the ^1H NMR spectrum of the mixture at δ 10.2 and 8.57 are assigned to the N–H · · · O and N–H · · · N hydrogen bridges of **19a** and **19b**, respectively. Both disappear in the presence of D_2O as a result of rapid exchange. The PCH_2 protons of L^2 give rise to a doublet of doublets for each isomer and the ^{31}P-{^1H} NMR spectrum confirms the *trans* arrangement of the phosphorus nuclei in each isomer (see Experimental section).

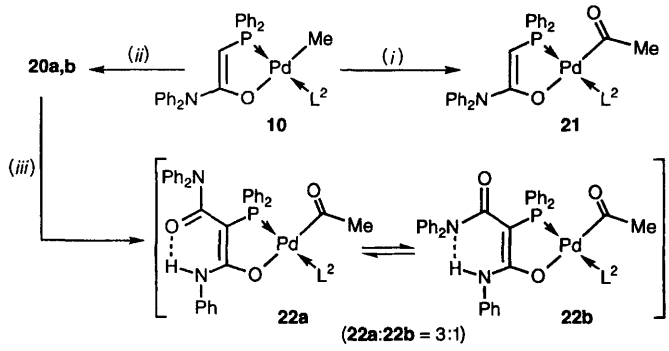
Isomerisation between complexes **19a** and **19b** involves rotation of the amide function about the C_{amide}–$C_{enolate}$ bond. It is interesting to contrast the *P*,*O* mode of chelation of the new functional enolate ligand in these complexes with the *P*,*N* mode found for its isomer in [Pd{Ph_2PCH[C(O)NR′]C(O)NPh_2}(dmba)][9] (dmba = *N*,*N*-dimethylbenzylamine, R′ = *p*-tolyl). The nature of the other ligands bound to palladium, phenyl, L^2 and dmba, respectively, has a profound influence on the co-ordination mode and isomeric structure of the anionic, functional phosphinoenolate moiety.

Complex **10** also reacted with PhNCO to give an isomeric



Scheme 12





Scheme 13 (*i*) CO, 1 atm, Et_2O, 2 h; (*ii*) PhNCO; (*iii*) CO, 1 atm, Et_2O, 12 h

mixture of **20a** and **20b** (Scheme 12). The spectroscopic data for these complexes (Experimental section) are similar to those for the phenyl derivatives **19a** and **19b**. After 1 min of reaction, quantitative conversion of **10** occurred and the ratio **20a**:**20b** was *ca.* 1:1. After 1 h this ratio stabilised to *ca.* 1:3 which corresponds to thermodynamic equilibrium. A similar ratio was observed with the phenyl derivatives (Scheme 12), although the complete conversion of **5** was less rapid and required *ca.* 15 min. This difference could be explained by the donor properties of the methyl ligand which renders the metal centre more electron rich and the phosphinoenolate ligand more susceptible to electrophilic attack by the organic isocyanate.

Reactions of complexes 10 and 20a, 20b with CO

The acetyl complex [Pd{C(O)Me}{$Ph_2PCH{\cdots}C(\cdots O)NPh_2$}$L^2$] **21** was obtained in high yield from **10** after 2 h under a CO atmosphere (Scheme 13). In the IR spectrum, the acyl vibration appears at 1660 cm^{-1} whereas the ν(C⋯C) + ν(C⋯O) vibration remains at 1483 cm^{-1}. For comparison, complete conversion of **20a**, **20b** into the corresponding acetyl complexes **22a**, **22b** required *ca.* 12 h. The presence of isomers was established by ^1H and ^{31}P-{^1H} NMR spectroscopy and the assignments were made by analogy with the spectra of **20a** and **20b**. These insertion reactions involve methyl migration from the metal to the co-ordinated CO, probably *via* a five-co-ordinated intermediate (or transition state) structurally similar to [PtMe(I)(CO)(phen)][10] (phen = 1,10-phenanthroline). Carbo-

nylation is irreversible and CO does not de-insert when these complexes are dried under reduced pressure. The less electron-donating character of the *P,O* ligand in **20a**, **20b** compared to **10** appears responsible for the decreased reactivity of the Pd–Me bond toward CO: complex **22a**, **22b** forms much more slowly than **21**. An opposite effect has been observed in the reactions of [PdMe{η^2-MeC(=O)=CH=C(=O)R}(PR$_3$)] when R varies from Me to CF_3.[11] That isomers **22a**, **22b** are air-stable in the solid state for weeks whereas **21** decomposes in solution after a few hours to give an almost insoluble red product, which was not identified, should be due to the electronic properties of the *P,O* chelates since steric effects cannot be invoked. It is interesting that the corresponding reaction of the nickel complex [NiPh{Ph$_2$PCH=C(=O)Ph}(PEt$_3$)] afforded a benzoyl complex although in this case the excess of CO reacted further and the final products were [Ni(CO)$_3$(PEt$_3$)] and the ester Ph$_2$PCH=C(Ph)OC(O)Ph, formed by reductive elimination of the chelate ring and the benzoyl group.[1e]

Reactions of complexes 16, 17 and 19a, 19b with ethylene

Preliminary experiments were carried out in order to evaluate the possibility of inserting ethylene into the Pd–C bond of these complexes. When a toluene solution of **16** was exposed to 5.0 MPa of ethylene at 110 °C for 1 h no significant pressure drop in the reactor was observed which would have indicated ethylene consumption (Scheme 14). After cooling, analysis of the gas phase showed only ethylene and formation of propylene in *ca.* 100% yield (see Experimental section). Propylene results from insertion of ethylene into the Pd–Me bond, followed by β-hydride elimination. The resulting palladium hydride, analogous to the nickel hydride species active in the SHOP catalysis, could not be detected by ^{1}H NMR spectroscopy of the liquid phase obtained after evaporation of toluene. It decomposes at the temperature required for its formation, accounting for the lack of further ethylene insertion and the formation of *cis*-[Pd{Ph$_2$PCH=C(=O)Ph}$_2$] and [Pd(PPh$_3$)$_3$], which were detected by ^{31}P-{^{1}H} NMR spectroscopy.

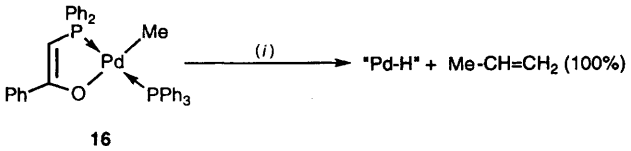
A similar experiment was carried out with complex **17** which contains the stabilising P(C$_6$H$_{11}$)$_3$ ligand. We decreased the reaction temperature to 80 °C, hoping to increase the lifetime of the palladium hydride species. However, after 1 h, no reaction had taken place and only **17** was detected by ^{1}H and ^{31}P-{^{1}H} NMR spectroscopy of the liquid phase.

When the aryl-palladium complexes **19a**, **19b** were similarly exposed to 4.0 MPa C_2H_4 at 100 °C for 2 h insertion took place since styrene was identified in the liquid phase, in *ca.* 60% yield. The palladium hydride resulting from the β-elimination reaction is again not stable under these conditions, which explains the formation of palladium metal and the lack of further ethylene insertion. As observed in the case of nickel complexes, the nature of the *P,O* chelate is crucial for catalysis to occur and *P,N* or *P,S* chelates of this metal have proved inactive.[12] Further modifications of our systems will therefore be required in order to observe catalytic activity towards olefins.

Experimental

Reagents and physical measurements

All reactions were performed in Schlenk-type flasks under nitrogen. Solvents were purified and dried under nitrogen by conventional methods. The ^{1}H and ^{31}P-{^{1}H} NMR spectra were recorded at 300.13 and 121.5 MHz, respectively, on a FT Bruker AC 300 instrument, IR spectra in the 4000–400 cm^{-1} range on a Bruker IFS66 FT spectrometer.



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Scheme 14 (*i*) CH$_2$=CH$_2$, 5.0 MPa, 110 °C, 1 h

Syntheses

The compounds Ph$_2$PCH$_2$C(O)Ph (L^1)[4a] and Ph$_2$PCH$_2$C(O)NPh$_2$ (L^2)[5] were prepared according to the literature. The complexes [Pd(dba)$_2$],[13] [PdPh(I)(tmen)],[14] [PdMe(Cl)(cod)],[7] **1** and **2**,[5] **12** and **16**–**18**[3b] were prepared according to the literature.

Reaction of [Pd(dba)$_2$] with excess of Ph$_2$PCH$_2$C(O)R. To a solution of [Pd(dba)$_2$] (0.300 g) in toluene (20 cm^3) was added a solution of 3 equivalents of Ph$_2$PCH$_2$C(O)R (L^1, R = Ph; L^2, R = NPh$_2$) in toluene (10 cm^3). After stirring for 3 h the solution was concentrated to half its original volume and filtered. A yellow-orange solution was obtained and characterised by ^{31}P-{^{1}H} NMR and infrared spectroscopy. It did not prove possible to separate the products [Pd(dba)L$^1_2$] **1** and [Pd(dba)L$^2_2$] **2** from dba and isolate them as pure solids due to similar solubility properties: **1**, IR (KBr) ν_{CO} 1672vs, (toluene) ν_{CO} 1677vs cm^{-1}; ^{31}P-{^{1}H} NMR (toluene–C$_6$D$_6$) AB spin system, δ_A 15.7, δ_B 11.8 [^2J(PP) = 14 Hz], −16.8 (L^1); **2**, IR (KBr) ν_{CO} 1662vs, (toluene) ν_{CO} 1653vs cm^{-1}; ^{31}P-{^{1}H} NMR (toluene–C$_6$D$_6$) AB spin system, δ_A 18.8, δ_B 13.1 [^2J(PP) = 15 Hz], −14.3 (L^2).

***trans*-[PdPh(I){Ph$_2$PCH$_2$C(O)Ph}$_2$] 3.** A mixture of [PdPh(I)(tmen)] (0.300 g, 0.70 mmol) and L^1 (0.427 g, 1.40 mmol) was stirred in thf (20 cm^3) for 2 h. The solvent was evaporated under reduced pressure to leave a white residue. Addition of pentane afforded a white powder which was filtered off, washed with pentane and dried *in vacuo*. Recrystallisation from CH$_2$Cl$_2$–pentane gave colourless crystals (0.585 g, 90%). IR (KBr): ν_{CO} 1676vs cm^{-1}. NMR (CDCl$_3$): ^{1}H, δ 7.81–7.16 (m, 35 H, aromatic) and 4.38 [virtual t, 4 H, PCH$_2$, ^{2+4}J(PH) = 6.8 Hz]; ^{31}P-{^{1}H}, δ 13.1 (s) (Found: C, 60.4, H, 4.40. Calc. for C$_{46}$H$_{39}$IO$_2$P$_2$Pd: C, 60.1; H, 4.30%).

***trans*-[PdPh(I){Ph$_2$PCH$_2$C(O)NPh$_2$}$_2$] 4.** Following a similar procedure to that for complex **3** but starting from [PdPh(I)(tmen)] (0.300 g, 0.70 mmol) and L^2 (0.556 g, 1.40 mmol), **4** was obtained as pale yellow crystals (0.720 g, 93%). IR: (KBr) ν_{CO} 1660vs, (CH$_2$Cl$_2$) ν_{CO} 1656vs cm^{-1}. NMR: ^{1}H (CDCl$_3$), δ 7.53–6.03 (m, 45 H, aromatic) and 3.87 [virtual t, 4 H, PCH$_2$, ^{2+4}J(PH) = 6.6 Hz]; ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 14.4 (s) (Found: C, 62.95; H, 4.55; N, 2.35. Calc. for C$_{58}$H$_{49}$IN$_2$O$_2$P$_2$Pd: C, 63.25; H, 4.50; N, 2.55%).

[PdPh{Ph$_2$PCH=C(=O)NPh$_2$}{Ph$_2$PCH$_2$C(O)NPh$_2$}] 5. An excess of NaOMe (0.068 g, 1.25 mmol) was added to a solution of complex **4** (0.700 g, 0.635 mmol) in toluene (30 cm^3). After being stirred for 2 h, the suspension was filtered and the solvent evaporated to leave a viscous yellow oil. Addition of pentane afforded a yellow powder which was filtered off and dried *in vacuo* (0.602 g, 97%). IR (CH$_2$Cl$_2$): ν_{CO} 1662vs, ν(C=C) + ν(C=O) 1482m cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ 7.80–6.77 (m, 45 H, aromatic), 3.78 [d, 1 H, PCH, ^2J(PH) = 5.1] and 3.20 [d, 2 H, PCH$_2$, ^2J(PH) = 7.9]; ^{31}P-{^{1}H}, AB spin system, δ_A 16.1 (P, O), δ_B 10.2 (L^2) [^2J(PP) = 393]; ^{13}C-{^{1}H}, δ 187.6 [s, *C*(=O)NPh$_2$], 179.1 [dd not assigned, J(P^{A}C) = 23.0, J(P^{B}C) = 18.0], 167.2 [s, *C*(=O)NPh$_2$], 149.5–122.4 (m, C, aromatic), 59.8 [dd, PCH, J(P^{A}C) = 64.8, J(P^{B}C) = 5.4] and 34.4 [filled-in d, PCH$_2$, ^1J(PC) = 23.7 Hz]. Mass spectrum: *m/z* (relative intensity) 972.8 (40, M^+), 895.9 (5, [M − Ph]$^+$) and 577.9 (8, [M − L^2]$^+$) (Found: C, 71.3; H, 4.85; N, 2.70. Calc. for C$_{58}$H$_{48}$N$_2$O$_2$P$_2$Pd: C, 71.55; H, 4.95; N, 2.90%).

[PdPh{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}{$Ph_2PCH_2C(O)NPh_2$}] 6. Complex **5** (0.060 g, 0.062 mmol) and solid L^1 (0.019 g, 0.062 mmol) were dissolved in C_6D_6 (0.3 cm^3). Proton and ^{31}P-{^1H} NMR spectra of the mixture were recorded after 0.5 h and indicated only the presence of **6** and free L^2. Complex **6** could not be isolated analytically pure owing to contamination with L^2 which has similar solubility properties. NMR (C_6D_6): ^1H, δ 8.05–6.75 (**6** + L^1, m, 60 H, aromatic), 5.16 (s, br, 1 H, PdPCH) and 3.33 (s, br, 4 H, $PdPCH_2$ + PCH_2 of free L^2); ^{31}P-{^1H}, AB spin system, δ_A 23.5 (br, P, O), δ_B 11.6 (br, L^2) [$^2J(PP)_{trans}$ = 385 Hz], −14.2 (s, br, L^2).

[PdPh{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}{$P(C_6H_{11})_3$}] 7. Complex **5** (0.063 g, 0.065 mmol) and solid $P(C_6H_{11})_3$ (0.018 g, 0.064 mmol) were dissolved in C_6D_6 (0.3 cm^3), forming a yellow solution. Proton and ^{31}P-{^1H} NMR spectra of the mixture were recorded after 15 min, and indicated only the presence of **7** and free L^2. Complex **7** could not be isolated analytically pure owing to contamination with L^2 which has similar solubility properties. NMR (C_6D_6): ^1H, δ 7.81–6.86 (m, 45 H, aromatic), 3.77 [d, 1 H, PCH, ^2J(PH) = 4.8], 3.18 (s, 2 H, PCH_2 of free L^2) and 1.90–0.94 (m, 33 H, C_6H_{11}); ^{31}P-{^1H}, AB spin system, δ_A 25.7 (P, O), δ_B 12.7 [$P(C_6H_{11})_3$] [$^2J(PP)_{trans}$ = 363 Hz], −14.2 (s, L^2).

***trans*-[PdMe(Cl){$Ph_2PCH_2C(O)NPh_2$}$_2$] 8.** Tetrahydrofuran (20 cm^3) was added to a mixture of [PdMe(Cl)(cod)] (0.400 g, 1.51 mmol) and L^2 (1.195 g, 3.03 mmol). After being stirred for 3 h a white suspension was obtained. A white solid product was filtered off, washed with pentane and dried *in vacuo*. Recrystallisation from CH_2Cl_2–pentane afforded colourless crystals (1.27 g, 89%). IR (KBr): ν_{CO} 1660vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.77–7.18 (m, 40 H, aromatic), 3.82 [virtual t, 4 H, PCH_2, ^{2+4}J(PH) = 6.4] and 0.38 [t, 3 H, CH_3, ^3J(PH) = 6.3]; ^{31}P-{^1H}, δ 23.6 (s); ^{13}C-{^1H}, δ 168.9 [s, C(=O)NPh_2], 143.1–126.2 (m, C, aromatic), 36.8 [virtual t, PCH_2, ^{1+3}J(PC) = 32.3 Hz] and 2.74 (s, CH_3) (Found: C, 67.15; H, 5.05; N, 2.85. Calc. for $C_{53}H_{47}ClN_2O_2P_2Pd$: C, 67.15; H, 5.00; N, 2.95%).

[PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}{$Ph_2PCH_2C(O)Ph$}] 9. This complex was obtained following a procedure similar to that detailed below for **10**. However, it could not be isolated pure and was characterised in solution by its ^{31}P-{^1H} NMR spectrum (C_6D_6): AB spin system, δ_A 27.3 (P, O), δ_B 16.7 (L^1) [$^2J(PP)_{trans}$ = 407 Hz].

[PdMe{$Ph_2PCH{\cdot\cdot}C(=O)NPh_2$}{$Ph_2PCH_2C(O)NPh_2$}] 10. Starting from complex **8** (0.300 g, 0.316 mmol) and NaOMe (0.034 g, 0.63 mmol), **10** was obtained as pale white powder (0.235 g, 89%). IR (CH_2Cl_2): ν_{CO} 1662s, ν(C=C) + ν(C=O) 1483s cm^{-1}. NMR (C_6D_6): ^1H, δ 7.81–6.83 (m, 40 H, aromatic), 3.73 [d, 1 H, PCH, ^2J(PH) = 4.8], 3.50 [d, 2 H, PCH_2, ^2J(PH) = 7.2] and 0.78 [dd, 3 H, CH_3, $^2J(P^AH)$ = 7.1, $^2J(P^BH)$ = 4.5]; ^{31}P-{^1H}, AB spin system, δ_A 20.7 (P, O), δ_B 15.8 (L^2) [^2J(PP) = 404]; ^{13}C-{^1H}, δ 179.3 [dd, C(=O)NPh_2, $^2J(P^AC)$ = 30.2, $^3J(P^BC)$ = 8.7], 167.7 [s, C(=O)NR_2], 148.0–126.7 (m, C, aromatic), 60.7 [dd, PCH, $^1J(P^AC)$ = 61.7, $^3J(P^BC)$ = 8.7], 35.1 [d, PCH_2, ^1J(PC) = 17.5 Hz] and −6.6 (s, CH_3) (Found: C, 69.85; H, 5.20; N, 2.85. Calc. for $C_{53}H_{46}N_2O_2P_2Pd$: C, 69.85; H, 5.10; N, 3.05%).

***trans*-[PdMe(Cl){$Ph_2PCH_2C(O)Ph$}$_2$] 13.** Following a similar procedure to that for complex **8**, but starting from [PdMe(Cl)(cod)] (0.200 g, 0.755 mmol) and L^1 (0.459 g, 0.151 mmol), **13** was obtained as colourless crystals (0.476 g, 85%). IR (KBr): ν_{CO} 1664vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 7.94–7.26 (m, 30 H, aromatic), 4.55 [virtual t, 4 H, PCH_2, ^{2+4}J(PH) = 7.0] and 0.04 [t, 3 H, CH_3, ^3J(PH) = 6.3 Hz]; ^{31}P-{^1H}, δ 22.4 (s) (Found: C, 64.3; H, 5.00. Calc. for $C_{39}H_{37}ClO_2P_2Pd$: C, 64.3; H, 4.85%).

[PdMe{$Ph_2PCH{\cdot\cdot}C(=O)Ph$}{$Ph_2PCH_2C(O)NPh_2$}] 15. Toluene (20 cm^3) was added to a mixture of complex **12** (0.200 g, 0.181 mmol) and L^1 (0.110 g, 0.362 mmol). After stirring for 0.5 h solid NaOMe (0.040 g, 0.740 mmol) was added. The mixture was stirred for 2 h then filtered through silica gel, and the solvent evaporated to leave a viscous yellow oil. The residue was dissolved in CH_2Cl_2 (5 cm^3), pentane (20 cm^3) added and the mixture stirred. A yellow powder precipitated, which was filtered off, washed with pentane (10 cm^3) and dried *in vacuo* (0.285 g, 96%). IR (KBr): ν_{CO} 1662vs, ν(C=C) + ν(C=O) 1504vs cm^{-1}. NMR (C_6D_6): ^1H, δ 7.98–6.84 (m, 35 H, aromatic), 5.13 [d, 1 H, PCH, ^2J(PH) = 4.8], 3.71 [d, 2 H, PCH_2, ^2J(PH) = 8.0] and 0.78 [dd, 3 H, CH_3, $^2J(P^AH)$ = 7.4, $^2J(P^BH)$ = 4.2]; ^{31}P-{^1H}, AB spin system, δ_A 27.9 (P, O), δ_B 17.4 (L^2) [^2J(PP) = 407]; ^{13}C-{^1H}, δ 184.7 [d, C(=O)Ph, ^2J(PC) = 19.2], 167.9 [s, C(=O)NR_2], 143.5–125.7 (m, C, aromatic), 76.2 [d, PCH, ^1J(PC) = 56.3], 35.2 [d, PCH_2, ^1J(PC) = 18.0 Hz] and −7.1 (s, CH_3) (Found: C, 68.95; H, 5.00; N, 1.95. Calc. for $C_{47}H_{41}NO_2P_2Pd$: C, 68.85; H, 5.05; N, 1.70%).

Reaction of complex 5 with *p*-tolyl isocyanate. *p*-Tolyl isocyanate (13 μl, 0.103 mmol) was added to a stirred solution of complex **5** (0.100 g, 0.102 mmol) in Et_2O (10 cm^3). After 15 min a white suspension was obtained. A white powder was filtered off, washed with pentane and dried *in vacuo*. Recrystallisation from CH_2Cl_2–pentane afforded colourless crystals (0.090 g, 78%). IR (CH_2Cl_2): ν_{CO} 1661vs, 1654vs and 1540s cm^{-1}. This product was identified as a mixture of isomers **19a** and **19b**. NMR: ^1H (C_6D_6), **19a**:**19b** = 3:1, δ 10.17 (**19a**, s, NH bonded, exchange with D_2O), 8.57 (**19b**, s, NH bonded, exchange with D_2O), 7.57–6.59 (**19a**, **19b**, m, 49 H, aromatic), 2.83 [**19b**, dd, 2 H, PCH_2, ^2J(PH) = 8.1, ^4J(PH) = 1.7], 2.80 [**19a**, dd, 2 H, PCH_2, ^2J(PH) = 8.3, ^4J(PH) = 1.3], 2.23 (**19a**, s, 3 H, *p*-tolyl) and 2.20 (**19b**, s, 3 H, *p*-tolyl); ^{31}P-{^1H} (CD_2Cl_2), AB spin system for **19a**, δ_A 30.0 (P, O), δ_B 12.1 (L^2) [$^2J(PP)_{trans}$ = 382], AB spin system for **19b**, δ_A 27.3 (P, O), δ_B 9.8 (L^2) [$^2J(PP)_{trans}$ = 386 Hz] (Found: C, 70.10; H, 4.80, N, 3.60. Calc. for $C_{66}H_{55}N_3O_3P_2Pd{\cdot}0.25CH_2Cl_2$: C, 70.55; H, 4.95; N, 3.70%).

Reaction of complex 10 with PhNCO. Phenyl isocyanate (10 μl, 0.092 mmol) was added to a stirred solution of complex **10** (0.080 g, 0.089 mmol) in Et_2O (10 cm^3). After 1 h the initially homogeneous pale yellow solution had not changed in physical appearance. Addition of pentane afforded a white powder which was washed with pentane and identified as isomers **20a** and **20b** in thermodynamic equilibrium. It was filtered off and dried *in vacuo* (0.075 g, 82%). IR (CH_2Cl_2): ν_{CO} 1661s, 1572w and 1546 m cm^{-1}. NMR (C_6D_6): ^1H, **20a**:**20b** = 3:1, δ 11.09 (**20a**, s, NH bonded), 8.80 (**20b**, s, NH bonded), 8.16–6.69 (**20a**, **20b**, m, 45 H, aromatic), 3.47 [**20a**, dd, 2 H, PCH_2, ^2J(PH) = 8.2 Hz, ^4J(PH) = 1.0], 3.37 [**20b**, dd, 2 H, PCH_2, ^2J(PH) = 8.6, ^4J(PH) = 1.2], 0.72 [**20b**, dd, 3 H, CH_3, $^2J(P^AH)$ not determined, $^2J(P^BH)$ = 4.0] and 0.69 [dd, 3 H, CH_3, $^2J(P^AH)$ = 7.8, $^2J(P^BH)$ = 4.0]; ^{31}P-{^1H}, AB spin system for **20a**, δ_A 32.5 (P, O), δ_B 15.9 (L^2) [^2J(PP) = 391], AB spin system for **20b**, δ_A 30.9 (P, O), δ_B 14.7 (L^2) [^2J(PP) = 397 Hz] (Found: C, 69.9; H, 4.65; N, 4.05. Calc. for $C_{60}H_{51}N_3O_3P_2Pd$: C, 69.95; H, 5.00; N, 4.10%). The rate of this insertion reaction was studied by ^1H NMR spectroscopy in C_6D_6 with the quantities described as above. After *ca.* 1 min, the spectrum showed quantitative conversion into **20** with a ratio **20a**:**20b** = 1:1. Thermodynamic equilibrium was reached after *ca.* 1 h with a ratio **20a**:**20b** = 3:1.

[Pd{C(O)Me}{Ph_2PCH⋯C(⋯O)NPh_2}{$Ph_2PCH_2C(O)NPh_2$}] 21. Carbon monoxide was bubbled through a solution of complex **10** (0.170 g, 0.186 mmol) in Et_2O (10 cm^3) for *ca.* 10 min. The yellow solution was then stirred for 1 h under an atmosphere of CO. The solvent was removed *in vacuo*. A white product was obtained which was washed with pentane and dried *in vacuo* (0.136 g, 78%). IR (CH_2Cl_2): ν_{CO} 1660vs, 1550w, ν(C⋯C) + ν(C⋯O) 1483s cm^{-1}. NMR (C_6D_6): ^1H, δ 7.82–6.83 (m, 40 H, aromatic), 3.68 (s, br, 1 H, PCH), 3.56 (s, br, 2 H, PCH_2) and 2.06 [s, br, 3 H, $C(=O)CH_3$]; ^{31}P-{^1H}, limiting case of AB pattern δ 9.20 (s) and 9.15 (s); ^{13}C-{^1H}, δ 233.3 [s, $C(=O)CH_3$], 179.3 [dd, $C(\cdots O)NPH_2$, $^2J(P^AC)$ = 22.0, $^3J(P^BC)$ = 17.2], 167.7 [s, $C(=O)NR_2$], 147.8–123.6 (m, C, aromatic), 59.1 [dd, PCH, $^1J(P^AC)$ = 45.4, $^3J(P^BC)$ = 28.2], 39.1 [t, $CH_3C(=O)$, $^{3+3}J(PC)$ = 17.0] and 35.8 [t, PCH_2, $^{1+3}J(PC)$ = 24.8 Hz] (Found: C, 69.1; H, 5.00; N, 2.60. Calc. for C, 69.05; H, 4.95; N, 3.00%).

Insertion of CO into complexes 20a, 20b. Carbon monoxide was bubbled through a suspension of isomers **20a, 20b** (0.090 g, 0.087 mmol) in Et_2O (10 cm^3) for *ca.* 10 min. The yellow suspension was then stirred for 12 h under an atmosphere of CO. The solvent was removed *in vacuo*. The yellow residue was dissolved in CH_2Cl_2 and filtered. The solvent was removed *in vacuo* and a yellow powder was obtained which was washed with pentane, dried *in vacuo* and identified as isomers **22a, 22b** (0.085 g, 92%). IR (CH_2Cl_2): ν_{CO} 1677m, 1660s and 1548s cm^{-1}. NMR (C_6D_6): ^1H, **22a**:**22b** = 7:3, δ 10.87 (**22b**, s, NH bonded), 8.74 (**22a**, s, NH bonded), 8.29–6.74 (**22a, 22b**, m, 45 H, aromatic), 3.47 [**22a, 22b**, d, 4 H, PCH_2, $^2J(PH)$ = 8.5], 1.97 [**22b**, s, 3 H, $C(O)CH_3$] and 1.91 [**22a**, s, 3 H, $C(O)CH_3$]; ^{31}P-{^1H}, AB spin system for **22a**, δ_A 21.5 (P, O), δ_B 9.4 (L^2) [$^2J(PP)$ = 272], AB spin system for **22b**, δ_A 20.6 (P, O), δ_B 8.2 (L^2) [$^2J(PP)$ = 277 Hz] Found: C, 69.25; H, 4.95; N, 3.90. Calc. for $C_{61}H_{51}N_3O_4P_2Pd$: C, 69.20, H, 4.85; N, 3.95%).

Insertion of ethylene. The reactions were performed in a stainless-steel reactor (80 cm^3), equipped with a double jacket for thermoregulation and a magnetic stirring bar. After drying and purging the reactor with ethylene, a toluene solution (20 cm^3) of complex **16**, **17** or **19a**, **19b** (0.3 mmol) was introduced. The temperature and pressure were slowly raised to reach the conditions given in Scheme 14. The total quantity of ethylene introduced was determined by weight difference of the cylinder. The reactor was isolated and the ethylene consumption was monitored by pressure variation on a manometer. After reaction the reactor was progressively cooled overnight, the gas phase depressurised and analysed by GC (Hewlett-Packard 5890, series II instrument) using a capillary PONA column (methylsilicone, 50 m, internal diameter 0.2 mm, film thickness 0.1 μm), an HP 3388 integrator and the following conditions: injection and flame ionisation detector 250 °C; held at 0 °C during 10 min, then increased at 8 °C min^{-1} to 250 °C, held at this temperature for 10 min.

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