

Synthesis of Methyl-palladium(II) and -platinum(II) Complexes containing Labile Chelates and Olefinic Tertiary Phosphine Ligands: Intramolecular Insertion of an Olefin into a Palladium–Carbon Bond, and Activation of a Carbon–Hydrogen Bond by a Platinum(II) Complex†

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The square planar complexes $[M(Me)(L-L)(L)]$ $\{M = Pd, L = dpvp [PPh_2(C_6H_4CH=CH_2-o)], L-L = acac$ (acetylacetonate), $bzsac$ (1-phenyl-3-sulfanylbut-2-en-1-onate) or $pyca$ (pyridine-2-carboxylate), $L = PPh_2(C_6H_4Et-o), L-L = acac$ or $pyca, L = P(CH_2-CH=CH_2)Ph_2, L-L = pyca; M = Pt, L = dpvp, L-L = bzsac$ or $pyca, L = PPh_2(C_6H_4Et-o), L-L = pyca\}$ have been synthesised and their thermal behaviour studied. Heating the palladium-dpvp complexes in benzene leads to intramolecular migratory insertion of the vinyl double bond of the phosphine into the Pd–Me bond to give complexes with a five-membered palladacyclic ring, $[Pd(L-L)\{PPh_2(C_6H_4CHCH_2Me)\}]$. In contrast, warming the platinum complex $[PtMe(pyca)(dpvp)]$ leads to a cyclometallation reaction forming a platinacycle with a platinum–alkenyl bond $[Pt(pyca)\{PPh_2(C_6H_4C=CH_2)\}]$. The platinum complex appears to react by oxidative addition of the vinyl C–H bond of dpvp to Pt^{II} ; methane is eliminated during the reaction. Although no such species has been identified, kinetic evidence suggests that the two thermal processes occur *via* a common four-co-ordinate intermediate containing a 'dangling' $pyca$ ligand and with dpvp chelated through the phosphorus and the vinyl double bond $[M(Me)(pyca)\{PPh_2(C_6H_4CH=CH_2)\}]$.

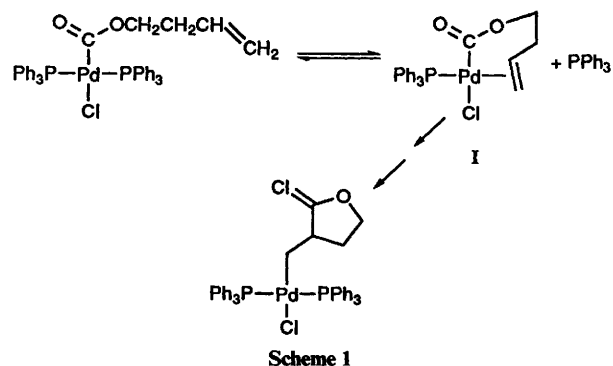
The insertion of an olefin into a metal–carbon bond (more correctly an alkyl migration^{1a}) is a critical step in many catalytic reactions, for example oligomerisation and polymerisation of olefins and the co-polymerisation of olefins with CO.

The generally accepted mechanism for an olefin insertion reaction requires prior co-ordination of the olefin in a site *cis* to the metal–hydrocarbyl bond before insertion occurs.¹ It is of interest to investigate the relationship between changes in an auxiliary ligand and the ease of the insertion step. The knowledge gained from a study of this type will benefit understanding of the catalytic process and aid in the design of new catalysts. However, despite the number of migratory insertion reactions known, the direct observation of olefin insertion into a metal–carbon bond has rarely been reported.² In a very recent paper Brookhart and Rix^{2g} have reported the identification and in one case isolation of intermediate complexes from the insertion of ethylene into palladium–alkyl bonds. The initial methylpalladium–ethylene complex was identified and the clean conversion of this complex to the ethylpalladium–ethylene complex and propylene was described. The latter, thermally unstable, complex was isolated (at $-78^\circ C$) and fully characterised by NMR spectroscopy. The reaction of the former complex with CO and the first direct observation of insertion of an acyl olefin complex has also been described.^{2g}

In studies on hydrocarbyl–platinum(II) and –palladium(II) complexes containing hemilabile, anionic, bidentate ligands we investigated ligand influences on the carbonylation reaction and on mechanistic steps in the CO insertion process.³ Subsequent to these modelling studies, a number of nickel(II) analogues were prepared and found to be active single component catalysts for ethylene oligomerisation and polymeri-

sation, and for ethylene–CO co-polymerisation.^{4,5} Consequently, it was of considerable interest to us to extend our research on the fundamental insertion steps to include reactions between the platinum and palladium complexes and olefins. However, many of the complexes investigated do not react with olefins, and other complexes whilst they do form insertion products their structures could not be determined due to their low stability. In order to overcome these difficulties, we have examined complexes in which an alkene is held in proximity to a metal–carbon bond through the use of a ligand with an olefinic moiety, in anticipation that an intramolecular insertion of the olefin into the metal–carbon bond may be promoted and the insertion product stabilised by the chelate effect.

In a previous study Samsel and Norton^{2b} carried out a detailed investigation of intramolecular alkyne and olefin insertion into a palladium–carbon bond. The intramolecular reaction involved the insertion of an unsaturated ligand moiety into the palladium–carbon bond of the same ligand (Scheme 1). Extensive kinetic and ³¹P NMR data were provided as evidence that the insertion step took place *via* a four-co-ordinate



† Non-SI unit employed: cal = 4.186 J.

intermediate, **I**, generated by the displacement of a phosphine by the unsaturated ligand moiety. The starting and final complexes could be clearly identified, however direct spectroscopic evidence for the presence of intermediates such as **I** could not be obtained.

Zero- and di-valent platinum, palladium and nickel complexes containing the olefinic tertiary phosphine $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}o)$ (dpvp) have been extensively investigated by Bennett and co-workers.⁶ It was demonstrated that it can function as a mono- or bi-dentate system, but generally as a bidentate chelate ligand, bonding through the phosphorus and the vinyl double bond. Spectroscopic data and ligand-exchange behaviour were found to be typical of olefin complexes of the nickel triad. Of particular interest was the observation that the zerovalent $\text{M}(\text{dpvp})_2$ complexes react with acid to give the divalent cationic species $[\text{M}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{CHCH}_3)\}(\text{dpvp})]^+$, in which one of the dpvp ligands is protonated and forms a five-membered chelate ring bonded through an alkyl carbon and the phosphorus.^{6b} More recently, we demonstrated that it was possible to initially co-ordinate dpvp as a monodentate ligand through the phosphorus (with the vinyl double bond free) and then, by providing a vacant *cis* co-ordination site, allow the vinyl group to co-ordinate, giving a chelated ligand co-ordinating through both the phosphorus and the olefin.⁷ The co-ordination of free olefin followed by the addition of metal and hydrogen (or hydrocarbyl group) to the double bond carbons mimics the first steps of the Cossee mechanism for olefin oligomerisation-polymerisation.⁸

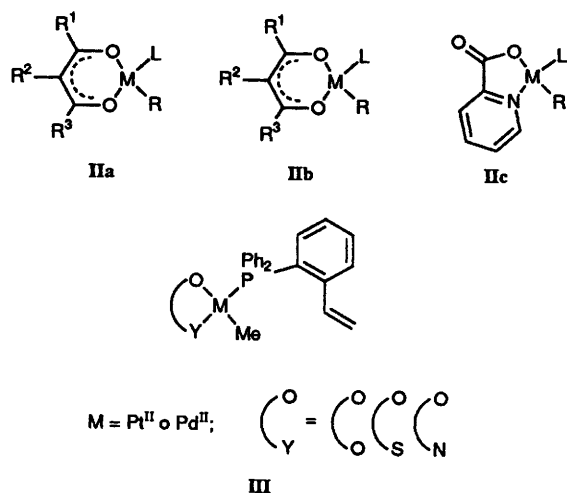
Accordingly, we have extended our studies on complexes of the type $[\text{MR}(\text{L-L})\text{L}]$, **IIa-IIIc** (where $\text{M} = \text{Pt}^{\text{II}}, \text{Pd}^{\text{II}}$; $\text{R} = \text{aryl}$ or alkyl ; $\text{L-L} = \beta$ -diketone, monothio- β -diketone, pyridine-carboxylate; $\text{L} = \text{tertiary phosphine}$ or other Lewis base). We report herein the preparation of methyl-palladium(II) and -platinum(II) complexes, **III**, containing a chelate ligand and diphenyl(*o*-vinylphenyl)phosphine. Thermally induced intramolecular reactions of the vinyl double bond have been investigated in detail and the reaction products fully characterised. From *in situ* NMR spectroscopy and other supporting experimental data a reaction pathway for olefin insertion has been proposed.

Experimental

Reagents.—Manipulations were generally carried out under dry, oxygen-free nitrogen using standard Schlenk techniques.⁹ Solvents were dried and purified by standard methods and freshly distilled before use. Chemical reagents were used as received. Diphenyl(*o*-vinylphenyl)phosphine,¹⁰ *trans*- $[\text{Pd}(\text{Me})(\text{PPh}_3)_2]$,¹¹ $[\{\text{Pd}(\text{Me})(\text{SMe}_2)(\mu\text{-I})\}_2]$,¹² $[\text{Pt}(\text{Me})(\text{pyca})(\text{py})]$ ($\text{py} = \text{pyridine}$)^{3d} and $\text{Ti}(\text{pyca})$ ^{3e} were prepared by literature methods.

Measurements.—Nuclear magnetic resonance spectra were recorded at 22 °C on a Bruker AM-300 NMR spectrometer at 300.13 (¹H), 75.48 (¹³C) and 121.50 MHz (³¹P). Chemical shifts (δ) are reported in ppm relative to internal SiMe_4 (¹H, ¹³C) or external 85% H_3PO_4 (³¹P). Coupling constants (J) are given in Hz and NMR peaks are given as singlet (s), doublet (d), triplet (t) and multiple (m). Unlabelled NMR peaks can be assumed to be singlets. Infrared spectra were recorded in absorbance units on a Digilab FTS 20E FT-IR spectrophotometer. Potassium bromide discs were used in the mid-IR range (4000–500 cm^{-1}). Absorption bands (cm^{-1}) are described as strong (s), medium (m) or weak (w) in intensity. Microanalyses were performed by the Central Science Laboratory, University of Tasmania.

Synthesis of Complexes.— $[\text{Pd}(\text{Me})(\text{pyca})(\text{dpvp})]$ **1**. To a solution of $[\{\text{Pd}(\text{Me})(\text{SMe}_2)(\mu\text{-I})\}_2]$ (0.09 g, 0.15 mmol) in acetonitrile (15 cm^3) at 0 °C was added $\text{Ti}(\text{pyca})$ (0.095 g, 0.29 mmol). After the mixture was stirred for *ca.* 15 min, dpvp (0.084 g, 0.29 mmol) was added. The mixture was stirred for 2 h,



allowed to warm to room temperature and stirred for another 1 h. The solvent was removed under vacuum, and the residue extracted with CH_2Cl_2 ($2 \times 10 \text{ cm}^3$). A small amount of yellow solid was removed by filtration and the pale yellow filtrate was evaporated to dryness. The oily residue was crystallised from benzene-light petroleum (b.p. 40–60 °C) to give a white solid (yield 0.16 g, 89%) (Found: C, 60.6; H, 4.60; N, 2.60. Calc. for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{Pd}$: C, 60.9; H, 4.55; N, 2.65%). ¹H NMR (CDCl_3) (refer to Table 1 for labelling of the protons): δ 0.61 [d, ³ $J(\text{PH})$ 3, Pd- CH_3], 5.1 [d, $J(\text{H}^a\text{H}^c)$ 12, $J(\text{H}^a\text{H}^b) < 1$, H^a], 5.6 [$J(\text{H}^b\text{H}^c)$ 17, H^b], 6.9 [dd, $J(\text{H}^a\text{H}^c)$ 12, $J(\text{H}^b\text{H}^c)$ 17 Hz, H^c]. ³¹P-¹H NMR (CDCl_3): δ 29.3 (s).

$[\text{Pd}(\text{Me})(\text{acac})(\text{dpvp})]$ (**2**). The complex was prepared by a similar method to that described for **1**. The complex was obtained as a white solid (yield 75%) (Found: C, 59.80; H, 5.60. Calc. for $\text{C}_{26}\text{H}_{27}\text{O}_2\text{PPd}\cdot\text{H}_2\text{O}$: C, 59.30; H, 5.50%). ¹H NMR (CDCl_3): δ 1.2 [d, 3 H, $J(\text{PH})$ 3, Pd- CH_3], 1.77 (br s), 2.05 (br s, 6 H, CH_3 of acac), 5.37 (s, 1 H, =CH), 4.9 [dd, 1 H, $J(\text{H}^a\text{H}^b)$ 1.2, $J(\text{H}^a\text{H}^c)$ 11, H^a], 5.4 [dd, 1 H, $J(\text{H}^a\text{H}^b)$ 1.2, $J(\text{H}^b\text{H}^c)$ 18, H^b], 6.9 [dd, 1 H, $J(\text{H}^a\text{H}^c)$ 11, $J(\text{H}^b\text{H}^c)$ 18 Hz, H^c]. ³¹P-¹H NMR ($[\text{C}_6\text{H}_6]$ /toluene): δ 32.4 (s). IR (KBr/ cm^{-1}): 1580vs, 1500vs, 1400vs [$\nu(\text{C}=\text{O})$ in acac]. The presence of water in the molecule is evident from its IR spectrum in CH_2Cl_2 solution.

$[\text{Pd}(\text{Me})(\text{bzac})(\text{dpvp})]$ (**3**). The complex was prepared by a similar method to that described above, by treating $[\{\text{Pd}(\text{Me})(\text{SMe}_2)(\mu\text{-I})\}_2]$ (0.05 g, 0.08 mmol) with $\text{Ti}(\text{bzac})$ (0.061 g, 0.16 mmol) and dpvp (0.047 g, 0.16 mmol). The complex was obtained as an orange solid (yield 0.08 g, 89%) by crystallising from MeOH (Found: C, 63.20; H, 5.15; S, 4.95. Calc. for $\text{C}_{31}\text{H}_{29}\text{OPPdS}$: C, 63.45; H, 5.00; S, 5.45%). ¹H NMR (CDCl_3): δ 0.45 [d, ³ $J(\text{PH})$ 5.4, Pd- CH_3], 2.56 (s, CH_3 of bzac), 4.9 [d, $J(\text{H}^a\text{H}^b) < 1$, $J(\text{H}^a\text{H}^c)$ 11, H^a], 5.4 [d, $J(\text{H}^b\text{H}^c)$ 18 Hz, H^b]. ³¹P-¹H NMR (CDCl_3): δ 29.0.

$[\text{Pd}(\text{Me})(\text{pyca})\{\text{PPh}_2(\text{C}_6\text{H}_4\text{Et-}o)\}]$ **4**. The complex was prepared by a similar method to that described for **1** except $\text{PPh}_2(\text{C}_6\text{H}_4\text{Et-}o)$ was used instead of dpvp. The complex was obtained as a pale orange solid (yield 57%) (Found: C, 60.40; H, 5.00; N, 2.80. Calc. for $\text{C}_{27}\text{H}_{26}\text{NO}_2\text{PPd}$: C, 60.75; H, 4.85; N, 2.60%). ¹H NMR (CDCl_3): δ 0.58 [d, 3 H, Pd- CH_3 , $J(\text{PH})$ 2.1], 1.05 [t, 3 H, PCH_2CH_3 , $J(\text{HH})$ 6], 3.03 [q, 2 H, PCH_2CH_3 , $J(\text{HH})$ 6 Hz]. ³¹P-¹H NMR (CDCl_3): δ 28.6 (s). IR (KBr/ cm^{-1}): 1650vs, 1350s [$\nu(\text{O}=\text{C}-\text{O})$].

$[\text{Pd}(\text{Me})(\text{acac})\{\text{PPh}_2(\text{C}_6\text{H}_4\text{Et-}o)\}]$ **5**. The complex was prepared by a similar method to that described for **4**. The complex was obtained as a yellow solid (yield 67%) (Found: C, 61.10; H, 5.70. Calc. for $\text{C}_{26}\text{H}_{29}\text{O}_2\text{PPd}$: C, 61.10; H, 5.70%). ¹H NMR (C_6D_6): δ 1.2 [d, 3 H, $J(\text{PH})$ 3, Pd- CH_3], 1.76(s), 2.06 (s, 3 H each, Me groups of acac), 5.4 (s, 1 H, =CH), 0.97 [t, 3 H, $J(\text{HH})$ 7.5, CH_2CH_3], 3.2 [dq, 2 H, $J(\text{HH})$ 7.5, $J(\text{PH})$ 1.8 Hz,

CH_2CH_3]. $^{31}\text{P}\{-^1\text{H}\}$ NMR (C_6D_6): δ 32.0 (s). IR ($\text{KBr}/\text{cm}^{-1}$): 1580vs, 1570vs, 1520vs, 1400vs [$\nu(\text{O}=\text{C}-\text{O})$].

[PtMe(pyca)(dpvp)] **6**. To a solution of [PtMe(pyca)(py)] (0.05 g, 0.12 mmol) in CH_2Cl_2 (10 cm^3) at room temperature was added dpvp (0.034 g, 0.12 mmol). The mixture was stirred for ca. 2 h. The solvent was removed *in vacuo* and the residue was crystallised from benzene–diethyl ether to give a white solid (yield 0.052 g, 70%) (Found: C, 52.20; H, 3.95; N, 2.65. Calc. for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{P}$: C, 52.25; H, 3.90; N, 2.25%). ^1H NMR (CDCl_3): two isomers: a (major): δ 0.62 [d, $J(\text{PH})$ 3, $J(\text{PtH})$ 79, Pt- CH_3], 5.08 [d, $J(\text{H}^*\text{H}^*)$ 11, H^*], 5.53 [d, $J(\text{H}^*\text{H}^*)$ 17, H^*]; b: δ 0.87 [d, $J(\text{PH})$ 3, $J(\text{PtH})$ could not be resolved, Pt- CH_3], 4.89 [d, $J(\text{H}^*\text{H}^*)$ 11, H^*], 5.34 [d, $J(\text{H}^*\text{H}^*)$ 17 Hz, H^*]. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): two isomers (ratio 3:1) δ 9.51 [s, $^1J(\text{PtP})$ 4423, major], 10.2 [s, $^1J(\text{PtP})$ 4690 Hz]. IR ($\text{KBr}/\text{cm}^{-1}$): 1660vs, 1640vs, 1600s.

[PtMe(bzsac)(dpvp)] **7**. The complex was prepared by a similar method to that described for **6** and it was obtained as an orange solid by crystallisation from benzene–light petroleum (yield 73%). This complex was characterised spectroscopically only. ^1H NMR (CDCl_3): δ 0.55 [d, 3 H, $J(\text{PH})$ 5.4, $^2J(\text{PtH})$ 83, Pt- CH_3], 2.3 (s, 3 H, CH_3 of bzsac), 4.75 [d, $J(\text{H}^*\text{H}^*)$ 12, H^*], 5.25 [d, $J(\text{H}^*\text{H}^*)$ 18 Hz, H^*]. $^{31}\text{P}\{-^1\text{H}\}$ NMR: δ 23.3 [$^1J(\text{PtP})$ 3689 Hz]. IR ($\text{KBr}/\text{cm}^{-1}$): 1550s, 1500s, 1480vs [$\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{S})$].

[PtMe(pyca){PPh₂(C₆H₄Et-o)}] **8**. The complex was prepared by a similar method to that described for its palladium analogue **4**, except that the residue was extracted with refluxing benzene for 30 min before being purified. The complex was obtained as a pale orange solid (yield 64%) (Found: C, 52.20; H, 4.25; N, 2.00. Calc. for $\text{C}_{27}\text{H}_{26}\text{NO}_2\text{P}$: C, 52.10; H, 4.20; N, 2.25%). ^1H NMR (C_6D_6): δ 0.86 [d, 3 H, $J(\text{PH})$ 3, $J(\text{PtH})$ 78, Pt- CH_3], 1.04 [t, 3 H, $J(\text{HH})$ 6, $\text{PC}_6\text{H}_4\text{CH}_2\text{CH}_3$ -o], 3.38 [q, 2 H, $J(\text{HH})$ 6 Hz, $\text{C}_6\text{H}_4\text{CH}_2\text{CH}_3$ -o]. $^{13}\text{C}\{-^1\text{H}\}$ NMR (C_6D_6): δ -17.0 [d, $J(\text{PC})$ 7.5, $J(\text{PtC})$ 717, Pt- CH_3], 14.4 (s, $\text{PC}_6\text{H}_4\text{CH}_2\text{CH}_3$ -o), 28.5 [d, $J(\text{PC})$ 7.5 Hz, $\text{PC}_6\text{H}_4\text{CH}_2\text{CH}_3$ -o]. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 9.4 [s, $^1J(\text{PtP})$ 4435 Hz]. IR ($\text{KBr}/\text{cm}^{-1}$): 1640vs, 1340vs [$\nu(\text{O}=\text{C}-\text{O})$].

[PdMe(pyca){PPh₂(CH₂-CH=CH₂)}] **9**. The complex, prepared by a similar method to that described for **1**, was obtained as a pale orange solid (Found: C, 55.4; H, 4.65; N, 3.10. Calc. for $\text{C}_{22}\text{H}_{22}\text{NO}_2\text{PPd}$: C, 56.2; H, 4.70; N, 3.00%). ^1H NMR (CDCl_3): δ 0.54 [d, 3 H, $^3J(\text{PH})$ 2, Pd- CH_3], 3.4 [dd, 2 H, $^2J(\text{PH})$ 12, $^3J(\text{HH})$ 9, P- CH_2], 4.9 [dd, 1 H, $J(\text{HH})$ 5.1, $J(\text{HH})$ 17, =CH], 5.0 [dd, 1 H, $J(\text{HH})$ 5.1, $J(\text{HH})$ 11 Hz, =CH], 5.9 (m, 1 H, =CH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 28.9. IR ($\text{KBr}/\text{cm}^{-1}$): 1640vs, 1600vs, 1340vs [$\nu(\text{O}=\text{C}-\text{O})$], 1570s [$\nu(\text{C}=\text{C})$].

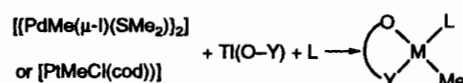
[Pd(pyca){PPh₂(C₆H₄(CHCH₂CH₃-o))}] **10**. A solution of **1** (0.09 g, 0.17 mmol) in benzene (15 cm^3) was refluxed for 4 h. The solvent was removed *in vacuo* and the residue was crystallised from benzene–light petroleum to give a white crystalline solid (yield 81%) (Found: C, 59.95; H, 5.00; N, 2.25. Calc. for $\text{C}_{27}\text{H}_{24}\text{NO}_2\text{PPd} \cdot 0.5\text{H}_2\text{O}$: C, 60.00; H, 4.65; N, 2.60%). The presence of traces of water in the molecule was evident from both ^1H NMR and IR spectra in CDCl_3 solution. ^1H NMR (CDCl_3): two isomers, δ 0.76 [t, $^3J(\text{HH})$ 7.5, major], 0.74 [t, 3 H, $^3J(\text{HH})$ = 7.5, CH_3], 1.8 (m, major), 2.2 (m, CH_2), 4.7 (q, major, J 6), 4.1 (J 6 Hz, Pd-CH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 50.8 (s, major), 46.9 (s). $^{13}\text{C}\{-^1\text{H}\}$ NMR (CDCl_3): two isomers were observed: δ 14.9 (s, major, CH_3), 32.0 (s, major), 32.9 (s, CH_2), 54.5 (s, major), 51.8 (s, PdCH), 172 (O=C-O). $^{13}\text{C}\{-^1\text{H}\}$ distortionless enhancements by polarisation transfer (DEPT) NMR spectrum: primary carbon: δ 14.9; secondary carbons: δ 32.0, 32.9; tertiary carbon: δ 54.5, 51.8. IR ($\text{KBr}/\text{cm}^{-1}$): 1640vs, 1600s, 1320vs [$\nu(\text{O}=\text{C}-\text{O})$ and $\nu(\text{C}=\text{C})$].

[Pd(acac){PPh₂(C₆H₄(CHCH₂CH₃-o))}] **11** and [Pd(bzsac){PPh₂(C₆H₄(CHCH₂CH₃-o))}] **12**. The complexes were prepared by a similar method to that described for **10**. The reaction was complete within 1–2 h. However, some decomposition of complex **12** took place at the reaction

temperature, therefore the insertion products have only been characterised spectroscopically. **11**: ^1H NMR (CDCl_3): δ 1.04 [t, 3 H, $^3J(\text{HH})$ 7.4 Hz, CH_3], 2.7 (m, 2 H, CH_2), 4.8 (q, 1 H, J 7 Hz, Pd-CH). $^{13}\text{C}\{-^1\text{H}\}$ NMR (CDCl_3): δ 15.1 (s, CH_3), 32.0 (s, CH_2), 51.2 (s, PdCH), 28.6 (s), 28.9 (s, CH_3 of acac), 99.9 (=CH of acac). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): 47.6 (s). IR ($\text{KBr}/\text{cm}^{-1}$): 1580vs, 1570vs, 1520s, 1380vs [$\nu(\text{O}=\text{C}-\text{O})$]. **12**: ^1H NMR (CDCl_3): two isomers, δ 0.78 [t, $^3J(\text{HH})$ 7.3], 0.80 [t, 3 H, $^3J(\text{HH})$ 7.3, CH_3], 1.75 (m), 1.90 (m, 2 H, CH_2), 4.1 (q, J 8.1), 4.5 (q, J 8.1 Hz, Pd-CH). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 53.5 (s), 40.1 (s). IR ($\text{KBr}/\text{cm}^{-1}$): 1581vs, 1570vs, 1525s, 1380vs [$\nu(\text{O}=\text{C}-\text{O})$].

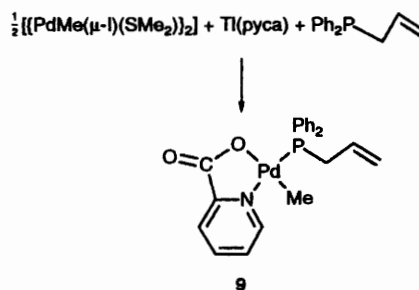
[Pt(pyca){PPh₂(C₆H₄C=CH₂-o)}] **13**. A solution of [PtMe(pyca)(dpvp)] in benzene (15 cm^3) was refluxed for ca. 6 h. The solution turned from colourless to pale yellow. After the solvent was evaporated *in vacuo*, the residue was crystallised from benzene–diethyl ether (Found: C, 51.30; H, 3.65; N, 2.20. Calc. for $\text{C}_{26}\text{H}_{20}\text{NO}_2\text{P}$: C, 51.65; H, 3.35; N, 2.30%). ^1H NMR (CDCl_3): δ 6.13 [d, $J(\text{PH})$ 2, $J(\text{PtH})$ 45, =CH], 6.2 [s, $J(\text{PtH})$ 62 Hz, =CH]. $^{13}\text{C}\{-^1\text{H}\}$ NMR (CDCl_3): δ 117.6 (s, =CH₂), 123 [d, $^2J(\text{PC})$ 15, $^1J(\text{PtC})$ 42 Hz, Pt-C=CH₂]. $^{13}\text{C}\{-^1\text{H}\}$ DEPT NMR spectrum: the only secondary carbon in the molecule was located at δ 117.5; two-dimensional heteronuclear chemical shift correlation (2DHETCOR) NMR spectrum: two protons at δ 6.10 and 6.14 are both correlated with the same carbon atom at δ 117.5. $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): δ 30.6 [$^1J(\text{PtP})$ 4550 Hz]. IR ($\text{KBr}/\text{cm}^{-1}$): 1650vs, 1600s, 1320vs [$\nu(\text{O}=\text{C}-\text{O})$ and $\nu(\text{C}=\text{C})$]. Mass spectrum: m/z 604 [M]⁺, 605 [$M - \text{H}$]⁺ and 480 ($M - \text{pyca}$). High resolution mass spectrum: m/z 604.0798. Calc. for $\text{C}_{26}\text{H}_{20}\text{NO}_2\text{P}$: 604.0880.

Kinetic Measurements.—Rates for the interchange of the acetylacetonate ligand in complex **2** were calculated from the differences in the chemical shifts of the two methyl singlets below the coalescence temperature using Gutowsky and Holm's equation.¹³ Samples were dissolved in 0.5 cm^3 of CDCl_3 which was contaminated with a trace of grease. The NMR tube was then fitted with a septum and secured with Teflon tape. The sample solution was made up to contain a concentration of 0.02 mol dm^{-3} of complex for each run. The extent of conversion to the insertion product was monitored by integration of the σ -methyl resonances of the complexes (at ca. δ 0.6) and the external standard (grease, δ 0.1). Each kinetic run consisted of four to eight points.



Isomer b also forms in some cases, see Table 1

	L	Y	O—Y
1 (6)	dpvp	N	pyca
2	dpvp	O	acac
3 (7)	dpvp	S	bzsac
4 (8)	PPh ₂ (C ₆ H ₄ Et-o)	N	pyca
5	PPh ₂ (C ₆ H ₄ Et-o)	O	acac



Scheme 2 M = Pd (Pt), cod = cycloocta-1,5-diene

Table 1 Selected NMR data for the dpvp containing complexes

Complex	¹ H NMR (δ) ^a			³¹ P- ¹ H NMR (δ) ^b
	M-CH ₃	H ^a	H ^b	
M = Pd				
1 (O-Y) = pyca (isomer a only)	0.61d (3)	5.1d (12)	5.6d (17)	29.3
2 (O-Y) = acac (isomer a only)	1.2d (3)	4.9dd (1.2/11)	5.4dd (1.2, 18)	32.4
3 (O-Y) = bzscac (isomer a only)	0.45d (5.4)	4.9dd (1.0/11)	5.4dd (1.0, 18)	29.0
M = Pt				
6 (O-Y) = pyca (two isomers, a : b = 5:1)				
a	0.62d (3, 79 ^c)	5.08d (11)	5.53d (17)	9.51 (4423)
b	0.87d (3)	4.89d (11)	5.34d (17)	10.2 (4690)
7 (O-Y) = bzscac (isomer a only)	0.55d (5.4, 83 ^c)	4.75d (12)	5.25d (18)	23.3 (3689)

^a Coupling constants $J(\text{HH})/\text{Hz}$ are given in parentheses. ^b Coupling constants $^1J(\text{PtP})/\text{Hz}$ are given in parentheses. ^c $^2J(\text{PtH})/\text{Hz}$.

Results and Discussion

Synthesis and Spectroscopic Properties of Complexes containing Olefinic Tertiary Phosphines.—The methyl-palladium(II) and -platinum(II) complexes 1–9 have been prepared using the methods shown in Scheme 2. Complexes 1–3, 6, 7 and 9 contain an ethylene moiety on the phosphine.

As previously reported for related complexes containing chelate ligands, e.g. [PtMe(O-Y)L] and [PdMe(O-Y)L] (Y = N, O or S), two isomers are expected from the synthesis: the methyl group may be either *trans* to a nitrogen or sulfur atom or to an oxygen atom.³ The predominant isomer expected (for O-Y = pyca), is **a** (Table 1), in which the two largest *trans* influence ligands avoid mutually *trans* positions. Identification of the isomers in solution is based on spectroscopic methods and by comparison with similar structures.³ In general, a higher selectivity for formation of one isomer is noted in palladium(II) complexes as they give only *cis*-isomers, **a**, while the platinum complexes could be obtained as a mixture of *cis* and *trans* isomers depending on the nature of the ligands (Table 1).

As shown in Table 1, the methyl ligands of these complexes appear in the ¹H NMR spectra in the region δ 0.5–1.5 as a doublet, due to coupling with *cis* phosphine. The coupling constants of these protons with phosphorus are typically 2–6 Hz. In platinum complexes these resonances are flanked by ¹⁹⁵Pt satellites, with coupling constants of 80 Hz. The smaller ¹⁹⁵Pt–³¹P coupling constant for the major isomer in the mixture of platinum complexes 6 implies that the *cis* structure, **a**, is preferred.

Olefinic protons of the diphenyl(*o*-vinylphenyl)phosphine ligand appear as two multiplets in the region δ 4–6, which are assigned to the vinyl protons H^a and H^b (Table 1). Resonances due to the α proton (H^c) in these complexes are masked by the aromatic resonances and are not observed in most cases. The chemical shift and coupling constants for the olefinic resonances are close to those of unco-ordinated dpvp and in the platinum complexes coupling between ¹⁹⁵Pt and the vinyl protons was not observed. These facts indicate that the vinyl

group of the dpvp ligands in these complexes is not bound to the central metal atom.

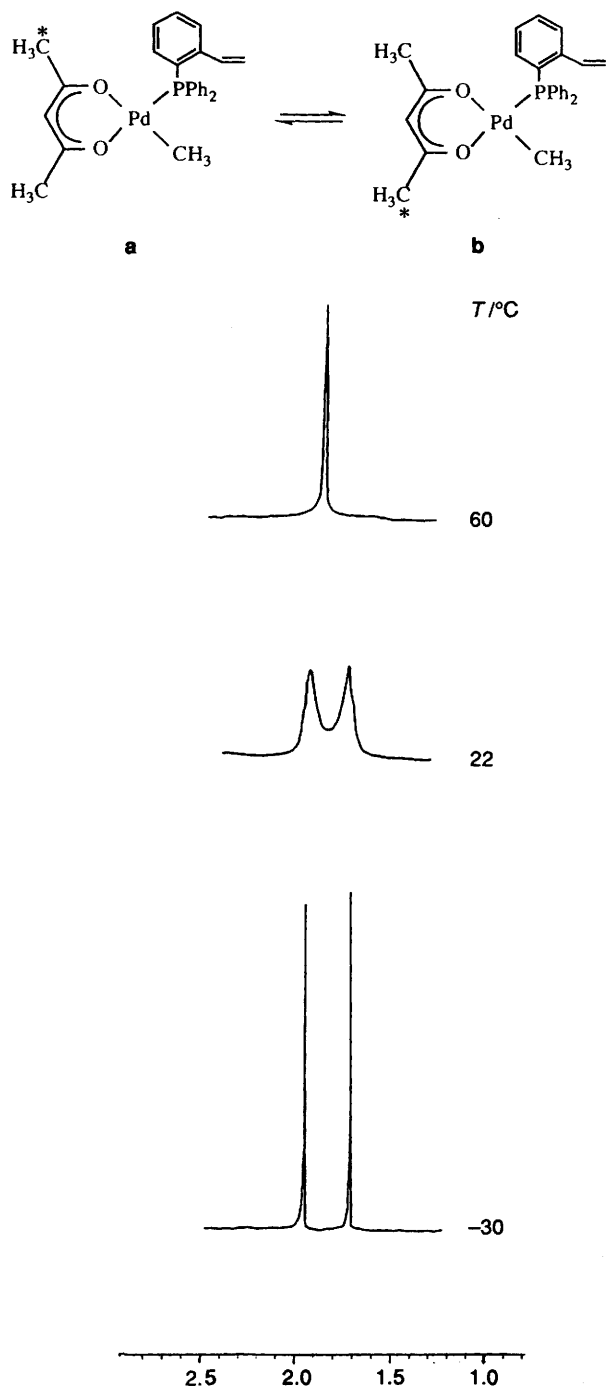
As shown in Fig. 1, two singlets at δ 1.77 and 2.05 in the ¹H NMR spectra of [PdMe(acac)(dpvp)], **2**, assigned to the two methyl groups of the acetylacetonate ligand, become two broadened singlets on raising the temperature from –30 to 22 °C and coalesce at 30–40 °C. Above this temperature, the coalesced singlet sharpens. This spectral change reflects the time-average field experienced by the two methyl groups of the acac ligand, and is interpreted as an increase in the exchange rate between **a** and **b** (Fig. 1) on raising the temperature. Rate constants *k*, for the exchange process were calculated from the Gutowsky and Holm equation.¹³ An Arrhenius plot of these *k* values leads to the activation parameters which are included in Table 2.

The two methyl groups of the acac ligand in **2** show only one resonance at δ 28.8 in the ¹³C NMR spectrum at 22 °C. This is in contrast to the spectra of other [PdR(acac)L] (R = Me, Ph; L = PPh₃) complexes, in which the two methyl groups always appear as two separate resonances.^{3a-c}

An Arrhenius activation energy, $E_a = 23 \text{ kcal mol}^{-1}$, has been reported for the palladium–oxygen bond rupture in the exchange reaction of [Pd(acac)₂] with ¹⁴C-labelled acetylacetone in anisole as solvent.¹⁴ In the co-ordinating solvent pyridine, a much smaller E_a value (6.2 kcal mol⁻¹) was obtained for [Pd(acac)(*r*-acac)(py)] [where *r*-acac = Me(O)CCHC(O)-Me].¹⁵ This was found to be consistent with an exchange mechanism involving solvent assisted M–O bond rupture and rotation of the unidentate acac around the remaining M–O bond and re-co-ordination of the carbonyl group to the metal.¹⁵ In the present study, a significantly smaller value for the activation energy was obtained ($E_a = 1.3 \text{ kcal mol}^{-1}$) in a non-co-ordinating solvent, which may indicate the existence of an interaction between the vinyl group of dpvp and the palladium atom. Since the palladium complex **2** has a 16-electron square-planar structure, dissociation of the co-ordinated acetylacetonate ligand is expected to proceed *via* a mechanism involving

Table 2 Selected kinetic data for some palladium(II) complexes containing acac ligands

Complexes	E_a /kcal mol ⁻¹	ΔH^\ddagger /kcal mol ⁻¹	ΔS^\ddagger /cal mol ⁻¹	ΔG^\ddagger /kcal mol ⁻¹
[Pd(acac)(r-acac)(py)]	6.16	5.82	-33.7	16.2 ¹⁵
Pd(acac) ₂ + ¹⁴ C-acac	23	—	—	— ¹⁴
2 [PdMe(acac)(dpvp)]	1.32	0.76	-46.5	15.5

**Fig. 1** Variable-temperature ¹H NMR spectra (in CDCl₃) of the acac methyl groups in the complex [Pd(Me)(acac)(dpvp)]

an 18-electron transition state formed by co-ordination of the vinyl group to the palladium centre. The vinyl group may then promote the partial dissociation of the acetylacetonate chelate. This interaction (described in Scheme 3) is similar to that of the solvent assisted exchange mechanism.

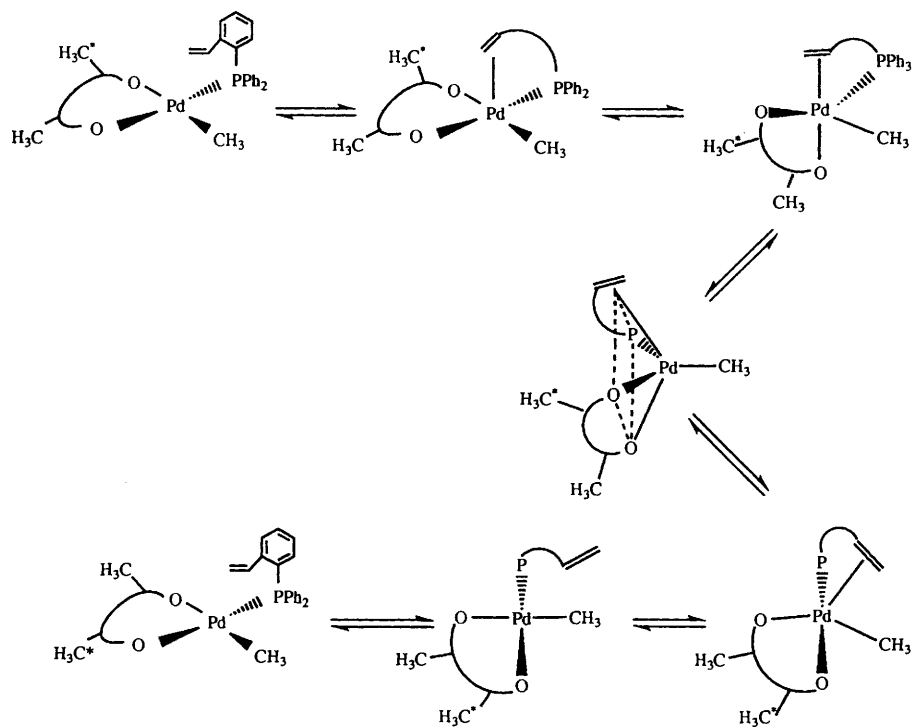
Variable-temperature NMR experiments between -50 and 50 °C have been unable to provide any evidence for either the existence of a five-co-ordinate intermediate or chelation of the olefinic tertiary phosphine. Thus the equilibrium must also lie well towards the unco-ordinated form and/or subsequent reaction of the co-ordinated vinyl group must be a rapid process at these temperatures. In order to provide evidence for this vinyl-group accelerated acac exchange reaction (Scheme 3), the complex [PdMe(acac){PPh₂(C₆H₄Et-*o*)}] **5** (which lacks a vinyl group) has been prepared. If pre-co-ordination of the vinyl group of the dpvp ligand to palladium is important for the exchange of the acetylacetonate chelate, such a mechanism will not be possible for the complex **5** containing PPh₂(C₆H₄Et-*o*). Consistent with this proposal, no broadening of the two methyl peaks of the acetylacetonate ligand in complex **5** is observed even at temperatures up to 55 °C. This behaviour is similar to that observed for [PdMe(acac)(PPh₃)] for which the dissociation-association of the acetylacetonate ligand can only be observed in a co-ordinating solvent such as pyridine.^{3b}

Pre-co-ordination of the olefin to a metal atom has been proposed as a key step in reactions in which an olefin inserts into a metal-carbon bond, and a computational modelling study favours a coplanar alignment of the alkene C=C bond with the M-C σ-bond in a *cis* position.^{1,2} Furthermore, in this favoured structure for the pre-insertion intermediate two large *trans* influence ligands are in mutually *trans* positions and will thus promote the methyl migration step.

Ethylene Insertion and Cyclometallation Reactions.—Migratory insertion of the vinyl group of the dpvp ligand into the M-Me bond may result in products formed by migration of the methyl group either to the terminal carbon or the internal carbon of the vinyl group. Thermolysis of the palladium complex [PdMe(pyca)(dpvp)] **1** at 60 °C generates a five-membered palladacycle, complex **10** only (Scheme 4), indicating that migration of the methyl ligand takes place to the terminal carbon of the vinyl group. Complex **10** appears as a pair of isomers **10a** and **10b** (ratio 3:1) with **10a** as the predominant product. Although the direct observation of alkene insertion into a Pd-alkyl bond is rare, the addition of nucleophiles to a co-ordinated olefin in palladium(II) complexes has been well documented.¹⁶ In general five-membered palladacycles are considerably more stable than either four- or six-membered ring systems.¹⁷ Thus, ring size is probably an important factor in determining the site of nucleophilic attack in these instances.

Isomers **10a** and **10b** appear in ³¹P-{¹H} NMR spectra as two singlets at δ 50.8 and 46.9 respectively (Table 3). The significant down-field shift of the two resonances compared with that observed for the precursor **1** (δ 29.3) is consistent with the formation of a five-membered alkylphosphine chelate in the molecule.¹⁸

The ¹H NMR spectrum of complex **10** shows two sets of triplets, one at δ 0.76 and the other at δ 0.74 [*J*(HH) 7.5 Hz], due to the methyl groups of **10a** and **10b**. The methine proton for each isomer is strongly deshielded with respect to normal benzyl protons and resonances appear as a pseudo-quartet [*J*(HH) 6 Hz] at δ 4.7 and 4.1, respectively. This splitting is in fact a complex combination of a doublet of doublets of doublets arising from the coupling of ³¹P nuclei and two diastereotopic methylene protons. Owing to the presence in **10** of an asymmetric carbon atom, the two diastereotopic hydrogen atoms appear as distinct multiplets at δ 1.8 and 2.2 in the ¹H



Scheme 3

Table 3 Selected spectroscopic data for intramolecular olefin insertion products

Complex	¹ H NMR (δ) ^a			³¹ P- ¹ H NMR (δ)	$\tilde{\nu}/\text{cm}^{-1}$
	CH	CH ₂	CH ₃		
10a	4.7q ^b (6)	1.8m 2.2m ^c	0.76t (7.5)	50.8	1640vs
10b	4.1q (6)	<i>d</i>	0.74t (7.5)	46.9	1640vs
11	4.8q (7)	2.7m	1.04t (7.4)	47.6	<i>e</i>
12a	4.1q (8.1)	1.7m	0.78t (7.3)	53.5	<i>f</i>
12b	4.5q (8.1)	1.9m	0.80t (7.3)	40.1	

^a Coupling constants in Hz are given in parentheses. ^b Collapsed quartet, the values reported as coupling constants for these resonances are the separation between lines and do not necessarily reflect the true coupling constants. ^c Two sets of multiplets for CH₂ for each isomer; group attached to chiral carbon. ^d Signals coincidentally the same as for isomer a. ^e 1580vs, 1570vs, 1520s, 1380vs, $\nu(\text{O}=\text{C})$ and $\nu(\text{C}=\text{C})$ of acetylacetonate ligand. ^f 1581vs, 1570vs, 1525s, 1380vs, $\nu(\text{C}=\text{O})$ and $\nu(\text{C}=\text{C})$ of bzvac ligand.

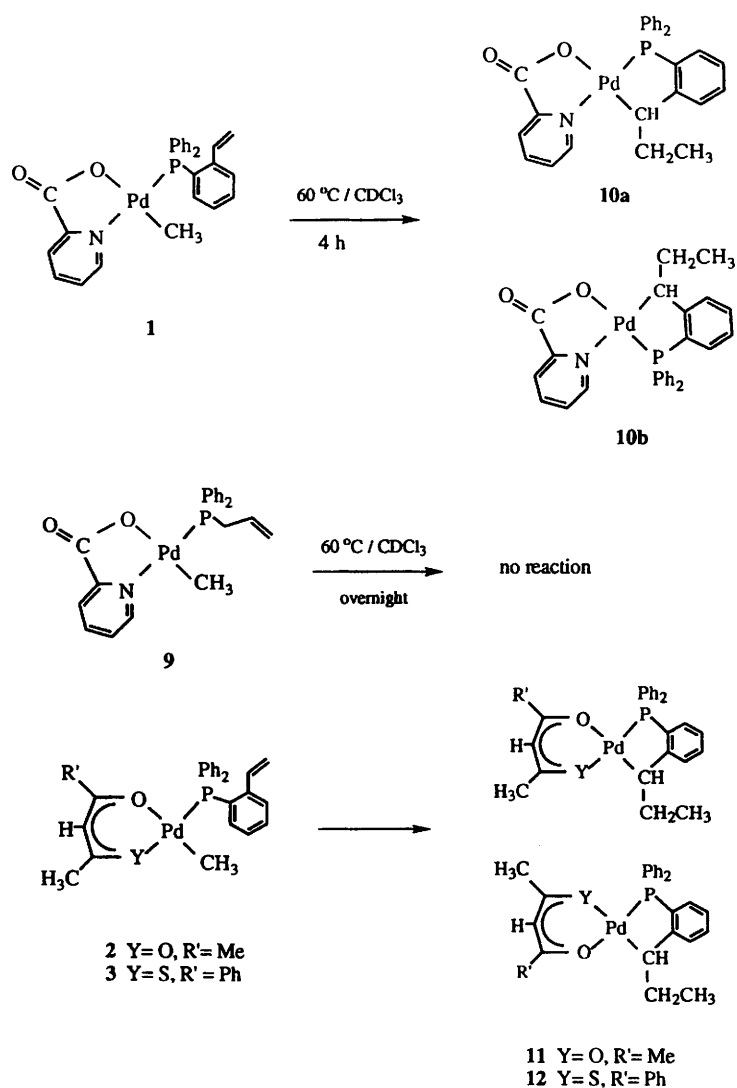
NMR spectrum. This multiplicity is due to couplings with the associated methyl group, the methine proton CH, and the neighbouring diastereotopic proton.¹⁹ The assignment of the structure of **10** has also been confirmed by ¹³C-¹H and ¹³C-¹H DEPT NMR spectroscopy.

The insertion of the ethylene moiety into the Pd-Me bonds in [PdMe(acac)(dpvp)] **2** and [PdMe(bzvac)(dpvp)] **3** also generates complexes with a five-membered chelate ring (Table 3). A pair of isomers for **12** are observed in the reaction of [PdMe(bzvac)(dpvp)] **3**, whereas [PdMe(acac)(dpvp)] **2** gives only one isomer **11**. However, some decomposition took place at the reaction temperature and the pure insertion products **11** and **12** have not been isolated.

Kinetic studies on the insertion reactions of **1-3** show that they obey a pseudo-first order rate law, in agreement with the

proposal that the reactions proceed *via* an intramolecular process. Reliable quantitative data could only be obtained for complex **2** ($k = 3.6 \times 10^{-4} \text{ s}^{-1}$, $T_{\frac{1}{2}} = 1925 \text{ s}$), a small amount of decomposition occurs with complex **3** and the reaction of complex **1** was too slow. However the relative reactivities were clear and the ease of the ethylene insertion reaction decreased in the following order: acac > bzvac > pyca. For example, insertion occurs in [PdMe(acac)(dpvp)] **2** at room temperature, while the same reaction can only be achieved in [PdMe(pyca)(dpvp)] **1** or [PdMe(bzvac)(dpvp)] **3** at temperatures above 40 °C.

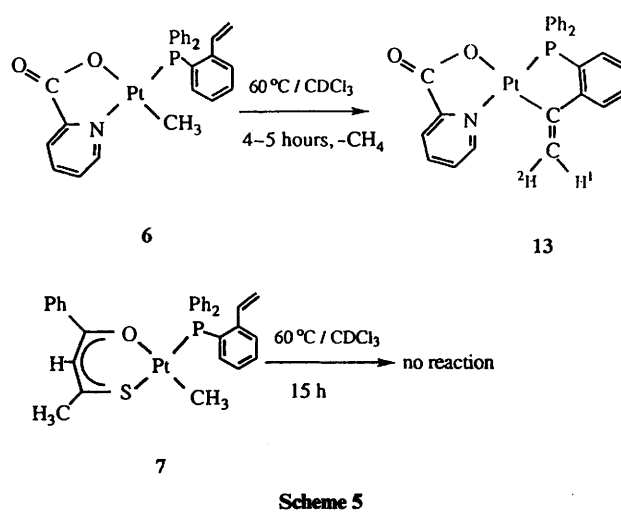
Interestingly, the complex [PdMe(pyca){PPh₂(CH₂CH=CH₂)}] **9**, which contains the ligand allyl(diphenyl)phosphine, does not undergo an insertion reaction under the same reaction conditions even after a prolonged reaction time. An



Scheme 4

explanation may be that the arrangement of the vinyl moiety in allyl(diphenyl)phosphine does not compel a close approach to the d_{π} orbital of the metal atom and hence hinders the required coplanar alignment of C=C in the co-ordination plane. More effective approach and alignment of the vinyl group of the dpvp ligand to the co-ordination plane favours the initial co-ordination and subsequent insertion reaction.

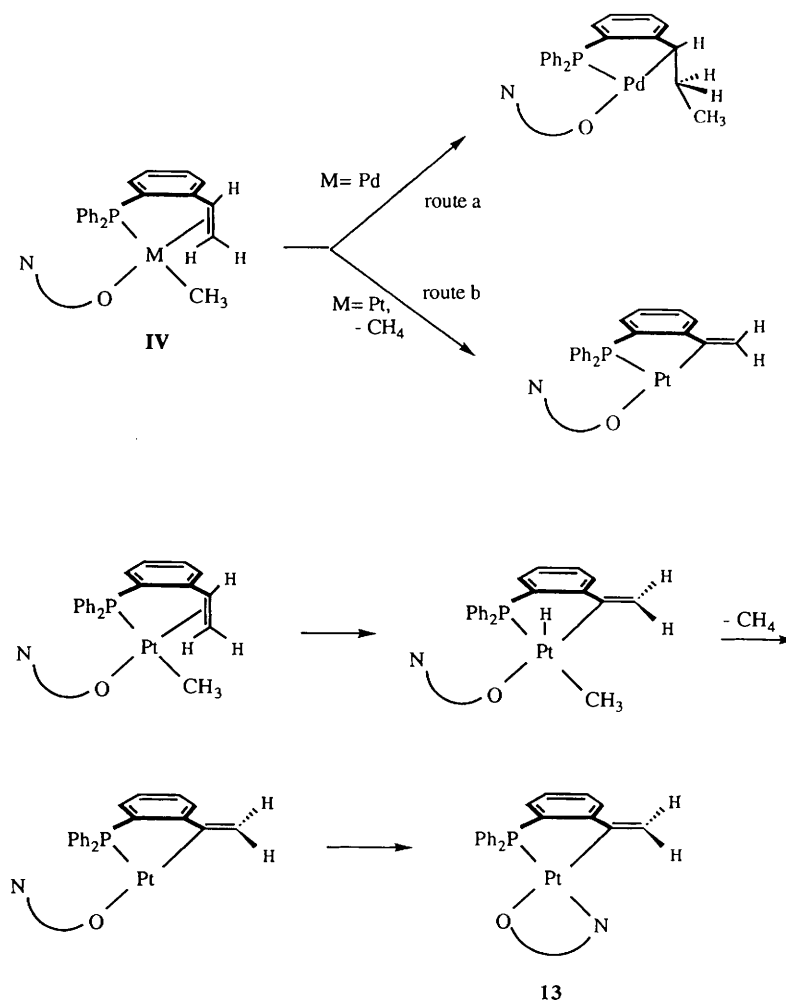
In contrast to the palladium complexes, the thermolysis of the platinum analogue, [PtMe(pyca)(dpvp)] **6** generates only a cyclometallated complex **13** rather than the expected insertion product (Scheme 5). When **6** was either refluxed in CDCl_3 or heated in the solid state at $70\text{ }^\circ\text{C}$ for several hours, the cyclometallated complex **13** formed almost quantitatively. Detailed ^1H , $^{13}\text{C}\{-^1\text{H}\}$ and $^{31}\text{P}\{-^1\text{H}\}$ spectral data for **13** are summarised in the Experimental section; assignments were confirmed by $^{13}\text{C}\{-^1\text{H}\}$ DEPT and $^{13}\text{C}\{-^1\text{H}\}$ HETCOR NMR spectroscopy. The two olefinic protons H^1 and H^2 in **13** appear in the ^1H NMR spectra as a singlet and doublet at δ 6.14 [$^2J(\text{PtH})$ 62] and 6.10 [$J(\text{PtH})$ 43 Hz] respectively. Both resonances are flanked by ^{195}Pt satellites. The DEPT and HETCOR experiments established that the two olefinic protons H^1 and H^2 are attached to the same carbon.²⁰ The chemical shifts and the coupling constants for the vinyl protons are consistent with those of known platinum vinyl complexes.²¹ Methane, generated in the reaction (Scheme 5), has been located at δ 0.2 from *in situ* ^1H NMR studies and its presence



Scheme 5

was confirmed separately by gas chromatography. A down-field shift in the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra from δ 9.5 and 10.2 in **6** to δ 30.6 in **13** is consistent with the formation of a chelated alkylphosphine ligand in **13**.¹⁸

As observed for the palladium complexes, differences in the



Scheme 6

nature of the hemilabile chelate ligand have a marked effect on the reaction rate. For example, the complex $[\text{PtMe}(\text{bzsac})(\text{dpvp})]$ **7**, containing a monothio- β -diketonate chelate, does not undergo reaction under the same conditions.

The reason for the formation of **13** rather than the expected analogue of **10** is clearly of interest. It is possible that **13** may be a decomposition product generated from further reaction of an intermediate analogous to the palladium complex **10**. However, a variable-temperature NMR study of **6** in CDCl_3 provided no spectroscopic evidence for an analogue of **10** or for any other intermediates. Furthermore, the occurrence of the reaction even in the solid state indicates that a pathway involving an intermediate with a similar structure to **10** is unlikely. A possible mechanism for the formation of **13**, which involves an intermediate formed from oxidative addition of a C–H bond to Pt^{II} , is proposed in Scheme 6.

The mechanism of thermal metallation of Pt^{II} complexes has been studied by Whitesides and co-workers.²² They found that the key steps in the reaction are; reversible dissociation of the phosphine ligand; oxidative addition of the C–H bond to the co-ordinately unsaturated three-co-ordinate complex; rate-limiting reductive elimination of the alkyl ligand and reassociation of the phosphine ligand. Our observations are in line with these proposals. The dissociation of the pyridine moiety of the pyca ligand in **6** provides an unsaturated species, which facilitates the oxidative addition of the olefinic C–H bond to the Pt^{II} atom, followed by reductive elimination of methane to give **13**. The bzsac ligand has been found to be quite strongly bound to Pt^{II} even in the presence of a donor ligand.^{3b}

This property may explain the absence of cyclometallation for $[\text{PtMe}(\text{bzsac})(\text{dpvp})]$.

It is proposed that both palladium and platinum complexes $[\text{MMe}(\text{pyca})(\text{dpvp})]$ have a common intermediate in the thermolysis reactions. We present it tentatively as **IV** (Scheme 6). From **IV**, two possible pathways may then ensue, *i.e.* insertion of the vinyl group into the M–Me bond (route a), or oxidative addition of an olefinic C–H bond to give a cyclometallation product (route b). To understand why the palladium complex **1** follows route a whereas the platinum analogue **6** prefers a cyclometallation reaction (route b) a consideration of the electronic properties of the two metals is informative. The electron affinity (which correlates with the σ -acceptor properties of the metal) of Pd^{II} and Pt^{II} are similar, however the electron promotion energy (which correlates inversely with metal π -donor properties) of Pd^{II} is significantly smaller than that of Pt^{II} , resulting in stronger initial binding between alkenes and Pd^{II} because of more efficient back-bonding.^{23,24} It can thus be assumed that π -back bonding to an anti-bonding orbital in the vinyl group is greater in the intermediate $[\text{PdMe}(\eta^1\text{-pyca})(\eta^3\text{-dpvp})]$ **IV** than in $[\text{PtMe}(\eta^1\text{-pyca})(\eta^3\text{-dpvp})]$, resulting in a greater reduction in the electron density between the olefinic carbons for the palladium complex and increasing the susceptibility of the olefin to nucleophilic attack by the Me group. Attack by a nucleophile is expected to occur away from the carbon bearing electron-withdrawing substituents.²³ In agreement with this prediction the σ -methyl group attacks the terminal carbon of the vinyl group, *i.e.* away from the carbon attached to the benzene ring.

In contrast, the oxidative addition of a C–H bond, which is largely related to the nucleophilicity of the metal centre, would be expected to occur more easily with Pt^{II} than Pd^{II}.^{22a,23,25} The platinum(II) centre is more nucleophilic and has been shown to undergo oxidative addition with considerably higher rates than does palladium(II). Furthermore, the greater stability of platinum(IV) compared to palladium(IV) is well known.²⁶

Conclusion

The intramolecular insertion of an olefin into a Pd–Me bond is a facile process in complexes 1–3 when compared to the intermolecular insertion of ethene. The resulting insertion products are readily identified by spectroscopic means as they are stabilised by the chelate effect. The ease of the reaction is related to the nature of the chelate ligands, among other factors, and decreases in the order: O–O(acac) > O–S(bzscac) > O–N(pyca). Although insertion from a five-co-ordinate intermediate cannot be ruled out it seems likely that the reaction pathway is a dissociative one, in which partial dissociation of a hemilabile chelate ligand occurs. In contrast, the platinum analogues do not undergo a similar insertion reaction. For these complexes the only product obtained was a platinacycle compound resulting from a metallation reaction, probably involving oxidative addition of the vinyl C–H bond to platinum(II).

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