Journal of Organometallic Chemistry, 461 (1993) 61-67

JOM 23737

Syntheses and NMR spectroscopic characterisation of transition metal complexes containing the azadiphosphetine ring system RP(NR′)P=CR′ (R = Et_3C, R′ = ^tBu) *

Peter B. Hitchcock, Robson M. Matos, Mohamed F. Meidine, John F. Nixon, Bernadette F. Trigo Passos
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ (UK)

Detlef Barion and Edgar Niecke
Institut für Anorganische Chemie, Gerhard-Domagk Strasse, Bonn (Germany)

(Received March 3, 1993)

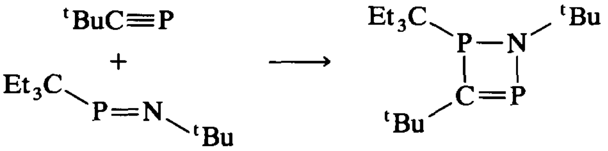
Abstract

The synthesis and characterisation of Pt^0, Pt^{II}, Pd^{II}, Rh^I, and W^0 complexes containing the RP(NR′)P=CR′(R = Et_3C, R′ = ^tBu) ring system are reported, and their NMR spectroscopic data are discussed. Low oxidation state metal fragments bond through the two-coordinate phosphorus, whereas the three-coordinate phosphorus atom is the donor towards Pd^{II} and Pt^{II}. Both phosphorus atoms are ligated in a dinuclear Pt^{II} complex.

1. Introduction

The chemistry of low-coordinated phosphorus has developed very rapidly in the past decade and already a number of reviews on phosphaalkynes (RC≡P), phosphaalkenes (R_2C=PR), and mono- and diphosphaallenes (R_2C=C=PR and RP=C=PR) have appeared [1]. More recently, there has been increasing interest in P–N multiple bonds compounds, typified by RP=NR′ and $(P{\equiv}NR')^+$ (R′ = $C_6H_2{}^tBu_3$) [2].

Niecke and coworkers [3] showed that $^tBuC{\equiv}P$ reacts with R–P=N–R′ (R=Et_3C, R′=^tBu) to produce the azadiphosphetine ring system RP(NR′)P=CR′ (1) *via* a [2 + 1] cycloaddition reaction and rearrangement of the three-membered ring intermediate



(I)

The availability of the novel four-membered azadiphosphetine ring I offers a rare opportunity to study the relative donor properties of the two- and three-coordinate phosphorus atoms within the same ring system.

Assuming ligation to only one transition metal *via* phosphorus, three bonding modes A–C for I can be envisaged. We thought it likely that the preferred interaction might depend on the electronic nature of the

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Correspondence to: Professor J.F. Nixon.

* A preliminary account of this work appeared in *J. Organomet. Chem., 390* (1990) C39.

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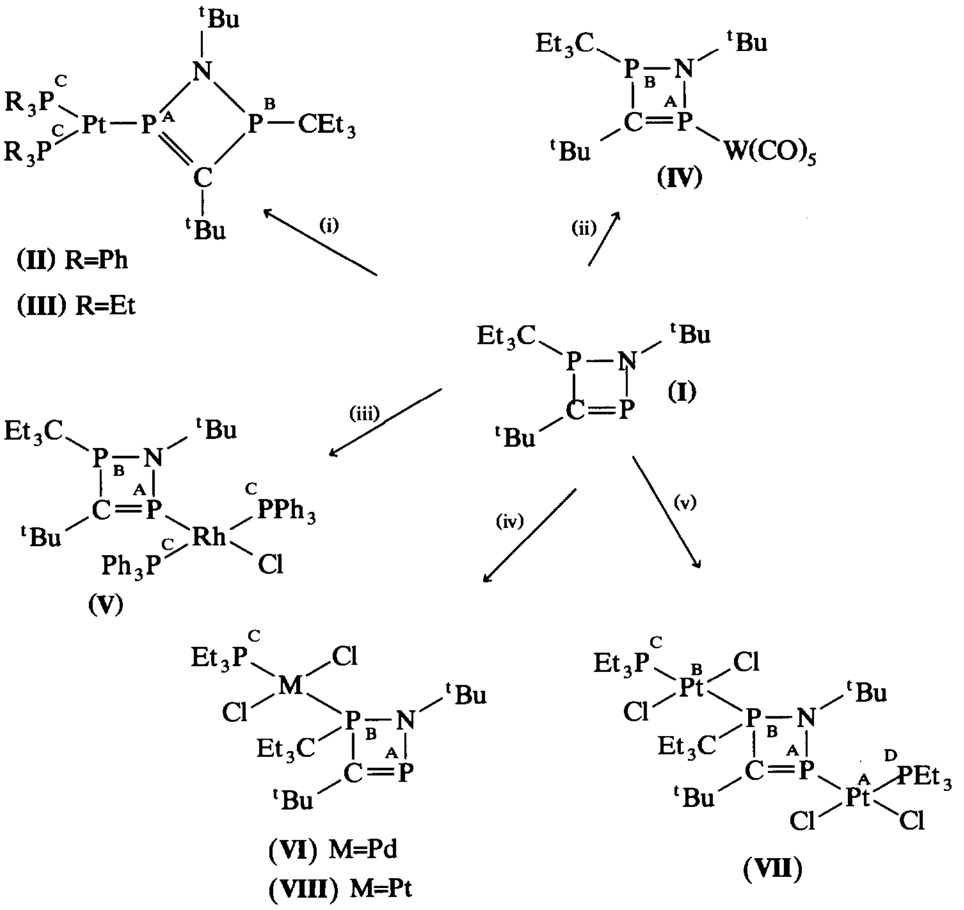


Scheme 1. (i): {Pt(PR$_3$)$_2$(C$_2$H$_4$)}, in toluene; (ii): [W(CO)$_5$THF], in THF; (iii): [RhCl(PPh$_3$)$_3$], in CH$_2$Cl$_2$; (iv): 1/2[M$_2$Cl$_4$(PEt$_3$)$_2$], in CH$_2$Cl$_2$; (v): [Pt$_2$Cl$_4$(PEt$_3$)$_2$], 1:1, in CH$_2$Cl$_2$.

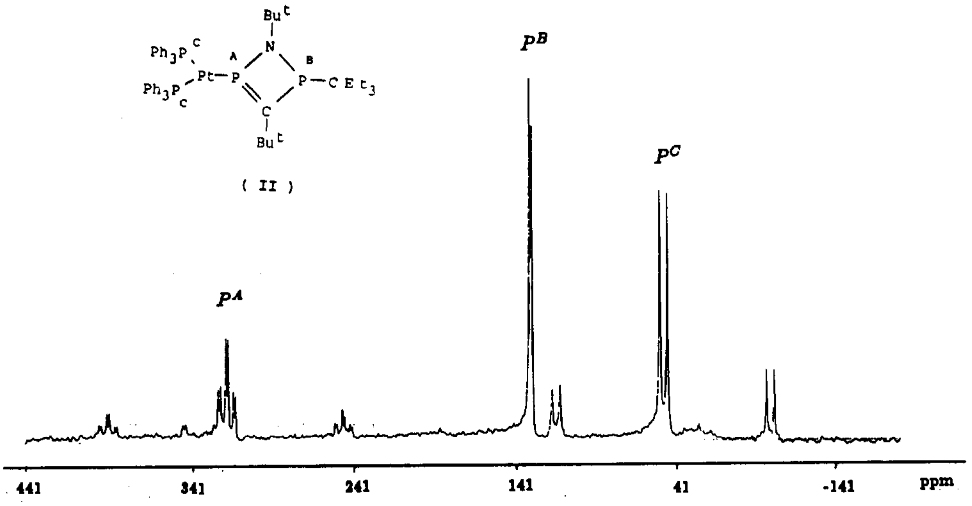
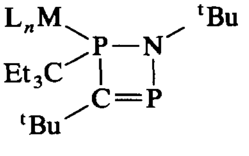
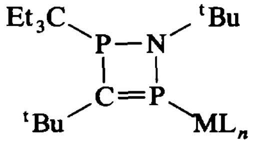


Fig. 1. ^{31}P-{^{1}H} NMR spectrum of [Pt(PPh$_3$)$_2$(Et$_3$C$\overline{\text{P(N}^t\text{Bu)P=C}}{}^t$Bu)] (II).

[ML$_n$] fragment, and particularly on the oxidation state of the transition metal atom.


(A)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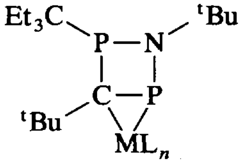

(C)

Thus, the softer P centre might interact more strongly with low oxidation state metal complexes.

2. Results and discussion

Treatment of the zerovalent platinum complexes [Pt(PR$_3$)$_2$(C$_2$H$_4$)] (R = Ph or Et) with I in toluene afforded the complexes [Pt(η^1-Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PPh$_3$)$_2$] (II) and [Pt(η^1-Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)$_2$] (III), respectively (see Scheme 1), in which the azadiphosphetine rings is η^1-ligated to platinum through the two-coordinate phosphorus atom.

The ^{31}P-{^{1}H} NMR data provided the strongest evidence for an η^1-bonded azadiphosphetine ring system in II and III. Complex II exhibits the pattern of lines corresponding to an [ABCX] spin system (A, B, C = ^{31}P, 100%; X = ^{195}Pt, 33.8%) (see Fig. 1). The two-coordinate phosphorus atom (P^A) exhibits a doublet of triplets with platinum satellites ($^1J_{\mathrm{PtP_A}}$ = 4683 Hz; $^2J_{\mathrm{P^AP^C}}$ = 152 Hz; and $^2J_{\mathrm{P^AP^B}}$ = 44 Hz), whereas the three-coordinate phosphorus atom (P^B) shows a simple doublet ($^2J_{\mathrm{P^AP^B}}$ = 44 Hz) without platinum satellites. The presence of a simple doublet resonance for the PPh$_3$ ligands ($^1J_{\mathrm{PtP^C}}$ = 4380 Hz) shows either that the plane of the azadiphosphetine ring system lies perpendicular to that containing Pt and the two PPh$_3$ ligands, or that there is rapid rotation around the Pt–P^A bond. The magnitude of the $^1J_{\mathrm{PtP^A}}$ (4683 Hz (II) and 4473 Hz (III)) is diagnostic of a coordination of the platinum through the lone-pair of the phosphorus nuclei [4]. Further confirmation of the proposed structure of II is provided by the ^{195}Pt-{^{1}H} NMR spectrum, which shows a doublet of triplets ($^1J_{\mathrm{PtP^A}}$ = 4684 Hz; $^1J_{\mathrm{PtP^C}}$ = 4383 Hz).

Treatment of I with the zerovalent tungsten complex [W(CO)$_5$THF] gives [W(CO)$_5$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)] (IV) (see Scheme 1), whose IR spectrum exhibits the expected four carbonyl stretching bands at 2100(m), 2060(w), 1990(m), and 1950(s) cm^{-1}, and these values are in accord with data for other complexes containing the [W(CO)$_5$] fragment [5,6]. An upfield shift of the ^{31}P resonance signal of P^A ($\Delta\delta_{\mathrm{P^A}}$ = −87.3 ppm) strongly suggests that it is coordinated to the tungsten atom. Additional evidence for the proposed structure comes from the observation of ^{183}W satellites around the

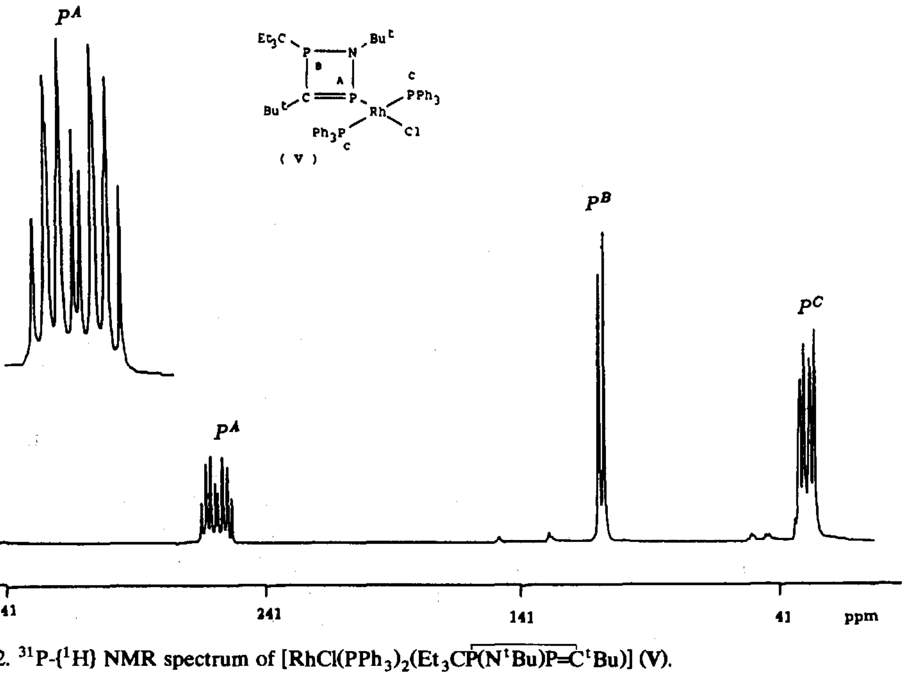


Fig. 2. ^{31}P-{^{1}H} NMR spectrum of [RhCl(PPh$_3$)$_2$(Et$_3$C$\overline{\mathrm{P(N^tBu)P{=}C}}$^{t}Bu)] (V).

resonance of P^A and the magnitude of the $^1J_{P^AW}$ coupling constant (254 Hz), which is typical for phosphane complexes (112–256 Hz) [4–6].

A similar η^1-bonded azadiphosphetine rhodium(I) complex [RhCl(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PPh$_3$)$_2$] (**V**) is obtained from the reaction of **I** with [RhCl(PPh$_3$)$_3$] (see Scheme 1). The ^{31}P-{^{1}H} NMR spectrum of **V** (Fig. 2) exhibits the pattern of lines corresponding to an [ABCX] spin system (A, B, C = ^{31}P, 100%; X = ^{103}Rh, 100%). The downfield resonance (260 ppm) is assigned to P^A, whereas the highfield signal (109.9 ppm) corresponds to P^B. The $^1J_{RhP^A}$ (210 Hz) is typical for one-bond coupling constants in square planar Rh$^{(I)}$-phosphane complexes, which usually lie in the range between 104 Hz and 217 Hz [4], again suggesting that it is the two-coordinate phosphorus, P^A, that preferentially ligates to the metal. The resonance corresponding to P^C consists of a doublet of doublets ($^1J_{RhP^C}$ = 136.8 Hz). Comparison between $^1J_{RhP^A}$ and $^1J_{RhP^C}$ coupling constants (210 and 136.8 Hz, respectively) provides further evidence for its geometry, since a phosphorus nucleus *trans* to a chloride gives a larger $^1J_{RhP}$ coupling constant than that *trans* to phosphorus [4].

In contrast to the above reactions, treatment of two equivalents of **I** with the dinuclear Pd$^{(II)}$ complex [Pd$_2$Cl$_4$(PEt$_3$)$_2$] in CH$_2$Cl$_2$ afforded a complex involving ligation of the three-coordinate phosphorus atom, *i.e.*, [PdCl$_2$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)] (**VI**) (see Scheme 1). A very simple ^{31}P-{^{1}H} NMR spectrum is observed for **VI**, consisting of a pattern of lines corresponding to an [ABC] spin system (A, B, C = ^{31}P, 100%). A downfield shift of the P^B resonance upon coordination ($\Delta\delta_{P^B}$ = 13.3 ppm), in addition to the absence of $^2J_{P^AP^B}$ and $^2J_{P^AP^C}$ coupling constants, rules out any coordination to the metal through the two-coordinate phosphorus atom P^A. Of particular interest is the magnitude of the $^2J_{P^BP^C}$ coupling constant (537 Hz), which suggests that P^B and P^C are mutually *trans* to each other in the square planar complex. Interestingly, $^2J_{P^AP^B}$ in **VI** is too small to be observed.

Similarly, treatment of **I** with the platinum(II) complex [Pt$_2$Cl$_4$(PEt$_3$)$_2$], in a 1:1 ratio, affords the dinuclear platinum(II) complex [Pt$_2$Cl$_4$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)$_2$] (**VII**), which shows that now *both* phosphorus atoms have become coordinated to the metals (see Scheme 1), presumably by a two stage process in which the first step is ligation *via* P^B.

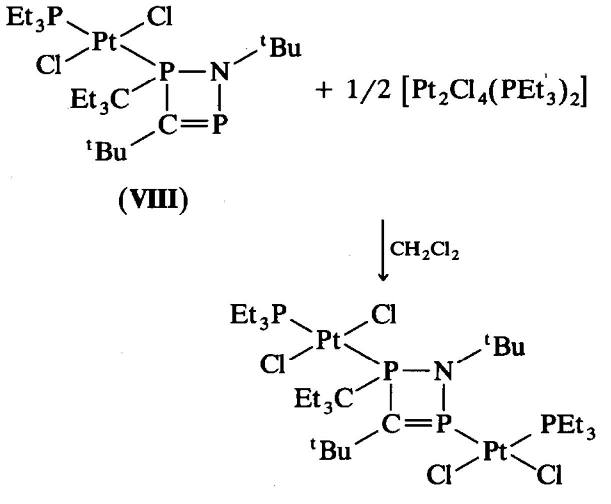
The ^{31}P-{^{1}H} NMR spectrum of **VII** provides useful structural information. It consists of an [ABCDXY] spin system (A, B, C, D, = ^{31}P, 100%; X, Y = ^{195}Pt, 33.8%). The magnitude of the $^2J_{P^BP^C}$ (468 Hz) and $^2J_{P^AP^D}$ (18 Hz) coupling constants clearly show that P^C lies *trans* to P^B, whereas P^D is *cis* to P^A; $^2J_{PP}$ couling constants of similar magnitude have been found in complexes of the type *trans*-[PtX$_2$(PR$_3$)(PR'$_3$)] or *cis*-[PtX$_2$(PR$_3$)(PR'$_3$)] [4,6–8], and some related coupling constant data are summarised in Table 1.

TABLE 1. $^2J_{PP}$ coupling constant (Hz) for some complexes of the type [PtX$_2$(PR$_3$)(PR'$_3$)]

Complex	$^2J_{P^AP^D}$ (*cis*)	$^2J_{P^BP^C}$ (*trans*)	Ref.
VII	18	468	this work
cis-[PtCl$_2$(MesP=CPh$_2$)(PEt$_3$)]	23	–	[7]
trans-[PtCl$_2$(MesP=CPh$_2$)(PEt$_3$)]	–	544	[7]
trans-[PtCl$_2$(PBu$_3$)(PEt$_3$)]	–	462	[8]
cis-[PtCl$_2$(PBu$_3$)(PEt$_3$)]	16	–	[8]
cis-[PtCl$_2$(PEt$_3$)$_2$]	17	–	[4]
cis-[PtCl$_2$(PEt$_3$)(PPh$_3$)]	17	–	[4]

It thus appears that the geometry around the coordinated azadiphosphetine rings is controlled by the steric hindrance around the phosphorus atoms P^A and P^B, since the more sterically demanding phosphorus nuclei P^B assumes a *trans* configuration. As would be expected, the one-bond Pt–P coupling constants for the phosphorus atoms *trans* to chloride are larger than those found for P atoms that are *trans* to another phosphorus [4,6–8] (*e.g.*, $^1J_{Pt^BP^B}$ = 2346 Hz; $^1J_{Pt^BP^C}$ = 2581 Hz; $^1J_{Pt^AP^A}$ = 4163 Hz; $^1J_{Pt^AP^D}$ = 3208 Hz). The ^{195}Pt-{^{1}H} NMR spectrum of [Pt$_2$Cl$_4$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)$_2$] (**VII**) confirmed the presence of two inequivalent platinum(II) nuclei (δ_{Pt^A} = −2483.6 and δ_{Pt^B} = −2233.6 ppm), and identical coupling parameters (within experimental error) for the J_{PtP} have been found (*e.g.*, $^1J_{Pt^AP^A}$ = 4196 Hz; $^1J_{Pt^AP^D}$ = 3201 Hz; $^3J_{Pt^AP^B}$ = 128 Hz; $^1J_{Pt^BP^B}$ = 2375 Hz; $^1J_{Pt^BP^C}$ = 2578 Hz; and $^3J_{Pt^BP^A}$ = 108 Hz).

The mononuclear platinum(II) complex [PtCl$_2$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)] (**VIII**) was obtained by treatment of two equivalents of **I** with [Pt$_2$Cl$_4$(PEt$_3$)$_2$] (see Scheme 1), indicating that coordination of the three-coordinate phosphorus P^B is preferred to that of the two-coordinate phosphorus P^A. Complex **VIII** has been characterised by ^{31}P-{^{1}H} NMR spectroscopy, three conformers were shown to be present, but could not be separated. The magnitudes of the $^2J_{P^BP^C}$ coupling constants (518, 526, and 526 Hz) found for each of the conformers suggest that (**VIII**) may have an structure analogous to that of the palladium(II) complex [PdCl$_2$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)] (**VI**). The $^1J_{PtP^B}$ and $^1J_{PtP^C}$ coupling constants are similar to those found for the dimeric platinum(II) complex [Pt$_2$Cl$_4$(Et$_3$CP(^{t}BuN)P=C^{t}Bu)(PEt$_3$)$_2$] (**VII**). It is interesting, however, that treatment of **VIII** with [Pt$_2$Cl$_4$(PEt$_3$)$_2$], in a 2:1 ratio, gives only one conformer of the known platinum(II) dimer complex **VII**, thus confirming that **VIII** is an intermediate for the formation of **VII**, *viz*.



(VIII)

(VII)

3. Conclusions

The clearly differing ligating behaviour of the two types of phosphorus in the azadiphosphospetine ring system **I** can, in the absence of any overriding steric effects, be understood in terms of the preference of the softer metal centre (low oxidation state) for interaction with the phosphorus lone-pair orbital having the greatest degree of s-character. This is in line with known differences between hard NR_3 and soft PR_3 ligands, for which the smaller bond angles at phosphorus imply a larger s-character in the P lone-pair orbital. PF_3 can be regarded as the softest of the PX_3 ligands because the electronegative fluorine substituents increase the character in the P lone-pair orbital [9]. Accordingly, PF_3 and its derivatives form a particularly wide range of stable complexes with transition metals in low oxidation states, *i.e.*, with soft metal centres. It is important to note, however, that in the PF_3 transition metal complexes there is also significant interaction between filled metal d-orbitals and σ^*-antibonding P–F orbitals [10].

Interestingly, no evidence was found during our studies for the formation of any complex of the type **C**, *i.e.*, containing the azadiphosphetine ring system bonded in an η^2-fashion through the P=C bond. However, formation of an η^2-azadiphosphetine platinum(0) complex might possibly be favoured if a less sterically demanding PR_3 ligand were used. It is well known from studies on certain phosphaalkene platinum(0) complexes that there is only a small energy difference between η^1- and η^2-ligating modes and, for example, an *inter*-conversion between η^1- and η^2-ligation in $[Pt(PPH_3)_2(Ph_2C{=}PMes)]$ occurs with a simple change of phase, as evidenced by ^{31}P-{^1H} NMR spectroscopic studies in solution and solid state, and a single crystal X-ray diffraction determination [11,12].

4. Experimental details

4.1. General procedures

All the reactions were carried out by standard procedures for manipulation of air-sensitive materials. All the glassware employed was flame-dried *in vacuo*, and solvents were dried, freshly distilled under a blanket of dinitrogen, and degassed prior to use.

Infrared spectra were recorded as Nujol mulls, or as KBr discs using a Perkin-Elmer Model 1720FT-IR spectrometer, calibrated relative to polystyrene.

Carbon, hydrogen, and nitrogen analyses were performed by the University of Sussex elemental analysis service.

NMR spectra were recorded on Bruker WP80SY (^{31}P) or WM360 (^{31}P, ^{195}Pt, ^1H) spectrometers operating in FT mode at 32.4, 145.8, 77.2, and 360.1 MHz, respectively. Chemical shifts are quoted relative to H_3PO_4 (^{31}P), K_2PtCl_4 (^{195}Pt), and $SiMe_4$ (^1H) as internal standard.

4.2. Synthesis of $[Pt(\eta^1\text{-}Et_3CP(^tBuN)P{=}C^tBu)(PPh_3)_2]$ (II)

A solution of **I** (1.78 mg, 0.6 mmol) in toluene (1 ml) was added dropwise to a solution of $[Pt(PPh_3)_2(C_2H_4)]$ (450 mg, 0.6 mmol) in toluene (5 ml). The mixture, which became red within minutes, was stirred for 24 h. Removal of the solvent gave [2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^4]-bis-(triphenylphosphane)platinum(0) (590 mg, 96%) as a red oil. ^{31}P-{^1H} NMR data (32.4 MHz, toluene-d_8, 25°C) δ_{P^A} 318.9 ppm; δ_{P^B} 131.6 ppm; δ_{P^C} 48.6 ppm; $^1J_{PtP^A} = 4683$ Hz; $^1J_{PtP^C} = 4380$ Hz; $^2J_{P^AP^B} = 44$ Hz; $^2J_{P^AP^C} = 152$ Hz. ^{195}Pt-{^1H} NMR data (77.2 MHz, toluene-d_8, 25°C) δ_{Pt} -3047.7 ppm; $^1J_{PtP^C} = 4383$ Hz; $^1J_{PtP^A} = 4684$ Hz.

4.3. Synthesis of $[Pt(\eta^1\text{-}Et_3CP(^tBuN)P{=}C^tBu)(PEt_3)_2]$ (III)

A solution of $Li[B(C_2H_5)_3H]$ (9.4×10^{-3} mg) in THF (1 ml) was added during 5 min tube to a solution of $[PtCl_2(PEt_3)_2]$ (100 mg, 0.2 mmol) contained in an NMR tube under an atmosphere of ethylene. A solution of **I** (60 mg, 0.2 mmol) in THF (0.2 ml) was then added, and formation of [2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^4]-bis-(triethylphosphane)platinum(0) was confirmed by the ^{31}P-{^1H} NMR spectrum. ^{31}P-{^1H} NMR data (32.4 MHz, THF, 25°C) δ_{P^A} 332.5 ppm; δ_{P^B} 130.3 ppm; δ_{P^C} 38.7 ppm; $^2J_{P^AP^B} = 44$ Hz; $^2J_{P^AP^C} = 151$ Hz; $^1J_{PtP^A} = 4473$ Hz; $^1J_{PtP^C} = 4146$ Hz.

4.4. Synthesis of $[W(CO)_5(Et_3CP(^{t}BuN)P{=}C^{t}Bu)$ (IV)

A solution of $[W(CO)_6]$ (250 mg, 0.7 mmol) in THF (10 ml) was irradiated with UV light for 4 h. A solution of **I** (178 mg, 0.6 mmol) in THF (1 ml) was then added and the mixture stirred for 24 h to give, after removal of the solvent, (pentacarbonyl-κ^5 : C)-[2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^4]-tungsten(0) (380 mg, 95%) as an oil, identified from ^{31}P-$\{^1H\}$ NMR and IR spectroscopic data. Infrared spectrum (Nujol) $\nu_{CO} = 2100$(m); 2060(w); 1990(m); 1950(s) cm^{-1}. ^{31}P-$\{^1H\}$ NMR data (32.4 MHz, THF, 25°C) δ_{P^A} 257.6 ppm; δ_{P^B} 141.0 ppm; $^1J_{P^AW} = 254$ Hz; $^2J_{P^AP^B} = 57$ Hz.

4.5. Synthesis of $[RhCl(Et_3CP(^{t}BuN)P{=}C^{t}Bu)(PPh_3)_2]$ (V)

A solution of $[RhCl(PPh_3)_3]$ (547 mg, 0.6 mmol) in CH_2Cl_2 was added to one of **I** (178 mg, 0.6 mmol) (CH_2Cl_2, 1 ml) and the mixtures was stirred for 24 h. Removal of the solvent and subsequent washing with pretroleum ether 60–80°C afforded [SP-4-2]-chloro-[2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^4]-bis-(triphenylphosphane)-rhodium(I) (400 mg, 70%) as a yellow solid. (Found: C, 65.13%; H, 6.33%; N, 1.29% $C_{52}H_{63}P_4NRhCl$ requires C, 64.8%; H, 6.5%; N, 1.5%). ^{31}P-$\{^1H]$ NMR data (32.4 MHz, CD_2-Cl_2, 25°C) δ_{P^A} 260.3 ppm; δ_{P^B} 109.8 ppm; δ_{P^C} 30.5 ppm; $^2J_{P^AP^B} = 63.5$ Hz; $^1J_{P^AC} = 122\ 1$ Hz; $^1J_{RhP^A} = 210$ Hz; $^1J_{RhP^C} = 136.8$ Hz. ^1H NMR data (360.1 MHz, $CdCl_3$, 25°C) δ 7.25–7.76 (m, 30H, 6Ph); δ 0.82–1.83 (m, 33H, 2^{t}Bu, 3Et).

4.6. Synthesis of $[PdCl_2(Et_3CP(^{t}BuN)P{=}C^{t}Bu)(PEt_3)]$ (VI)

To a solution of **I** (178 mg, 0.6 mmol) in CH_2Cl_2 (1 ml) was added one of $[Pd_2Cl_4(PEt_3)_2]$ (175 mg, 0.3 mmol) (CH_2Cl_2, 1 ml) and the mixture was stirred for 24 h. Removal of the solvent and subsequent washing with petroleum ether 60–80°C gave the pale yellow solid [SP-4-1]-dichloro-[2-(1,1′-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^2]-bis-(triethylphosphane)palladium(II) (0.32 mg, 90%) (Found: C, 44.32%; H, 8.45%; N, 2.70%. $C_{22}H_{48}P_3NPdCl_2$ requires C, 44.3%; H, 8.1%; N, 2.4%). ^{31}P-$\{^1H\}$ NMR spectroscopic data (32.4 MHz, CD_2Cl_2, 25°C) δ_{P^A} 339.8 ppm; δ_{P^B} 144.5 ppm; δ_{P^C} 29.8 ppm; $^2J_{P^AP^B}$ *ca.* 0 Hz; $^2J_{P^BP^C}$ 537.1 Hz; ^1H NMR data (360.1 MHz, $CDCl_3$, 25°C) δ 3.74–3.78 (m, 12H, $6CH_2$); δ 3.05–3.13 (m, 18H, $6CH_3$); δ 1.99 (s, 18H, 2^{t}Bu).

4.7. Synthesis of $[Pt_2Cl_4(Et_3CP(^{t}BuN)P{=}C^{t}Bu)$-$(PEt_3)_2]$ (VII)

A solution of $[Pt_2Cl_4(PEt_3)_2]$ (230 mg, 0.3 mmol) in CH_2Cl_2 (1 ml) was added to one of **I** (89 mg, 0.3 mmol) (CH_2Cl_2, 1 ml) and the mixture was stirred for 24 h. Removal of the solvent and washing of the resulting oil with petroleum ether 60–80°C gave the yellow solid 1-[SP-4-1]-2-[SP-4-2]-tetrachloro-[μ-{2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-1κ : P^2 : 2κ : P^4}]-bis-(triethylphosphane)diplatinum(II) (250 mg, 81%). (Found: C, 31.78%; H, 6.13%; N, 1.52%. $C_{28}H_{63}P_4Pt_2Cl_4$ requires C, 31.6%; H, 5.9%; N, 1.32%). ^{31}P-$\{^1H\}$ NMR data (145.8 MHz, CD_2Cl_2, 25°C) δ_{P^A} 204 ppm; δ_{P^B} 122.6 ppm; δ_{P^C} 14.5 ppm; δ_{P^D} 9.6 pmm; $^1J_{Pt^AP^A} = 4163$ Hz; $^3J_{Pt^AP^B} = 127$ Hz; $^1J_{Pt^AP^D} = 3208$ Hz; $^1J_{Pt^BP^B} = 2346$ Hz; $^1J_{Pt^BP^C} = 2581$ Hz; $^2J_{P^AP^B} = 28$ Hz; $^2J_{P^AP^B} = 18$ Hz; $^2J_{P^BP^C} = 468$ Hz; $^4J_{P^CP^A} = 18$ Hz. ^{195}Pt-$\{^1H\}$ NMR data (77.2 MHz, CD_2Cl_2, 25°C) δ_{Pt^A} -2483.6 ppm; δ_{Pt} -2233.6 ppm; $^1J_{Pt^AP^A} = 4196$ Hz; $^1J_{Pt^AP^D} = 3201$ Hz; $^3J_{Pt^AP^B} = 128$ Hz; $^1J_{Pt^BP^B} = 2375$ Hz; $^1J_{Pt^BP^C} = 2578$ Hz; $^3J_{Pt^BP^A} = 108$ Hz. ^1H NMR data (360.1 MHz, CD_2Cl_2, 25°C) δ 1.17–2.25 (m, 45H, 9Et); δ 1.11 (bs, 18H, 2^{t}Bu).

4.8. Synthesis of $[PtCl_2(Et_3CP(^{t}BuN)P{=}C^{t}Bu)(Et_3)]$ (VIII)

The procedures outlined above were used for $[Pt_2Cl_4(PEt_3)_2]$ (230 mg, 0.3 mmol) and **I** (178 mg, 0.6 mmol) in CH_2Cl_2 (2 ml), and gave three conformers of [SP-4-1]-dichloro-[2-(1,1-diethylpropyl)-1,3-di-t-butyl-Δ^3-1,2,4-azadiphosphetine-κ : P^2]-(triethylphosphane)-platinum(II) (353 mg, 85%) identified on the basis of their ^{31}P-$\{^1H\}$ NMR spectra. Complex **VIII** was not isolated, but further addition of $[Pt_2Cl_4(PEt_3)_2]$ (230 mg, 0.3 mmol) was show to give the dimeric species **VII**. ^{31}P-$\{^1H\}$ NMR data (145.8 MHz, CD_2Cl_2, 25°C) (1): δ_{P^A} 343 ppm; δ_{P^B} 113.2 ppm; δ_{P^C} 7.4 ppm; $^1J_{PtP^B} = 3073$ Hz; $^1J_{PtP^C} = 2227$ Hz; $^2J_{P^AP^B} =$ *ca.* 0 Hz; $^2J_{P^BP^C} = 518$ Hz; (2): δ_{P^A} 343 ppm; δ_{P^B} 124.8 ppm; δ_{P^C} 7.2; $^1J_{PtP^B} = 3039$ Hz; $^1J_{PtP^C} = 2220$ Hz; $^2J_{P^AP^B} =$ *ca.* 0 Hz; $^2J_{P^BP^C} = 526$ Hz; (3) δ_{P^A} 343 ppm; δ_{P^B} 138.1 ppm; δ_{P^C} 61.1 ppm; $^1J_{PtP^B} = 2314$ Hz; $^1J_{PtP^C} = 2954$ Hz; $^2J_{P^BP^C} = 526$ Hz.

Acknowledgements

We thank the SERC for continuing support for the work, the Brazilian Government (CNPq) for financial support (for R.M.M. and B.F.T.P.), Dr. A.G. Avent for help with the NMR spectroscopy, and Johnson Matthey plc for the loan of some platinum salts.

References

1 J.F. Nixon, *Chem. Rev.*, *88* (1988) 1327; M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, *27* (1988) 1484; R. Appel and F. Knoll, *Adv. Inorg. Chem. Radiochem.*, *33* (1989) 259; R. Appel, in M. Regitz and O.J. Scherer (eds.), *Multiple Bonds and Low*

Coordination in Phosphorus Chemistry, Thieme Verlag, Stuttgart, 1990, p. 157; M. Regitz, *Chem. Rev., 90* (1990) 191.

2 E. Niecke and D. Gudat, *Angew. Chem., Int. Ed. Engl., 30* (1991) 217; E. Niecke, in M. Regitz and O.J. Scherer (eds.), *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, Thieme Verlag, Stuttgart, 1990, p. 293; J. Hein, E. Niecke, M.F. Meidine, B.F. Trigo Passos and J.F. Nixon, *J. Chem. Soc., Chem. Commun.*, (1991) 41.

3 E. Niecke and D. Barion, *Tetrahedron Lett., 30* (1989) 459.

4 J.F. Nixon and A. Pidcock, *Ann. Rev. NMR Spectrosc., 2* (1969) 345; J.G. Verkade and J.A. Mosbo, in J.G. Verkade and L.D. Quin (eds.), *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, Weinheim, 1987, p. 425.

5 L.K. Peterson and S. Huang, *Inorg. Chim. Acta, 203* (1993) 87.

6 B. Deschamps, F. Mathey, J. Fischer and J.H. Nelson, *Inorg. Chem., 23* (1984) 3455; R. Bartsch, A. Gelessus, P.B. Hitchock and J.F. Nixon, *J. Organomet. Chem., 430* (1992) C10; C.C. Santini, J. Fischer, F. Mathey and A. Mitschler, *J. Am. Chem. Soc., 102* (1980) 5809.

7 H.W. Kroto, J.F. Nixon, M.J. Taylor, A.A. Frew and K.W. Muir, *Polyhedron, 1* (1982) 89.

8 F.H. Allen and S.N. Sze, *J. Chem. Soc. (A)*, (1971) 2054.

9 H.A. Bent, *J. Chem. Ed., 37* (1960) 616; H.A. Bent, *J. Chem. Phys., 33* (1960) 1259; H.A. Bent, *Chem. Rev., 61* (1961) 275.

10 J.F. Nixon, *Adv. Inorg. Chem. Radiochem., 29* (1985) 41.

11 T.A. van der Knaap, F. Bickelhaupt, J.G. Kraaykamp, G. van Koten, J.P.C. Bernards, H.T. Edzes, W.S. Veeman, E. de Boer and E.J. Baerends, *Organometallics, 3* (1984) 1804.

12 H.W. Kroto, S.I. Klein, M.F. Meidine, J.F. Nixon, R.K. Harris, K.J. Packer and P. Reams, *J. Organomet. Chem., 280* (1985) 281.