An η² Transition State for the Insertion of M(PR₃)₂ Fragments (M = Pd or Pt) into the Phosphorus–Carbon Bonds of Pentacarbonyl(phosphirane)tungsten Complexes†

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The reaction of (*E*)- and (*Z*)-[W(CO)₅(PPhCHPhCHPh)] complexes with [M(PR₃)₂(C₂H₄)] [M = Pd, (PR₃)₂ = dppe (Ph₂PCH₂CH₂PPh₂); M = Pt, PR₃ = PPh₃] has been studied and the following products [which result from insertion of the M(PR₃)₂ fragment into the phosphirane ring] have been fully characterised by NMR spectroscopy: (2*R**,3*S**,4*S**)-(±)-, (2*R**,3*R**,4*R**)-(±)- and (2*R**,3*S**,-4*R**)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅]; (2*S**,3*S**,4*S**)-(±)-, (2*S**3*R**4*R**)-(±)- and (2*S**,-3*S**,4*R**)-(±)-[(Ph₃P)₂Pt(CHPhCHPhPPh)W(CO)₅]; and *trans*-(2*S**,3*S**,4*R**)-(±)-[(Ph₃P)(OC)Pt-(CHPhCHPhPPh)W(CO)₅]. The crystal and molecular structures of (*Z*)-[W(CO)₅(PPhCHPhCHPh)], (2*R**,3*S**,4*R**)-(±)- and (2*R**,3*S**,4*S**)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅] have been determined. The configurations of the products are interpreted in terms of a transition state in which a P–C bond is η²-co-ordinated to the M(PR₃)₂ fragment.

Because of the synthetic importance of phosphane-supported organometallic compounds, the preparation of phosphane ligands which are resistant to decomposition by reactive transition metals is still an area of active academic study.[1,2] The most appropriate way to evaluate these decomposition processes is over protracted periods under the conditions of high temperature and pressure which may be encountered in the industrial environment, but such studies are complicated by side-reactions and the tendency of the first-formed products to undergo further chemistry.[3] We were therefore interested to develop a simpler model for the problem, through the generation of phosphane ligands which incorporate artificially reactive P–C bonds, and a study of their interactions with metal centres. Such an approach has been used successfully to model the metal-induced intermolecular C–C bond-cleavage reaction, where cyclopropane and its derivatives are very useful and reactive substrates, because of their ring strain.[4] It therefore seemed likely that phosphorus analogues of cyclopropane and cyclopropene (phosphirane and phosphirene respectively) would provide interesting information concerning the co-ordination chemistry of the phosphorus–carbon bond.

In recent papers we have demonstrated the mild activation of the free and complexed phosphirene, PPhCPh=CPh, by insertion of d¹⁰ nickel, palladium, and platinum[5–7] and d⁸ rhodium centres[8] into its P–C ring bond, and we now describe the reactivity of the analogous P-co-ordinated phosphirane complexes (*E*)- and (*Z*)-[W(CO)₅(PPhCHPhCHPh)] **1** and **2** towards M(PR₃)₂ centres (M = Pd or Pt). These reactions are of particular interest because the phosphirane complexes have a well defined stereochemistry, which permits an evaluation of the mechanism of the phosphorus–carbon bond-cleavage reaction.

Reactions of M(PR₃)₂ (M = Ni, Pd or Pt) fragments with three-membered ring systems which incorporate first-row
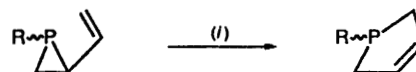
Scheme 1 (*i*) [Ni(cod)₂] or [Pd(C₃H₅)₂]

elements have been studied extensively. Ring-opening reactions tend to predominate and thus tetracyano- and tricyano-oxiranes undergo insertion of Pt(PPh₃)₂ into the carbon–oxygen bond,[9,10] 1,1,2,2-tetracyanocyclopropane also inserts Pt-(PPh₃)₂ fragments,[11] and [Pd(PPh₃)₄]-mediated insertion of CO into functionalised aziranes probably proceeds *via* Pd⁰-promoted C–N cleavage.[12,13] In contrast, the less-activated 1,2-dicyanocyclopropane is unchanged on treatment with [Pt(PPh₃)₂(C₂H₄)].[14] A ring-closure reaction, which involves formation of 2,2-dimethyloxirane from [Ni(PPh₃)₂(OCMe₂-CH₂)], demonstrates that these metal-insertion reactions may be reversible.[15]

Fewer reports of the interaction of M(PR₃)₂ fragments with rings containing heavier congeners have appeared, but thiirane is not apparently cleaved by [Pt(PPh₃)₂(C₂H₄)].[16] The report that CH₂CH₂SO does not undergo C–S bond cleavage upon reaction with [Pt(PPh₃)₂(C₂H₄)][16] is not established, in our view.[17]

The chemistry of phosphiranes is well developed,[18,19] but reactions at transition-metal centres[20–22] have received little attention. Richter[23–25] has reported a symmetry-forbidden isomerisation of *C*-vinylphosphiranes to phosphol-3-enes (Scheme 1) but no evidence for phosphametallacyclobutane intermediates was presented, and the reaction may conceivably proceed *via* the intermediacy of free radicals stabilised by the vinyl group.[26] Significantly, 2-ethylphosphiranes R PCH₂CHEt (R = Buᵗ, C₆H₁₁, Ph or menthyl) are unchanged by treatment with [Ni(cod)₂] (cod = cycloocta-1,5-diene).[25]

Electronic Structures and Syntheses of Phosphiranes.—Before considering the reactivity of co-ordinated phosphiranes in detail, it is instructive to consider the electronic structures of the

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Table 1 Bond distances (Å) and angles (°) for complex **2** with estimated standard deviations (e.s.d.s) in the least significant figures in parentheses

W–P	2.493(1)	C(9)–C(10)	1.389(8)	C(1)–C(2)	1.532(7)	C(17)–C(18)	1.35(1)
W–C(21)	2.034(7)	C(9)–C(14)	1.395(7)	C(1)–C(9)	1.485(7)	C(18)–C(19)	1.38(1)
W–C(22)	2.034(7)	C(10)–C(11)	1.392(8)	C(2)–C(15)	1.478(7)	C(19)–C(20)	1.40(1)
W–C(23)	2.026(6)	C(11)–C(12)	1.358(9)	C(3)–C(4)	1.379(8)	C(21)–O(21)	1.136(9)
W–C(24)	2.031(8)	C(12)–C(13)	1.390(9)	C(3)–C(8)	1.389(8)	C(22)–O(22)	1.15(1)
W–C(25)	1.989(8)	C(13)–C(14)	1.389(8)	C(4)–C(5)	1.38(1)	C(23)–O(23)	1.154(8)
P–C(1)	1.858(6)	C(15)–C(16)	1.387(9)	C(5)–C(6)	1.36(1)	C(24)–O(24)	1.14(1)
P–C(2)	1.827(5)	C(15)–C(20)	1.377(9)	C(6)–C(7)	1.36(1)	C(25)–O(25)	1.15(1)
P–C(3)	1.822(5)	C(16)–C(17)	1.393(9)	C(7)–C(8)	1.392(9)		
P–W–C(21)	95.7(2)	P–C(3)–C(8)	120.7(4)	C(24)–W–C(25)	88.2(3)	C(9)–C(14)–C(13)	121.0(5)
P–W–C(22)	87.6(2)	C(4)–C(3)–C(8)	118.6(5)	W–P–C(1)	127.7(2)	C(2)–C(15)–C(16)	118.9(5)
P–W–C(23)	89.1(2)	C(3)–C(4)–C(5)	120.7(6)	W–P–C(2)	134.5(2)	C(2)–C(15)–C(20)	121.1(5)
P–W–C(24)	89.6(2)	C(4)–C(5)–C(6)	120.4(6)	W–P–C(3)	118.5(2)	C(16)–C(15)–C(20)	119.3(5)
P–W–C(25)	177.4(2)	C(5)–C(6)–C(7)	120.3(6)	C(1)–P–C(2)	49.1(2)	C(15)–C(16)–C(17)	120.0(6)
C(21)–W–C(22)	90.8(3)	C(6)–C(7)–C(8)	120.2(6)	C(1)–P–C(3)	105.8(2)	C(16)–C(17)–C(18)	120.4(7)
C(21)–W–C(23)	93.1(3)	C(3)–C(8)–C(7)	119.8(6)	C(2)–P–C(3)	101.8(2)	C(17)–C(18)–C(19)	120.7(7)
C(21)–W–C(24)	174.7(3)	C(1)–C(9)–C(10)	118.0(5)	P–C(1)–C(2)	64.4(3)	C(18)–C(19)–C(20)	119.3(8)
C(21)–W–C(25)	86.5(3)	C(1)–C(9)–C(14)	124.7(5)	P–C(1)–C(9)	120.0(4)	C(15)–C(20)–C(19)	120.2(7)
C(22)–W–C(23)	175.0(3)	C(10)–C(9)–C(14)	117.3(5)	C(2)–C(1)–C(9)	123.8(5)	W–C(21)–O(21)	175.3(7)
C(22)–W–C(24)	90.0(3)	C(9)–C(10)–C(11)	121.7(5)	P–C(2)–C(1)	66.5(3)	W–C(22)–O(22)	178.4(7)
C(22)–W–C(25)	93.8(3)	C(10)–C(11)–C(12)	120.1(6)	P–C(2)–C(15)	128.9(4)	W–C(23)–O(23)	174.7(6)
C(23)–W–C(24)	86.3(3)	C(11)–C(12)–C(13)	119.9(6)	C(1)–C(2)–C(15)	127.4(5)	W–C(24)–O(24)	177.2(6)
C(23)–W–C(25)	89.4(3)	C(12)–C(13)–C(14)	120.0(6)	P–C(3)–C(4)	120.7(4)	W–C(25)–O(25)	178.1(8)
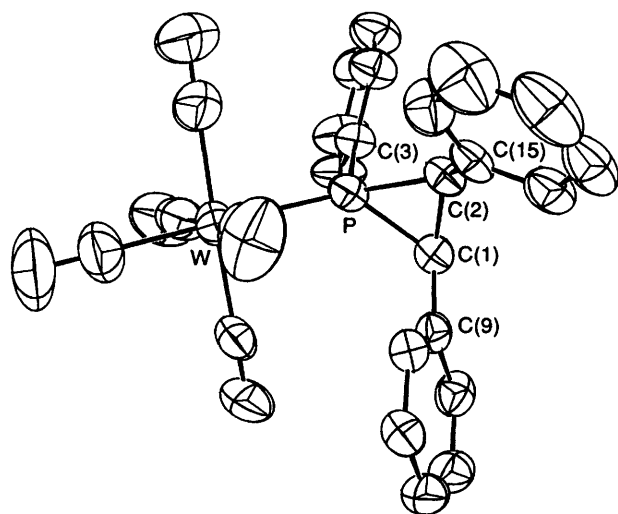
Fig. 1 The molecular structure of (Z)-[W(CO)₅(PPhCHPhCHPh)] **2**

parent compounds. No molecular orbital calculations or photoelectron spectroscopy (PES) studies of P-co-ordinated phosphiranes are available, but useful data relating to free phosphiranes exist. Microwave-determined geometries of phosphirane HPCH₂CH₂ and its derivatives[27] have been used as the basis for semiempirical calculations, which compare the photoelectron spectra of phosphirane, oxirane, azirane, and thiirane.[28] The phosphirane highest occupied molecular orbital (HOMO) (−9.75 eV) involves a lone-pair hybrid of high s character, and the antisymmetrical P–C σ-bonding hybrid also lies at high energy (−10.20 eV). Recent STO 4.31G* and 6.31G* calculations reproduce the microwave and PES data for HPCH₂CH₂, and identify the low-lying P–C σ* combination (5.19 eV) as the lowest unoccupied molecular orbital (LUMO).[29,30] Phosphirane has a large dipole moment [1.12 D (ca. 3.73 × 10⁻³⁰ Cm)] and relatively polar P–C bonds (Q_P = +0.207, Q_C = −0.478),[27] which result from a strong repulsion of electrons in the P–C bonds close to phosphorus, induced by the small C–P–C angle (47.4°). It is noteworthy that the

calculated frontier-orbital orderings of phosphirane[29] and phosphirene[31] are comparable, which suggests parallel reactivities for the two ring systems.

The P-co-ordinated phosphiranes are accessible either by direct routes,[32,33] or through co-ordination of W(CO)₅ to free phosphiranes.[19] Olefin cyclopropanation by naked phosphinidenes is not a viable synthetic method, because of the low electronegativity and low reactivity of the R–P triplet ground state.[19] On the other hand, the singlet complex [W(CO)₅(=PPh)] leads directly to P-co-ordinated phosphiranes *via* a stereospecific [2 + 1] cycloaddition, in which the configuration of the alkene is retained.[32,34] This procedure is suited to stereochemical studies since pure (E)- and (Z)-phosphiranes are produced, and the complexes used in this study were therefore prepared from [W(CO)₅(=PPh)] and *trans*-or *cis*-stilbene, respectively.[32] Their purity was confirmed by ³¹P-{¹H} NMR spectroscopy (signal-to-noise ratio ⩾ 2⁸ : 1) prior to use.

Any meaningful analysis of the insertion reaction clearly must depend on the establishment of the configurations of the starting complexes. The complex (E)-[W(CO)₅(PPhCHPhCHPh)] **1** exists as a single isomer and therefore requires no structural clarification, but the stereochemistry of the (Z) isomer **2** is potentially ambiguous. An X-ray diffraction study, carried out on a single crystal taken from the bulk sample of **2**, established the configuration shown in Fig. 1; relevant bond lengths and angles are in Table 1, and atomic coordinates in Table 2.

Results and Discussion

Generation and Molecular Structures of (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅] **3** *and* (2R*, 3S*, 4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅]·0.5CHCl₃**5**.†—The rapid reaction of (E)-[W(CO)₅(PPhCHPhCHPh)] **1** with [Pd(dppe)(C₂H₄)] (dppe = Ph₂PCH₂CH₂PPh₂) occurred below room temperature and yielded two new metallacycles, **3** and **4** (relative yields of 97:3, as monitored by ³¹P-{¹H} NMR

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† The stereochemical description of the metallacycles described here follows a recent Chemical Abstracts convention.[35] It should be noted that all products are racemates.

spectroscopy). The major component was fully structurally characterised by a single-crystal X-ray diffraction study, but the minor isomer was not isolated. The corresponding reaction of [Pd(dppe)(C$_2$H$_4$)] with (Z)-[W(CO)$_5$(PPhCHPhCHPh)] 2 more slowly yielded a single, orange, air-stable crystalline product, 5, which was shown to be neither 3 nor 4, and whose metallacyclic structure was also determined by a single-crystal

X-ray diffraction study. The molecular structures of 3 and 5 are shown in Fig. 2, and relevant bond lengths and angles are listed in Tables 3 and 5 respectively, and atomic coordinates in Tables 4 and 6.

The crystallographic studies confirm that insertion of Pd(dppe) into the (E)- and (Z)-phosphirane complexes occurs with retention of configuration in each case. The principal difference between the resulting puckered products concerns the configuration at C(7) (Fig. 2). In (2R*,3S*,4S*)-(±)-[(dppe)-Pd(CHPhCHPhPPh)W(CO)$_5$] 3 the aryl group is equatorially disposed above P(1), C(6) and C(7), whereas for (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$] 5 it lies axially and below the P(1)C(6)C(7) plane, where its interaction with the W(CO)$_5$ centre causes severe distortions of the palladium co-ordination sphere. This overcrowding permits a much smaller W–P(1)–Pd angle for 3 [115.8(1)°] than for 5 [133.04(9)°], whose value is comparable with the formally sp^2-hybridised phosphorus donors in [Pd(dppe){(OC)$_5$W(PhP=PPh)W-(CO)$_5$}] [129.8(2), 131.9(2)°].[36] The W–P(1) bond in 5 [2.589(2) Å] is also longer, and the Pd–P(1) length [2.366(2) Å] greater than found in 3 [2.556(3) and 2.320(4) Å, respectively]. The short Pd · · · C(14) separation (approximately 2.74 Å) in 5 and enlarged P(1)–Pd–C(7) angle over 3 [71.5(2) and 68.9(4)°, respectively] offer further proof of steric hindrance. The folds along P(1)–C(6) axes (32.2° in 3, 30.4° in 5) are large for metallacyclobutanes (typically 0–30°),[37] but small for η^3-oxodimethylenemethyl complexes (43–52°),[38,39] and preclude Pd–C(6) transannular interactions.

Interaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] *with* (E)- *and* (Z)-[W(CO)$_5$(PPhCHPhCHPh)].—The results above suggested that insertions of M(PR$_3$)$_2$ fragments into phosphirane complexes give mutually exclusive products; however, small amounts of impurities present in solutions of Pd(dppe) fragments made it difficult to evaluate the reaction pathway fully. In order to provide better defined conditions, the reactions of 1 and 2 with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] were examined.

Treatment of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with a tetrahydrofuran (thf) solution of (E)-[W(CO)$_5$(PPhCHPhCHPh)] 1 at 304 K yielded an 11:1 mixture of two isomers of [(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]. The major product was formul-

Table 2 Positional parameters and their e.s.d.s for complex 2

Atom	x	y	z
W	0.968 54(3)	0.573 68(1)	0.720 06(2)
P	1.190 5(2)	0.634 31(6)	0.794 8(1)
C(1)	1.209 9(6)	0.712 6(2)	0.783 6(5)
C(2)	1.341 7(6)	0.678 0(2)	0.730 5(5)
C(3)	1.288 2(6)	0.615 1(2)	0.929 0(5)
C(4)	1.433 5(7)	0.588 2(3)	0.932 1(5)
C(5)	1.505 5(8)	0.572 3(3)	1.033 4(6)
C(6)	1.432 0(9)	0.581 2(3)	1.131 7(6)
C(7)	1.287 7(9)	0.607 3(4)	1.131 4(6)
C(8)	1.213 9(7)	0.624 3(3)	1.030 1(5)
C(9)	1.089 3(6)	0.745 6(2)	0.717 2(5)
C(10)	1.020 5(6)	0.791 9(3)	0.768 8(5)
C(11)	0.898 6(7)	0.822 8(3)	0.715 5(6)
C(12)	0.843 9(7)	0.807 9(3)	0.610 5(6)
C(13)	0.912 4(6)	0.762 7(3)	0.555 1(5)
C(14)	1.035 5(6)	0.732 4(2)	0.607 7(5)
C(15)	1.389 7(5)	0.679 3(3)	0.611 9(4)
C(16)	1.438 8(7)	0.730 3(3)	0.566 4(5)
C(17)	1.507 7(7)	0.731 1(4)	0.461 3(5)
C(18)	1.523 8(8)	0.682 8(4)	0.402 1(6)
C(19)	1.476(1)	0.631 4(4)	0.445 6(7)
C(20)	1.408 5(8)	0.630 0(3)	0.551 6(6)
C(21)	1.003 0(9)	0.590 6(3)	0.554 5(6)
C(22)	1.126 1(8)	0.508 4(3)	0.716 9(7)
C(23)	0.818 9(7)	0.640 1(3)	0.736 9(6)
C(24)	0.915 7(8)	0.552 9(3)	0.880 7(7)
C(25)	0.786 0(9)	0.526 2(4)	0.666 6(7)
O(21)	1.013 5(8)	0.597 7(3)	0.460 2(5)
O(22)	1.214 8(7)	0.471 3(3)	0.717 9(6)
O(23)	0.733 7(5)	0.677 0(2)	0.755 3(5)
O(24)	0.879 9(6)	0.541 9(3)	0.969 8(5)
O(25)	0.681 6(7)	0.498 9(3)	0.632 8(7)
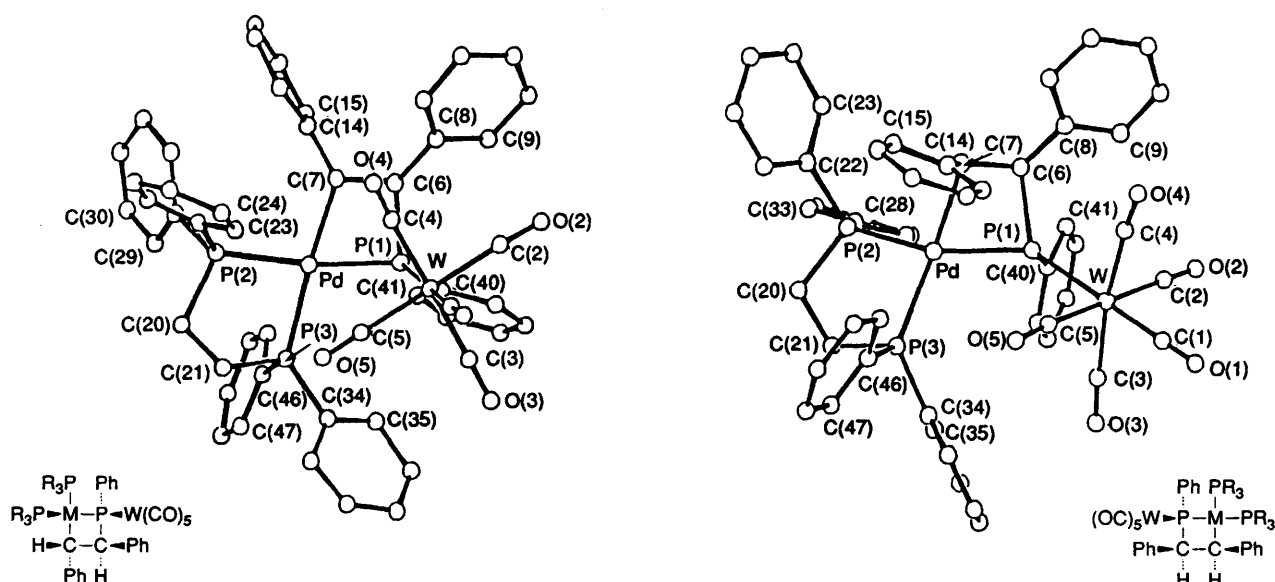
Fig. 2 Molecular structures of (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$] 3 (left) and (2R*,3S*,4R*)-(±)-[(dppe)Pd-(CHPhCHPhPPh)W(CO)$_5$] 5 (right)
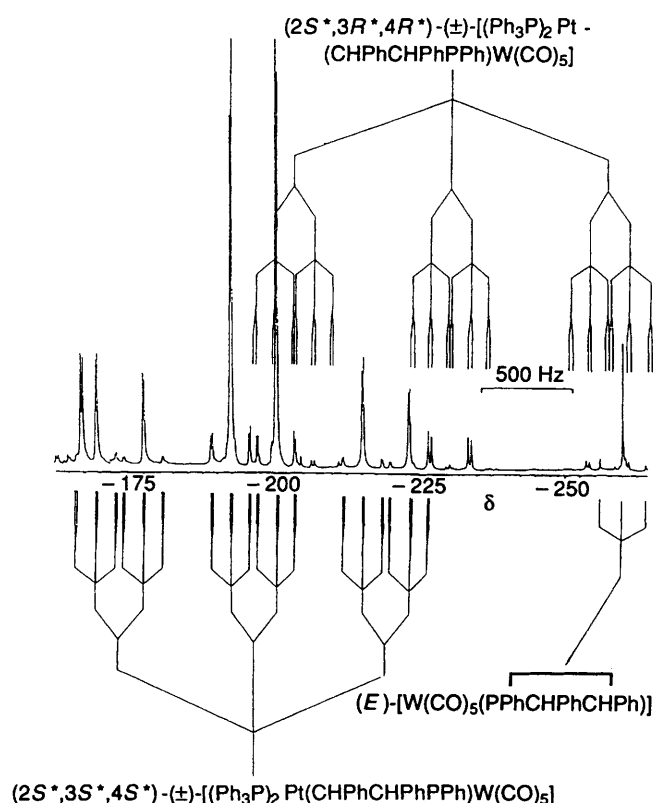
Fig. 3 ^{31}P-$\{^1$H$\}$ NMR spectrum of a crude reaction mixture containing [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] and (E)-[W(CO$_5$)(PPhCHPhCHPh)] 1. For clarity, only the high-field P$_X$ region is shown
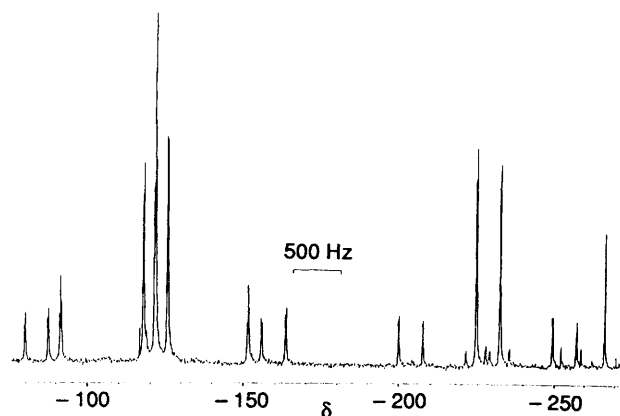

Fig. 4 ^{31}P-$\{^1$H$\}$ NMR spectrum measured on a Bruker WP80SY spectrometer (32.432 MHz) of a crude reaction mixture in thf at 304 K containing [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] and (Z)-[W(CO)$_5$(PPhCHPhCHPh)] 2

ated as (2S*,3S*,4S*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W-(CO)$_5$] **6**, on the basis of spectroscopic similarities with (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]† **3**, and the complex was fully characterised by ^{1}H, ^{31}P-$\{^1$H$\}$, ^{195}Pt-$\{^1$H$\}$, ^{13}C-$\{^1$H$\}$ NMR and IR spectroscopy, and elemental analysis. The minor component could not be isolated, but may be assigned the formula (2S*,3R*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPh-CHPhPPh)W(CO)$_5$] **7**, from mechanistic considerations. The slower reaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with (Z)-[W(CO)$_5$-(PPhCHPhCHPh)] **2** yielded two further products, assigned as (2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$] **8** and trans-(2S*,3S*,4R*)-(±)-[(Ph$_3$P)(OC)Pt(CHPhCHPhP-Ph)W(CO)$_5$] **9**, on the basis of ^{1}H, ^{31}P-$\{^1$H$\}$, ^{195}Pt-$\{^1$H$\}$, NMR and IR spectroscopy, and elemental analysis.

The unanticipated generation of complex **9** presumably reflects the high trans influence of the CHPh donor, and a steric congestion in the parent complex **8**, which can be inferred from the X-ray results on the analogous palladium compound (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$] **5**. The stability of (2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPh-PPh)W(CO)$_5$] **8** is solvent-dependent, and conversion into **9** was complete within 24 h in CHCl$_3$ at ambient temperature,‡ but was much slower in thf.

These results indicate that insertions of M(PR$_3$)$_2$ fragments into (E)-and (Z)-[W(CO)$_5$(PPhCHPhCHPh)] yield mutually exclusive products. Spectroscopic examinations of crude

mixtures derived from (E)-[W(CO)$_5$(PPhCHPhCHPh)] **1** and [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] showed no traces of complexes **8** and **9** (Fig. 3), and therefore establish a stereoselectivity in excess of 99.7%. Insertion of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] into (Z)-[W(CO)$_5$(PPhCHPhCHPh)] **2** was also shown not to produce **6** or **7**, as indicated by ^{31}P NMR spectroscopy (Fig. 4). Solutions containing **6** and **7** showed no evidence of **8** upon standing at room temperature for 3 months, thus implying that the product distribution is kinetically controlled.

A competition experiment, which involved treatment of a one-third molar equivalent of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with a mixture containing equimolar quantities of [W(CO)$_5$-(PPhCPh=CPh)], (E)-[W(CO)$_5$(PPhCHPhCHPh)] **1** and (Z)-[W(CO)$_5$(PPhCHPhCHPh)] **2** in thf at 25 °C, established that the cyclic complexes were consumed at significantly different rates: [W(CO)$_5$(PPhCPh=CPh)] 59(3) > 1 39(2) ≫ 2 3(3)%. After allowing for the generation of two different products from **1**, the formation rates for the product metallacycles decrease in the ratio 17(2) for **7** : 15(2) for (4R)-[(Ph$_3$P)$_2$Pt(CPhCPhPPh)W(CO)$_5$] 11 : 2(1) for **8** : 1(2) for **9**.

Proton NMR Stereochemical Studies on the Phosphametalla-cyclobutanes.—The ^{1}H NMR technique has been extensively applied to the evaluation of metallacyclobutane stereo-chemistry.[40] Variable-temperature measurements show only minor changes in chemical shift and couplings between 203 and 308 K for complexes **3** and **9** (Table 7), and rule out conformational exchange in solution on the NMR time-scale.[39] Therefore the spectroscopic characteristics of the phospha-metallacyclobutanes can be related to the crystallographically determined structures of **3** and **5**.

The ^{1}H NMR spectra of complexes **3–9** are characterised by a low-field multiplet (doublet of doublets, or pseudo-triplet) and a more complex high-field resonance. The lower-field resonances may be attributed to the PCHPh protons on the basis of their low multiplicity, invariance of the $^2J(P_{ring}H)$ coupling (12–15 Hz), and small values of $^nJ_{PtH}$ for **6**, **8** and **9**. This assignment is in agreement with a ^{31}P-[^{1}H] nuclear Overhauser effect (NOE) difference investigation, which reveals that irradiation of the

† The apparent inversion of the 2 position in these complexes is an anomaly merely reflecting the relative priority of the metal atoms, where Pt > W > Pd. It should be stressed that complexes **3** and **6** have analogous geometries.

‡ Upon standing at room temperature for 7 d, thf solutions of complex **8** also showed some evidence for phosphane transfer from Pt to W, as ^{31}P-$\{^1$H$\}$ and ^{195}Pt-$\{^1$H$\}$ NMR spectroscopy revealed resonances consistent with the formation of the new complex trans-(2S*,3S*,4R*)-(±)-[(Ph$_3$P)(OC)Pt(CHPhCHPhPPh)W(CO)$_4$(PPh$_3$)] **10**: δ(^{195}Pt) −2327 [ddd, J_{PtP} 2038, 1238, 99]; δ(^{31}P) −240 [$^1J_{PtP}$ 1236, $^2J_{PP}$ 203, 27 Hz].

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Table 3 Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for complex **3**

W–P(1)	2.556(3)	W–C(1)	1.978(14)	C(20)–C(21)	1.52(2)	C(22)–C(23)	1.40(2)
W–C(2)	2.01(2)	W–C(3)	2.030(13)	C(22)–C(27)	1.38(2)	C(23)–C(24)	1.42(2)
W–C(4)	2.04(2)	W–C(5)	1.99(2)	C(24)–C(25)	1.41(3)	C(25)–C(26)	1.32(3)
Pd–P(1)	2.320(4)	Pd–P(2)	2.337(4)	C(26)–C(27)	1.42(3)	C(28)–C(29)	1.39(3)
Pd–P(3)	2.324(4)	Pd–C(7)	2.135(13)	C(28)–C(33)	1.38(2)	C(29)–C(30)	1.45(2)
P(1)–C(6)	1.872(12)	P(1)–C(40)	1.860(13)	C(30)–C(31)	1.31(3)	C(31)–C(32)	1.43(3)
P(2)–C(20)	1.90(2)	P(2)–C(22)	1.82(2)	C(32)–C(33)	1.40(2)	C(34)–C(35)	1.38(3)
P(2)–C(28)	1.826(13)	P(3)–C(21)	1.86(2)	C(34)–C(39)	1.43(2)	C(35)–C(36)	1.45(2)
P(3)–C(34)	1.802(13)	P(3)–C(46)	1.83(2)	C(36)–C(37)	1.42(3)	C(37)–C(38)	1.41(3)
O(1)–C(1)	1.13(2)	O(2)–C(2)	1.14(2)	C(38)–C(39)	1.38(3)	C(40)–C(41)	1.37(2)
O(3)–C(3)	1.13(2)	O(4)–C(4)	1.14(2)	C(40)–C(45)	1.40(2)	C(41)–C(42)	1.37(2)
O(5)–C(5)	1.14(2)	C(6)–C(7)	1.54(2)	C(42)–C(43)	1.40(2)	C(43)–C(44)	1.38(2)
C(6)–C(8)	1.50(2)	C(7)–C(14)	1.48(2)	C(44)–C(45)	1.39(2)	C(46)–C(47)	1.35(2)
C(8)–C(9)	1.39(2)	C(8)–C(13)	1.38(2)	C(46)–C(51)	1.37(2)	C(47)–C(48)	1.47(3)
C(9)–C(10)	1.45(3)	C(10)–C(11)	1.39(3)	C(48)–C(49)	1.37(2)	C(49)–C(50)	1.37(3)
C(11)–C(12)	1.39(3)	C(12)–C(13)	1.41(3)	C(50)–C(51)	1.39(2)		
C(14)–C(15)	1.40(2)	C(14)–C(19)	1.42(2)				
C(15)–C(16)	1.41(2)	C(16)–C(17)	1.41(2)				
C(17)–C(18)	1.36(2)	C(18)–C(19)	1.38(2)				
P(1)–W–C(1)	177.6(5)	P(1)–W–C(2)	90.4(4)	C(9)–C(10)–C(11)	119(2)	C(10)–C(11)–C(12)	120(2)
P(1)–W–C(3)	93.6(3)	P(1)–W–C(4)	92.0(4)	C(11)–C(12)–C(13)	120(2)	C(8)–C(13)–C(12)	121(2)
P(1)–W–C(5)	88.9(4)	C(1)–W–C(2)	90.0(6)	C(7)–C(14)–C(15)	123(1)	C(7)–C(14)–C(19)	119(1)
C(1)–W–C(3)	88.8(6)	C(1)–W–C(4)	85.7(6)	C(15)–C(14)–C(19)	118(1)	C(14)–C(15)–C(16)	121(1)
C(1)–W–C(5)	90.8(6)	C(2)–W–C(3)	89.7(6)	C(15)–C(16)–C(17)	119(1)	C(16)–C(17)–C(18)	120(1)
C(2)–W–C(4)	91.6(7)	C(2)–W–C(5)	179.3(6)	C(17)–C(18)–C(19)	122(2)	C(14)–C(19)–C(18)	120(1)
C(3)–W–C(4)	174.3(5)	C(3)–W–C(5)	90.2(7)	P(2)–C(20)–C(21)	109(1)	P(3)–C(21)–C(20)	110.0(9)
C(4)–W–C(5)	88.7(7)	P(1)–Pd–P(2)	164.5(1)	P(2)–C(22)–C(23)	117(1)	P(2)–C(22)–C(27)	123(1)
P(1)–Pd–P(3)	106.1(1)	P(1)–Pd–C(7)	68.9(4)	C(23)–C(22)–C(27)	120(1)	C(22)–C(23)–C(24)	119(1)
P(2)–Pd–P(3)	83.8(1)	P(2)–Pd–C(7)	100.3(4)	C(23)–C(24)–C(25)	119(2)	C(24)–C(25)–C(26)	122(2)
P(3)–Pd–C(7)	174.0(3)	W–P(1)–Pd	115.8(1)	C(25)–C(26)–C(27)	120(2)	C(22)–C(27)–C(26)	120(2)
W–P(1)–C(6)	117.2(5)	W–P(1)–C(40)	117.9(4)	P(2)–C(28)–C(29)	119(1)	P(2)–C(28)–C(33)	121(1)
Pd–P(1)–C(6)	84.1(5)	Pd–P(1)–C(40)	112.9(5)	C(29)–C(28)–C(33)	119(1)	C(28)–C(29)–C(30)	117(2)
C(6)–P(1)–C(40)	103.5(5)	Pd–P(2)–C(20)	108.8(5)	C(29)–C(30)–C(31)	123(2)	C(30)–C(31)–C(32)	121(2)
Pd–P(2)–C(22)	110.0(6)	Pd–P(2)–C(28)	124.7(5)	C(31)–C(32)–C(33)	117(2)	C(28)–C(33)–C(32)	123(2)
C(20)–P(2)–C(22)	101.7(7)	C(20)–P(2)–C(28)	102.8(7)	P(3)–C(34)–C(35)	115(1)	P(3)–C(34)–C(39)	122(1)
C(22)–P(2)–C(28)	106.4(7)	Pd–P(3)–C(21)	103.3(5)	C(35)–C(34)–C(39)	123(1)	C(34)–C(35)–C(36)	118(2)
Pd–P(3)–C(34)	125.1(6)	Pd–P(3)–C(46)	114.2(4)	C(35)–C(36)–C(37)	120(2)	C(36)–C(37)–C(38)	118(2)
C(21)–P(3)–C(34)	105.5(7)	C(21)–P(3)–C(46)	101.9(7)	C(37)–C(38)–C(39)	123(2)	C(34)–C(39)–C(38)	117(2)
C(34)–P(3)–C(46)	104.2(7)	W–C(1)–O(1)	178(2)	P(1)–C(40)–C(41)	119(1)	P(1)–C(40)–C(45)	121(1)
W–C(2)–O(2)	174(1)	W–C(3)–O(3)	175(1)	C(41)–C(40)–C(45)	120(1)	C(40)–C(41)–C(42)	120(1)
W–C(4)–O(4)	170(1)	W–C(5)–O(5)	177(1)	C(41)–C(42)–C(43)	121(1)	C(42)–C(43)–C(44)	119(2)
P(1)–C(6)–C(7)	95.1(8)	P(1)–C(6)–C(8)	120.0(9)	C(43)–C(44)–C(45)	120(2)	C(40)–C(45)–C(44)	120(1)
C(7)–C(6)–C(8)	118(1)	Pd–C(7)–C(6)	99.3(8)	P(3)–C(46)–C(47)	119(1)	P(3)–C(46)–C(51)	119(1)
Pd–C(7)–C(14)	119(1)	C(6)–C(7)–C(14)	114(1)	C(47)–C(46)–C(51)	122(1)	C(46)–C(47)–C(48)	116(1)
C(6)–C(8)–C(9)	118(1)	C(6)–C(8)–C(13)	123(1)	C(47)–C(48)–C(49)	120(2)	C(48)–C(49)–C(50)	122(2)
C(9)–C(8)–C(13)	119(2)	C(8)–C(9)–C(10)	120(2)	C(49)–C(50)–C(51)	117(1)	C(46)–C(51)–C(50)	123(2)

low-field proton multiplet enhances the relaxation of P_X, whilst irradiation of the higher resonance affects only the phosphane ligands. In contrast to earlier studies,[39,40] the MCHPh resonance appears to higher field with the proton situated axially (δ 3.16–3.18) than equatorially (δ 3.44–3.76) in the complexes investigated here. Magnitudes of PtH, PH and HH coupling constants are useful stereochemical probes of metallacyclobutane structures, and $^2J_{P_{II}H}$ is predictably[39] found to be lower for equatorially than axially disposed PtCHPh protons [^2J(PtH$_{eq}$) 69, ^2J(PtH$_{ax}$) 103 Hz for **6** and **9**, respectively]. Additionally, PtCHPh protons which are oriented equatorially show complex multiplets (ΣJ_{PH} ca. 32 Hz), whilst those which are axially disposed give simpler patterns (ΣJ_{PH} ca. 18 Hz). A two-dimensional ^{31}P–^{1}H shift correlation experiment for **3** indicates that this simplicity results from the absence of coupling between H and P_A (Fig. 5). If it is assumed the axial H atom of **3** occupies a similar position to that of C(14) in **5**, and that $^3J_{PH}$ is under Karplus control,[39] then the very small $^3J(P_AH)$ coupling follows logically from an 80.0° P(2)PdC(7)H dihedral angle, and further supports the hypothesis that **3** is conformationally rigid in solution.

Since $^3J_{HH}$ couplings within the metallacyclobutane backbone have similar magnitudes for axial/equatorial [(Z)-] and axial/axial [(E)-] orientations (ca. 12 and 14 Hz, respectively),

reliable stereochemical assignments cannot be made from analysis of $^3J_{HH}$. Fortunately, ^{1}H-[^{1}H] NOE difference spectroscopy provides an excellent guide to backbone stereochemistry, since the cis-disposed H atoms of complex **5** show a 17% enhancement of the PdCHPh resonance upon irradiation of the downfield PCHPh multiplet, whereas no discernible enhancement is observed under identical conditions for **3** (Fig. 6).

^{31}P NMR Studies.—The ^{31}P-$\{^1$H$\}$ NMR spectrum of $(2S^*,3S^*,4R^*)$-($\pm$)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$] **8** (Fig. 3) is typical of the phosphametallacyclobutanes studied here. Spectra are of a simple AMX type and show additional satellite features which reflect couplings to tungsten [I (^{183}W) = $\frac{1}{2}$, 14% abundant] and, where appropriate, to platinum [I (^{195}Pt) = $\frac{1}{2}$, 34% abundant]. In all cases, the bridging phosphide resonance appears at high field, and is deshielded relative to the corresponding phosphametallacyclobutene.[7] Comparison of data for complex **3** with those for **5**, and of **6** with **8**, reveals a lower-field shift for the (E) isomer than its (Z) counterpart. These high-field shifts are in accord with X-ray structural data in implying the absence of metal–metal bonds [r(Pd–W) = 4.13 for **3**, 4.54 Å for **5**].

Differences in the trans influence of the P and C donors in the platinum complexes are more exaggerated in phosphametalla-

Table 4 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for complex 3

Atom	x	y	z	Atom	x	y	z
W	−8.0(6)	−91.6(5)	2730.7(4)	C(22)	−2797(13)	−3548(12)	4208(9)
Pd	−995.7(8)	−3321.2(8)	2594.6(6)	C(23)	−2528(14)	−2439(11)	4317(10)
P(1)	−448(3)	−2055(3)	1827(2)	C(24)	−3116(16)	−1792(14)	4920(11)
P(2)	−1897(3)	−4304(3)	3512(2)	C(25)	−3945(16)	−2293(16)	5398(13)
P(3)	776(3)	−3449(3)	3291(2)	C(26)	−4209(16)	−3340(15)	5282(12)
O(1)	400(12)	2281(9)	3838(7)	C(27)	−3625(16)	−3997(14)	4684(11)
O(2)	−542(13)	678(9)	1062(8)	C(28)	−2783(13)	−5691(11)	3138(9)
O(3)	2736(9)	438(10)	2488(8)	C(29)	−2198(18)	−6520(14)	3055(14)
O(4)	−2640(11)	−178(10)	3233(9)	C(30)	−2921(20)	−7609(15)	2685(15)
O(5)	573(11)	−770(9)	4424(7)	C(31)	−4077(18)	−7827(16)	2436(14)
C(1)	266(15)	1416(12)	3446(9)	C(32)	−4677(17)	−6984(15)	2474(13)
C(2)	−390(13)	350(11)	1645(9)	C(33)	−3979(14)	−5930(13)	2819(11)
C(3)	1750(12)	202(10)	2549(9)	C(34)	2196(12)	−2486(12)	3453(10)
C(4)	−1733(12)	−244(12)	3008(11)	C(35)	2673(13)	−2370(13)	2693(12)
C(5)	372(15)	−547(12)	3797(9)	C(36)	3823(16)	−1617(15)	2780(15)
C(6)	−1982(12)	−2666(11)	1212(9)	C(37)	4379(16)	−958(16)	3623(14)
C(7)	−2536(10)	−3029(10)	1976(8)	C(38)	3815(18)	−1109(17)	4363(15)
C(8)	−2601(12)	−2014(10)	776(9)	C(39)	2777(15)	−1881(16)	4310(13)
C(9)	−2180(14)	−1791(12)	24(9)	C(40)	562(11)	−2437(10)	993(8)
C(10)	−2792(15)	−1220(13)	−451(10)	C(41)	661(13)	−3477(11)	738(9)
C(11)	−3761(16)	−859(12)	−114(11)	C(42)	1416(16)	−3767(13)	132(11)
C(12)	−4179(16)	−1102(15)	630(12)	C(43)	2085(17)	−3012(12)	−234(10)
C(13)	−3552(14)	−1629(12)	1094(10)	C(44)	1959(14)	−1971(12)	−2(9)
C(14)	−3647(12)	−3904(10)	1695(8)	C(45)	1201(12)	−1675(11)	617(9)
C(15)	−3718(14)	−4866(12)	1049(10)	C(46)	1143(12)	−4752(11)	2890(9)
C(16)	−4806(14)	−5654(12)	769(10)	C(47)	2034(14)	−4979(13)	3346(10)
C(17)	−5831(14)	−5467(13)	1163(11)	C(48)	2256(16)	−6053(14)	3009(11)
C(18)	−5756(14)	−4558(14)	1818(12)	C(49)	1590(17)	−6749(12)	2262(11)
C(19)	−4691(12)	−3782(12)	2104(10)	C(50)	667(17)	−6504(14)	1832(12)
C(20)	−693(12)	−4369(12)	4353(9)	C(51)	479(13)	−5482(11)	2159(10)
C(21)	402(13)	−3470(12)	4411(9)				
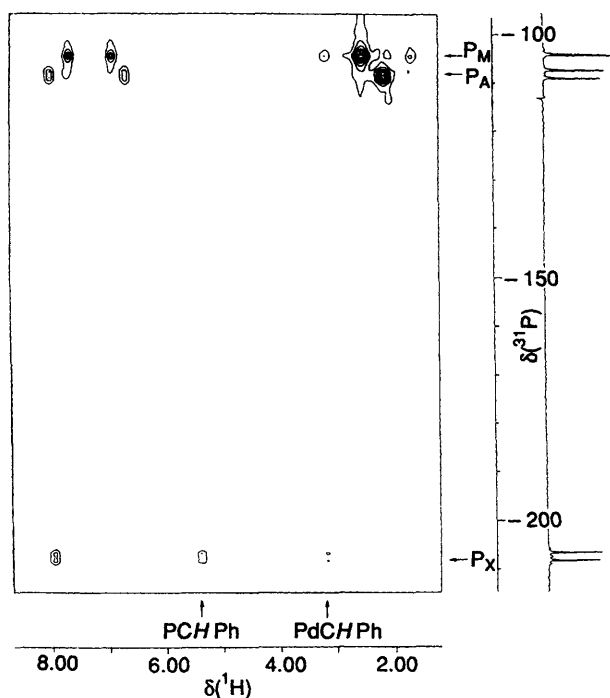
Fig. 5 The ^{31}P-^{1}H shift-correlated NMR spectrum of $(2R^*,3S^*,4S^*)$-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$] 3 showing an absence of coupling between P$_A$ and the axially oriented PdCHPh proton

cyclobutanes than in the analogous phosphametallacyclo-butenes,[5] and a non-dissociative rotational process is implied by the lineshapes and intensities associated with the P$_X$ resonance of 5 in both thf and CHCl$_3$ (Fig. 7).[41] Complex 3 is

non-rigid only in the latter solvent and no evidence of rotation is observed in either solvent for their phosphametallacyclo-butene analogues or the platinum complexes 6, 8 and 9.

Conclusion

The insertion of M(PR$_3$)$_2$ fragments into the co-ordinatively saturated phosphirane ring system provides an example of unequivocally *inter*molecular P–C bond cleavage, and establishes a reaction pathway which may also be relevant to the insertions into [W(CO)$_5$(PPhCPh=CPh)] discussed in our previous paper.[7]

Comparison of the molecular structures of $(2R^*,3S^*,4S^*)$-(±)- and $(2R^*,3S^*,4R^*)$-(±)-[(dppe)Pd(CHPhCHPhPPh)W-(CO)$_5$] 3 and 5, respectively reveals that the latter has a more sterically encumbered co-ordination sphere, and microscopic reversibility arguments therefore require that its formation be disfavoured on both kinetic and thermodynamic grounds. Since 5 is the sole insertion product from [Pd(dppe)(C$_2$H$_4$)] and (Z)-[W(CO)$_5$(PPhCHPhCHPh)] 2, reaction mechanisms which involve either S$_N$2 attack of the M(PR$_3$)$_2$ fragment upon the phosphirane complex or the intermediacy of free radicals can be excluded, since both of these processes involve acyclic intermediates whose ability to undergo inversion and bond rotation should lead to the more favoured $(2R^*,3S^*,4S^*)$-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$] 3.

The most plausible mechanism which permits exclusive formation of a kinetically and thermodynamically disfavoured product is a concerted insertion process, *via* a transition state which features η^2 co-ordination of the P–C bond to the metal centre. This process involves donation of electrons from the high-lying σ_{PC} combination into a vacant metal dsp^2 hybrid with back donation of metal d-electron density into the σ^*_{PC} orbital (Scheme 2), and is consistent with current theories concerning P–C bond cleavage at electron-rich metal centres.[3]

Table 5   Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for complex **5**

W–P(1)	2.589(2)	W–C(1)	1.965(10)	C(17)–C(18)	1.41(2)	C(18)–C(19)	1.411(13)
W–C(2)	2.018(10)	W–C(3)	2.027(10)	C(20)–C(21)	1.551(13)	C(22)–C(23)	1.381(12)
W–C(4)	2.032(10)	W–C(5)	2.008(10)	C(22)–C(27)	1.382(13)	C(23)–C(24)	1.391(13)
Pd–P(1)	2.366(2)	Pd–P(2)	2.310(2)	C(24)–C(25)	1.370(15)	C(25)–C(26)	1.39(2)
Pd–P(3)	2.348(2)	Pd–C(7)	2.131(8)	C(26)–C(27)	1.413(15)	C(28)–C(29)	1.403(13)
P(1)–C(6)	1.894(8)	P(1)–C(40)	1.850(8)	C(28)–C(33)	1.385(13)	C(29)–C(30)	1.400(13)
P(2)–C(20)	1.850(9)	P(2)–C(22)	1.815(9)	C(30)–C(31)	1.38(2)	C(31)–C(32)	1.37(2)
P(2)–C(28)	1.817(8)	P(3)–C(21)	1.867(9)	C(32)–C(33)	1.392(14)	C(34)–C(35)	1.406(12)
P(3)–C(34)	1.806(9)	P(3)–C(46)	1.832(8)	C(34)–C(39)	1.379(13)	C(35)–C(36)	1.389(14)
O(1)–C(1)	1.144(13)	O(2)–C(2)	1.138(13)	C(36)–C(37)	1.37(2)	C(37)–C(38)	1.377(14)
O(3)–C(3)	1.121(13)	O(4)–C(4)	1.136(12)	C(38)–C(39)	1.41(2)	C(40)–C(41)	1.374(13)
O(5)–C(5)	1.152(14)	C(6)–C(7)	1.517(12)	C(40)–C(45)	1.384(12)	C(41)–C(42)	1.446(13)
C(6)–C(8)	1.538(11)	C(7)–C(14)	1.498(11)	C(42)–C(43)	1.35(2)	C(43)–C(44)	1.41(2)
C(8)–C(9)	1.388(13)	C(8)–C(13)	1.383(12)	C(44)–C(45)	1.380(13)	C(46)–C(47)	1.398(13)
C(9)–C(10)	1.389(14)	C(10)–C(11)	1.37(2)	C(46)–C(51)	1.374(11)	C(47)–C(48)	1.363(15)
C(11)–C(12)	1.42(2)	C(12)–C(13)	1.394(13)	C(48)–C(49)	1.402(15)	C(49)–C(50)	1.37(2)
C(14)–C(15)	1.429(13)	C(14)–C(19)	1.369(13)	C(50)–C(51)	1.408(13)	C(52)–Cl(1)	1.748(10)
C(15)–C(16)	1.41(2)	C(16)–C(17)	1.39(2)	C(52)–Cl(2)	1.535(13)	C(52)–Cl(3)	1.576(8)
P(1)–W–C(1)	179.5(3)	P(1)–W–C(2)	87.1(3)	C(11)–C(12)–C(13)	120.2(9)	C(8)–C(13)–C(12)	119.5(8)
P(1)–W–C(3)	92.0(3)	P(1)–W–C(4)	95.5(3)	C(7)–C(14)–C(15)	117.5(8)	C(7)–C(14)–C(19)	123.4(8)
P(1)–W–C(5)	91.1(3)	C(1)–W–C(2)	93.2(4)	C(15)–C(14)–C(19)	119.0(8)	C(14)–C(15)–C(16)	119(1)
C(1)–W–C(3)	87.6(4)	C(1)–W–C(4)	84.9(4)	C(15)–C(16)–C(17)	122(1)	C(16)–C(17)–C(18)	119(1)
C(1)–W–C(5)	88.6(4)	C(2)–W–C(3)	89.7(4)	C(17)–C(18)–C(19)	119(1)	C(14)–C(19)–C(18)	122.3(9)
C(2)–W–C(4)	90.0(4)	C(2)–W–C(5)	177.2(4)	P(2)–C(20)–C(21)	107.3(6)	P(3)–C(21)–C(20)	107.5(6)
C(3)–W–C(4)	172.5(4)	C(3)–W–C(5)	88.2(4)	P(2)–C(22)–C(23)	118.4(6)	P(2)–C(22)–C(27)	120.8(7)
C(4)–W–C(5)	92.3(4)	P(1)–Pd–P(2)	152.67(8)	C(23)–C(22)–C(27)	120.6(8)	C(22)–C(23)–C(24)	119.7(8)
P(1)–Pd–P(3)	112.95(8)	P(1)–Pd–C(7)	71.5(2)	C(23)–C(24)–C(25)	120.5(9)	C(24)–C(25)–C(26)	121(1)
P(2)–Pd–P(3)	83.33(8)	P(2)–Pd–C(7)	97.9(2)	C(25)–C(26)–C(27)	119(1)	C(22)–C(27)–C(26)	119.6(9)
P(3)–Pd–C(7)	166.6(2)	W–P(1)–Pd	133.04(9)	P(2)–C(28)–C(29)	118.6(6)	P(2)–C(28)–C(33)	121.5(7)
W–P(1)–C(6)	122.6(3)	W–P(1)–C(40)	109.6(3)	C(29)–C(28)–C(33)	119.6(8)	C(28)–C(29)–C(30)	119.0(9)
Pd–P(1)–C(6)	82.3(3)	Pd–P(1)–C(40)	100.9(3)	C(29)–C(30)–C(31)	121(1)	C(30)–C(31)–C(32)	120(1)
C(6)–P(1)–C(40)	102.8(4)	Pd–P(2)–C(20)	109.7(3)	C(31)–C(32)–C(33)	120(1)	C(28)–C(33)–C(32)	120.5(9)
Pd–P(2)–C(22)	124.9(3)	Pd–P(2)–C(28)	108.5(3)	P(3)–C(34)–C(35)	119.5(7)	P(3)–C(34)–C(39)	121.1(7)
C(20)–P(2)–C(22)	104.9(4)	C(20)–P(2)–C(28)	102.0(4)	C(35)–C(34)–C(39)	119.4(8)	C(34)–C(35)–C(36)	120.4(9)
C(22)–P(2)–C(28)	104.5(4)	Pd–P(3)–C(21)	107.9(3)	C(35)–C(36)–C(37)	119.7(9)	C(36)–C(37)–C(38)	121(1)
Pd–P(3)–C(34)	130.2(3)	Pd–P(3)–C(46)	106.3(3)	C(37)–C(38)–C(39)	120(1)	C(34)–C(39)–C(38)	119.6(9)
C(21)–P(3)–C(34)	101.7(4)	C(21)–P(3)–C(46)	101.6(4)	P(1)–C(40)–C(41)	123.5(6)	P(1)–C(40)–C(45)	116.6(6)
C(34)–P(3)–C(46)	105.7(4)	W–C(1)–O(1)	178.6(9)	C(41)–C(40)–C(45)	119.9(8)	C(40)–C(41)–C(42)	119.2(9)
W–C(2)–O(2)	178.9(9)	W–C(3)–O(3)	174.9(9)	C(41)–C(42)–C(43)	120(1)	C(42)–C(43)–C(44)	119(1)
W–C(4)–O(4)	174.0(9)	W–C(5)–O(5)	177.6(9)	C(43)–C(44)–C(45)	120(1)	C(40)–C(45)–C(44)	120.8(9)
P(1)–C(6)–C(7)	100.6(5)	P(1)–C(6)–C(8)	120.9(6)	P(3)–C(46)–C(47)	121.4(6)	P(3)–C(46)–C(51)	118.8(6)
C(7)–C(6)–C(8)	120.3(7)	Pd–C(7)–C(6)	100.1(5)	C(47)–C(46)–C(51)	119.6(8)	C(46)–C(47)–C(48)	120.6(9)
Pd–C(7)–C(14)	96.6(5)	C(6)–C(7)–C(14)	121.3(7)	C(47)–C(48)–C(49)	120(1)	C(48)–C(49)–C(50)	119(1)
C(6)–C(8)–C(9)	118.1(7)	C(6)–C(8)–C(13)	120.9(7)	C(49)–C(50)–C(51)	120.6(9)	C(46)–C(51)–C(50)	119.6(9)
C(9)–C(8)–C(13)	120.7(8)	C(8)–C(9)–C(10)	119.4(9)	Cl(1)–C(52)–Cl(2)	115.2(6)	Cl(1)–C(52)–Cl(3)	114.4(5)
C(9)–C(10)–C(11)	122(1)	C(10)–C(11)–C(12)	119(1)	Cl(2)–C(52)–Cl(3)	130.4(7)		

For the (*Z*) complex **2**, concerted insertion of Pd(dppe) into either P–C bond can result only in the formation of **5**, whereas two different products are expected from the non-equivalent PC bonds of **1**, Scheme 3. On this basis, the minor isomers obtained by insertion of Pd(dppe) and Pt(PPh₃)₂ into **1** may be assigned the structures (2*R**,3*R**,4*R**)-[(dppe)Pd(CHPhCHPhPPh)W-(CO)₅] **4** and (2*S**,3*R**,4*R**)-[(Ph₃P)₂Pt(CHPhCHPhPPh)-W(CO)₅] **7**, respectively, which result from concerted insertion into the P–C bond having the *trans*-disposed phenyl groups.

In principle, the insertion of M(PR₃)₂ into [W(CO)₅-(PPhCPh=CPh)] could proceed through co-ordination of the metal to the intracyclic C=C bond, a pathway proposed for the inclusion of platinum(0) fragments into diphenylcyclo-propenone OCCPh=CPh[42–44] and almost certainly operative in the Pd⁰-induced generation of SO₂ from thiirane dioxides,[45] but neither our studies with [W(CO)₅(PPhCPh=CPh), nor those of Hughes and co-workers[46] on F₂CCF=CF, show any low-temperature solution evidence for the involvement of such η²-co-ordination complexes. In both of these cases, where the ring σ bonds lie at much higher energy than π(C=C), insertion probably proceeds *via* direct attack of the M(PR₃)₂ moiety upon the ring bond. This hypothesis receives support from the similar insertion rates of Pt(PPh₃)₂ into [W(CO)₅-(PPhCPh=CPh)] and (*E*)-[W(CO)₅(PPhCHPhCHPh)], which suggest that insertion into [W(CO)₅(PPhCPh=CPh] is not assisted by preassociation of the intracyclic C=C bond with Pt(PPh₃)₂.

Numerous studies suggest that the mode of concerted oxidative addition of phosphorus–carbon bonds to co-ordinatively unsaturated low-valent metal centres, which we observed here, provides the decomposition pathway for metal–phosphane catalyst decomposition in industrial processes.[3] In phosphirene and phosphirane complexes this oxidative-addition process must be accelerated by unusually favourable energetics which result from a high radical extension and low σ ⟶ σ* promotion potential associated with the strained ring P–C bonds. In principle, these characteristics should enable phosphirane complexes to be used as low-temperature probes of the relationship between the substituents at phosphorus and the ease of P–C bond-cleavage reactions, providing steric factors affecting the metal insertion rate are minimised.

Preliminary results suggest that such steric effects may exert a significant influence over the product distribution for insertion reactions into (*E*)- and (*Z*)-[W(CO)₅(PPhCHPhCHPh)]. In

Table 6 Fractional atomic coordinates (× 10⁴) with e.s.d.s in parentheses for complex **5**

Atom	x	y	z	Atom	x	y	z
W	1510.2(3)	2301.2(2)	1234.8(2)	C(24)	−4275(8)	4924(5)	2535(5)
Pd	−1920.4(5)	2939.2(3)	1413.1(3)	C(25)	−4748(8)	4702(6)	3127(5)
P(1)	−171(2)	3023(1)	1033(1)	C(26)	−4959(9)	4043(6)	3207(5)
P(2)	−3666(2)	3282(1)	1433(1)	C(27)	−4630(8)	3603(5)	2685(5)
P(3)	−2716(2)	1929(1)	1139(1)	C(28)	−4067(7)	3653(4)	570(4)
O(1)	3530(7)	1436(4)	1477(5)	C(29)	−3345(8)	3653(5)	31(5)
O(2)	2501(7)	3123(4)	20(4)	C(30)	−3675(9)	3901(6)	−649(5)
O(3)	702(8)	1271(4)	74(5)	C(31)	−4679(9)	4168(5)	−778(5)
O(4)	2722(6)	3156(4)	2445(4)	C(32)	−5383(8)	4166(5)	−248(5)
O(5)	437(8)	1447(4)	2389(5)	C(33)	−5082(8)	3903(5)	424(5)
C(1)	2778(8)	1747(5)	1387(6)	C(34)	−2399(7)	1325(4)	485(4)
C(2)	2148(8)	2831(5)	463(5)	C(35)	−2722(8)	1422(5)	−245(5)
C(3)	947(9)	1655(5)	479(6)	C(36)	−2467(9)	970(5)	−758(5)
C(4)	2252(8)	2878(5)	2001(5)	C(37)	−1915(9)	417(5)	−548(5)
C(5)	812(8)	1769(5)	1971(6)	C(38)	−1591(10)	314(6)	164(6)
C(6)	−260(7)	3864(4)	1435(4)	C(39)	−1836(8)	772(5)	689(5)
C(7)	−1174(6)	3770(4)	1912(4)	C(40)	−455(7)	3173(4)	60(4)
C(8)	750(6)	4232(4)	1718(4)	C(41)	−312(8)	3765(5)	−260(5)
C(9)	1575(7)	4294(5)	1266(5)	C(42)	−572(9)	3834(6)	−1025(5)
C(10)	2454(8)	4673(5)	1481(6)	C(43)	−940(10)	3323(6)	−1420(5)
C(11)	2537(9)	4982(5)	2132(7)	C(44)	−1070(10)	2718(6)	−1082(6)
C(12)	1681(9)	4925(5)	2586(5)	C(45)	−835(8)	2652(5)	−352(5)
C(13)	798(7)	4543(4)	2377(5)	C(46)	−2752(6)	1494(4)	1994(4)
C(14)	−995(7)	3482(4)	2649(4)	C(47)	−3394(8)	946(5)	2060(5)
C(15)	−1795(8)	3592(6)	3142(5)	C(48)	−3483(9)	662(5)	2713(6)
C(16)	−1688(10)	3288(8)	3821(5)	C(49)	−2923(9)	915(6)	3329(5)
C(17)	−841(10)	2876(7)	4013(6)	C(50)	−2285(9)	1448(5)	3267(5)
C(18)	−30(10)	2795(5)	3538(5)	C(51)	−2189(7)	1741(5)	2592(5)
C(19)	−140(8)	3098(4)	2858(5)	C(52)	5000	0	0
C(20)	−4562(7)	2570(4)	1438(5)	Cl(1)	5742(8)	−561(4)	−459(5)
C(21)	−4164(7)	2070(4)	896(5)	Cl(2)	4490(12)	549(6)	−465(7)
C(22)	−4154(6)	3836(4)	2092(4)	Cl(3)	4999(9)	−126(5)	833(4)
C(23)	−3974(7)	4493(4)	2013(4)				

The occupancy for the Cl atoms is 0.5
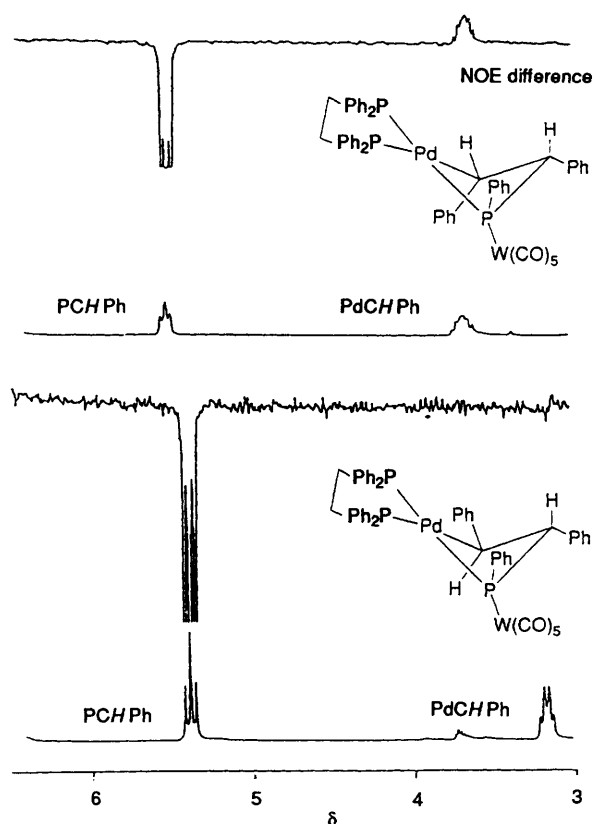
Fig. 6 ¹H-[¹H] NOE difference spectra of (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅] **5** (upper) and (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅] **3** (lower)
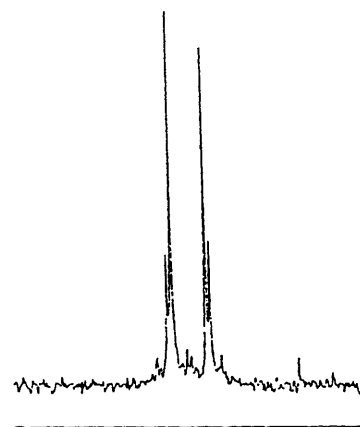
Fig. 7 ³¹P-{¹H} NMR spectrum of the PW(CO)₅ resonance of (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)₅] **5**, showing lineshapes and intensities characteristic of an intramolecular rotational process

competition for Pt(PPh₃)₂, the disfavoured products **7** and **8** share a congested axial orientation of the C(6) aryl group, and have rates of formation which are much lower than that of the more sterically favoured **6**. Changes are therefore necessary at sites remote from the P–C bonds if electronic effects are to dominate. Several phosphirane complexes having the electronically diverse substituents [W(CO)₅-(PPhCH₂CHR] (R = C₆H₄X-p, X = MeO, Me, Ph, F, H, Cl or Br), which would be useful for more extended studies, are available.⁴⁷

Table 7 Proton NMR data for phosphametallacyclobutane complexes

Complex	Solvent	T/K	$\delta(H_\alpha)$	$\delta(H_\beta)$	$^2J(H_\alpha H_\beta)$	$\Sigma J(PH_\alpha)$	$\Sigma J(PH_\beta)$	$^2J(PtH_\alpha)$	$^2J(PtH_x)$
3 (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]	CDCl$_3$	298	3.181	5.394	12.4	20.4	12.4	n.a.	n.a.
	CD$_2$Cl$_2$	183	3.036	5.271			a		
5 (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]	CDCl$_3$	293	3.780	5.630	11.6	32.3	11.6	n.a.	n.a.
	CD$_2$Cl$_2$	183	3.594	5.663			a		
6 (2S*,3S*,4S*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]	CDCl$_3$	298	3.160	5.076	12.3	16.1	12.3	69.1	25.4
8 (2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]	CD$_2$Cl$_2$	283	3.444	5.460	9.1	43.3	13.1	b	b
	CD$_2$Cl$_2$	203	3.425	5.431	9.4	43.4	13.1	b	b
9 trans-(2S*,3S*,4R*)-(±)-[(Ph$_3$P)(OC)Pt(CHPhCHPhPPh)W(CO)$_5$]	CD$_2$Cl$_2$	308	3.485	5.534	9.9	32.9	14.7	102.9	17.6
	CD$_2$Cl$_2$	213	3.504	5.609	9.5	32.0	15.1	b	
	CD$_2$Cl$_2$ c	163	3.532	5.681			a		

Chemical shifts in ppm, positive to high frequency of SiMe$_4$, J in Hz. Measured on a Bruker WM360SY spectrometer operating at 360.1 MHz. n.a. = Not applicable.
a Broad lines precluded these measurements. b Not resolved. c Measured in CD$_2$Cl$_2$–CCl$_3$F.

Table 8 ^{31}P-{^{1}H} NMR data for phosphametallacyclobutane complexes

| Complex	$\delta(P_A)$	$\delta(P_M)$	$\delta(P_x)$	$^2J(P_A P_x)$	$^2J(P_M P_x)$	$^2J(P_A P_M)$	$^1J(P_x W)$	$^1J(PtP_A)$	$^1J(PtP_M)$	$^1J(PtP_x)$
3 (2R*,3S*,4S*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]	−107.7	−104.6	−207.9	250	12	18	208	n.a.	n.a.	n.a.
4 (2R*,3R*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]	—	—	−246.3	222	21	—	—	n.a.	n.a.	n.a.
5 (2R*,3S*,4R*)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]	−101.3	−105.0	−260.6	235	26	24	192	n.a.	n.a.	n.a.
6 (2S*,3S*,4S*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]	−124.3	−127.6	−196.4	261	7	10	215	2515	1909	1487
7 (2S*,3R*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]	−118.5	−120.4	−230.5	227	20	12	208	2676	1895	1753
8 (2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]	−121.9	−121.7	−228.6	250	10	10	205	2465	1947	1603
9 trans-(2S*,3S*,4R*)-(±)-[(Ph$_3$P)(OC)Pt(CHPhCHPhPPh)W(CO)$_5$]	−122.8	n.a.	−255.5	208	n.a.	n.a.	208	2197	n.a.	1259

Chemical shifts in ppm, positive to high frequency of P(OMe)$_3$, J in Hz. Measured in thf at 304 K, on a Bruker WP80SY spectrometer at 32.432 MHz.

Experimental

Standard procedures for the manipulation of air-sensitive materials were employed throughout this work. Unless otherwise stated, all manipulations were carried out under an atmosphere of dry dinitrogen using Schlenk, syringe, and high-vacuum techniques. Glassware was flame dried *in vacuo* and solvents were distilled under a blanket of dinitrogen prior to use: tetrahydrofuran and diethyl ether were from sodium–benzophenone; toluene, benzene and light petroleum (b.p. 60–80 °C) (from sodium metal; di- and tri-chloromethane from phosphorus pentoxide; and methanol and ethanol from the corresponding magnesium alkoxide.

The NMR spectra were recorded upon either Bruker WP80SY (^{1}H 80.1, ^{31}P 32.4, ^{13}C 20.1, ^{195}Pt 17.1 MHz) or WM360SY (^{1}H 360.1, ^{31}P 145.8, ^{13}C 90.4, ^{195}Pt 77.1 MHz) Fourier-transform machines, and are referenced to external SiMe$_4$, P(OMe)$_3$ or K$_2$[PtCl$_4$], as appropriate, *via* the deuterium lock signal from the solvent resonance. Chemical shifts are quoted with positive values to high frequency of the reference. Infrared spectra were recorded as Nujol mulls or potassium bromide discs on a Perkin Elmer PE 1430 continuous-wave instrument, and were calibrated relative to polystyrene at 1601 and 1028 cm^{-1}. Carbon and hydrogen microanalyses were performed in the University of Sussex microanalysis service by Ms. K. Plowman. The complexes (*E*)-and (*Z*)-[W(CO)$_5$(PPhCHPhCHPh)] were prepared as described previously.[32]

Preparations.—(2*R**,3*S**,4*S**)-(±)-[(dppe)Pd(CHPhCHPh PPh)W(CO)$_5$] **3**. Addition of (*E*)-[W(CO)$_5$(PPhCHPhCHPh)] (71.5 mg, 1.17 × 10^{-4} mol) to a solution of [Pd(dppe)(C$_2$H$_4$)] (prepared by dropwise treatment of a powdered suspension of [PdCl$_2$(dppe)] (67.3 mg, 1.16 × 10^{-4} mol) with LiBEt$_3$H (84.6 mg, 8.00 × 10^{-4} mol) in ethylene-purged thf (1.8 cm^3)
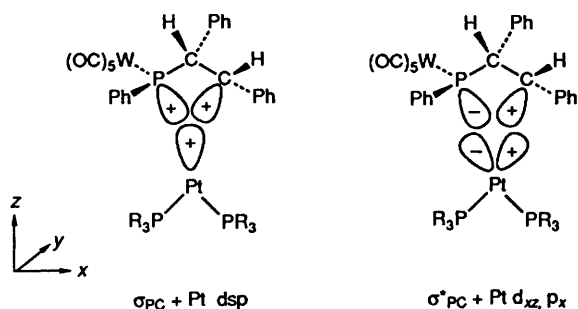
Scheme 2 A mechanism for the concerted insertion of a Pt(PR$_3$)$_2$ fragment into [W(CO)$_5$(PPhCHPhCHPh)]
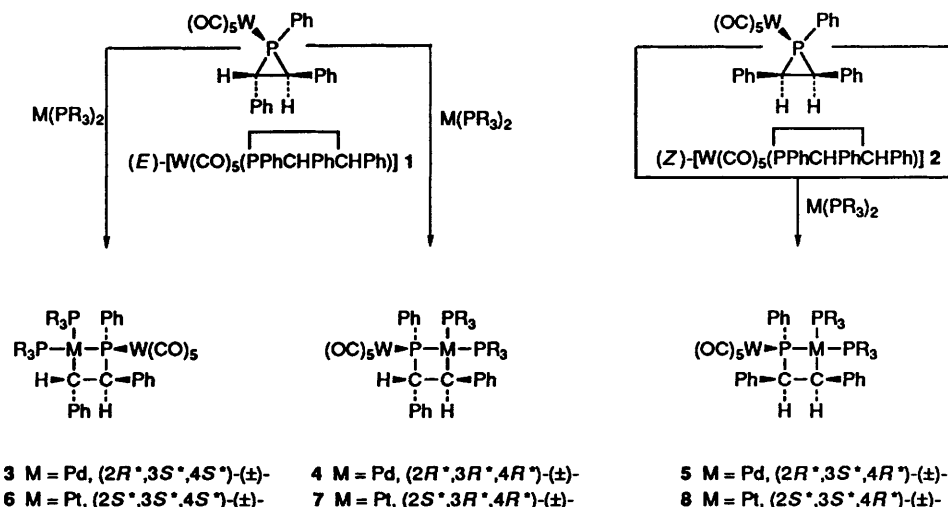
caused an evolution of gas and a colour change from orange to deep red. After 30 min at room temperature, ethanol (1 drop) was added and further ethanol (3 cm^3) was allowed to diffuse slowly into the mixture. Orange crystals of (2*R**,3*S**,4*S**)-1,2-bis(diphenylphosphino)ethane-2κ^2*P*-pentacarbonyl-1κ^5*C*-μ-(1,2,3-triphenyl-1-phospha-1 : 2κ^2*P*-propane-1,3-diyl-2κ*C*^{3})-palladium(ɪɪ)tungsten(o) were collected after 24 h, washed with ethanol (3 × 4 cm^3), diethyl ether (2 × 2 cm^3), and dried *in vacuo* (75.6 mg, 67%) (Found: C, 54.45; H, 3.85. C$_{51}$H$_{41}$O$_5$P$_3$PdW requires C, 54.85; H, 3.70%); ν$_{max}$(CO) 2055 (sh), 1957w, 1909s and 1895cm^{-1} (Nujol); δ$_H$ in Table 7; δ$_C$ (thf–C$_7$D$_8$) 23.3 (1 C, dd, *J*$_{PC}$ 79, 10, $^1J_{CH}$ 136, PdC), 25.8 (1 C, dd, *J*$_{PC}$ 22, 16, PCH$_2$), 27.6(1 C, *J*$_{PC}$ 23, 16, PCH$_2$), 56.7(1 C, d, $^1J_{PC}$ 16, $^1J_{CH}$ 133, PCHPh), 120–150 (m, Ph), 198.1 (4 C, d, $^2J_{PC}$ 5, $^1J_{WC}$ 120, *cis*-WCO) and 200.3 (1 C, d, $^2J_{PC}$ 20 Hz, *trans*-WCO); δ$_P$ in Table 8.

(2*R**,3*S**,4*R**)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]

5. The complex (*Z*)-[W(CO)$_5$(PPhCHPhCHPh)] (122.7 mg, 2.00 × 10^{-4} mol) was added to a sample of [Pd(dppe)(C$_2$H$_4$)] which had been freshly prepared from [PdCl$_2$(dppe)] (114.0 mg, 1.98 × 10^{-4} mol) and LiBEt$_3$H (104.7 mg, 1.00 × 10^{-3} mol) in ethylene-saturated thf (1.5 cm^3). Gas was evolved and the colour changed from pale straw to deep red. After 30 min, methanol (1 drop) was added, and further methanol (4 cm^3) was allowed to diffuse into the thf layer overnight. Orange microcrystals of (2*R**,3*S**,4*R**)-(±)-1,2-bis(diphenylphosphino)ethane-2κ^2*P*-pentacarbonyl-1κ^5*C*-μ-(1,2,3-triphenyl-1-phospha-1 : 2κ^2*P*-propane-1,3-diyl-2κ*C*^{3})-palladium(ɪɪ)-tungsten(o) **5** were collected, washed with methanol (2 × 1 cm^3) and dried *in vacuo* (161.9 mg, 73%), m.p. 124–130 °C (Found: C, 54.85; H, 4.10. C$_{51}$H$_{41}$O$_5$P$_3$PdW requires C, 54.85; H, 3.70%); ν$_{max}$(CO) 2060 (sh), 1962vw, 1919s, 1896m and 1883m, cm^{-1} (Nujol); δ$_H$ in Table 7, δ$_P$ in Table 8.

A small sample crystallised from CHCl$_3$–MeOH was employed in the crystal structure analysis of (2*R**,3*S**,4*R**)-(±)-[(dppe)Pd(CHPhCHPhPPh)W(CO)$_5$]·0.5CHCl$_3$ (Found: C, 51.80; H, 3.85. C$_{103}$H$_{83}$Cl$_3$O$_{10}$P$_6$Pd$_2$W$_2$ requires C, 52.55; H, 3.55%).

(2*S**,3*S**,4*S**)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$]

6. The complex (*E*)-[W(CO)$_5$(PPhCPhCHPh)] (231.2 mg, 3.77 × 10^{-4} mmol) was added to an acetone (1 cm^3) suspension of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (280.2 mg, 3.74 × 10^{-4} mol) at room temperature. Colourless crystals which formed after 12 h were collected, washed with diethyl ether (2 × 1 cm^3), and shown to be (2*S**,3*S**,4*S**)-(±)-pentacarbonyl-1κ^5*C*-μ-(1,2,3-triphenyl-1-phospha-1 : 2κ^2*P*-propane-1,3-diyl-2κ*C*^{3})-bis(triphenylphosphine)-2κ^2*P*-platinum(ɪɪ)tungsten(o) **6** (327.4 mg, 75%) (Found: C, 55.00; H, 3.85. C$_{61}$H$_{45}$O$_5$P$_3$PtW requires C, 54.85; H, 3.75%);

3 M = Pd, (2*R**,3*S**,4*S**)-(±)-
6 M = Pt, (2*S**,3*S**,4*S**)-(±)-

4 M = Pd, (2*R**,3*R**,4*R**)-(±)-
7 M = Pt, (2*S**,3*R**,4*R**)-(±)-

5 M = Pd, (2*R**,3*S**,4*R**)-(±)-
8 M = Pt, (2*S**,3*S**,4*R**)-(±)-

Scheme 3 Insertion of M(PR$_3$)$_2$ into phosphirane complexes **1** and **2**

v_{max}(CO) 2055 (sh), 1961 (sh), 1913 (br) and 1900 (br) cm^{-1} (Nujol); δ_H(CDCl$_3$) in Table 7; δ_C(thf–CD$_3$COCD$_3$) (selected) 21.6 (1 C, dd, $^2J_{PC}$ 86, 11, $^1J_{PtC}$ 455, $^1J_{CH}$ 138, PtC) and 64.4 (1 C, d, $^1J_{PC}$ 22, $^2J_{PtC}$ 92, $^1J_{CH}$ 133 Hz, PtPCPh); δ_P(thf) in Table 8; δ_{Pt}(thf) −2653 (1 Pt, ddd, $^1J_{PtP}$ 2515, 1909, 1487 Hz).

(2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt($\overline{\text{CHPhCHPhPPh}}$)W(CO)$_5$] 8. The complex (Z)-[W(CO)$_5$($\overline{\text{PPhCHPhCHPh}}$)] (121.0 mg, 1.98 × 10^{-4} mol) was added with stirring to a tetrahydrofuran (1 cm^3) solution of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (140.1 mg, 1.87 × 10^{-4} mol) at −40 °C. The mixture was warmed to room temperature for 12 h after which time conversion into (2S*,3S*,4R*)-(±)-[(Ph$_3$P)$_2$Pt(CHPhCHPhPPh)W(CO)$_5$] was 95% complete, according to ^{31}P-{^{1}H} NMR spectroscopy. Absolute ethanol (3 cm^3) was added, and the solution was cooled to −40 °C. After several weeks, yellow microcrystals of (2S*,3S*,4R*)-(±)-pentacarbonyl-1κ^{5}C-μ-(1,2,3-triphenyl-1-phospha-1 : 2κ^{2}P-propane-1,3-diyl-2κC^3)-bis(triphenyl-phosphine)-2κ^{2}P-platinum(II)tungsten(0) 8 were collected, washed with ethanol (2 × 1 cm^3), and dried *in vacuo* (152.2 mg, 61%) (Found: C, 55.15; H, 3.85. C$_{61}$H$_{47}$O$_5$P$_3$PtW requires C, 55.00; H, 3.55%); v_{max}(CO) 2059 (sh), 1965w, 1918s (br), 1911s (br) and 1800w (br) cm^{-1} (Nujol); δ_H in Table 7, δ_P in Table 8.

trans-(2S*,3S*,4R*)-(±)-[(Ph$_3$P)(OC)Pt($\overline{\text{CHPhCHPhPPh}}$)-W(CO)$_5$] 9. The complex (Z)-[W(CO)$_5$($\overline{\text{PPhCHPhCHPh}}$)] (125.0 mg, 2.04 × 10^{-4} mol) was added to a chloroform (1 cm^3) solution of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (154.5 mg, 2.07 × 10^{-4} mol). No evolution of gas was observed at room temperature, and the solution was therefore allowed to stand for 24 h. Methanol (3 cm^3) was added to the green solution and the mixture was allowed to stand at room temperature. After 1 week, colourless crystals of *trans*-(2S*,3S*,4R*)-hexacarbonyl-1κ^{5}C,2κC-μ-(1,2,3-triphenyl-1-phospha-1 : 2κ^{2}P-propane-1,3-diyl-2κC^3)-triphenylphosphine-2κP-platinum(II)tungsten(0) 9 were collected, washed with methanol (3 × 1 cm^3) and diethyl ether (2 × 1 cm^3), and dried *in vacuo* (149.1 mg, 54.5%) (Found: C, 47.70; H, 3.30. C$_{44}$H$_{32}$O$_5$P$_3$PtW requires C, 48.15; H, 3.30%); v_{max}(CO) 2062 (sh), 2045 (sh), 1953w, 1924 (br), 1910 (br) and 1902 (br) cm^{-1} (Nujol); δ_H in Table 7, δ_P in Table 8; δ_{Pt}(thf) − 2540 (1 Pt, $^1J_{PtP}$ 2188, 1254 Hz).

Competition Experiment for [Pt(PPh$_3$)$_2$(C$_2$H$_4$)].—The ^{31}P-{^{1}H} NMR spectrum of a tetrahydrofuran (1.5 cm^3) solution containing [W(CO)$_5$($\overline{\text{PPhCPh=CPh}}$)] (51.2 mg, 8.39 × 10^{-4} mol), (E)-[W(CO)$_5$($\overline{\text{PPhCHPhCHPh}}$)] 1 (51.5 mg, 8.41 × 10^{-4} mol) and (Z)-[W(CO)$_5$($\overline{\text{PPhCHPhCHPh}}$)] 2 (51.4 mg, 8.40 × 10^{-4} mol) was measured over 800 transients using a 25° pulse and a repetition time of 5 s, and recorded on a disc. The complex [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (63.0 mg, 8.40 × 10^{-4} mol) was added at 25 °C, and the procedure was repeated under identical conditions. The relative reaction rates of the three complexes were obtained by evaluation of the proportion of the starting material consumed during the reaction. As the low rate of insertion into the bond of (E)-[W(CO)$_5$-($\overline{\text{PPhCHPhCHPh}}$)] having mutually *trans*-oriented phenyl groups precluded a direct comparison of the relative proportions of 6 and 7 generated, it was necessary to assume that their relative rates of formation were 11 : 1, as is observed in tetrahydrofuran at 25 °C and much higher concentration. The experiment was performed in duplicate, and gave the results discussed in the text.

Crystal-structure Determinations.—X-Ray diffraction studies were performed on an Enraf-Nonius CAD4 diffractometer and the crystal structure solved and refined using the SDP-PLUS program package[48] on a microVax computer. Graphite-mono-chromated Mo-Kα radiation (λ = 0.710 69 Å) was employed.

Complex 2. Crystals were grown at −18 °C from a pentane solution of the compound. Data were collected at 21 ± 1 °C.

Crystal data. C$_{25}$H$_{17}$O$_5$PW, M = 616.2, monoclinic, space group P2$_1$/c, a = 8.434(1), b = 23.589(4), c = 11.853(1) Å, β = 92.09(1)°, U = 2356.75(89) Å^3, Z = 4, D$_c$ = 1.725 g cm^{-3}, μ = 51.0 cm^{-1}, F(000) = 1184.

A total of 6597 unique reflections were recorded for a crystal of size 0.3 × 0.3 × 0.3 mm in the range 2 ≤ 2θ ≤ 60.0° of which 3947 were considered as unobserved [$F^2 < 2.0\sigma(F^2)$], leaving 2650 for solution and refinement. The positions of the tungsten and phosphorus atoms were obtained from a Patterson map. The positions of the hydrogen atoms were refined in the final stages of least-squares while using anisotropic thermal parameters for all other atoms. A non-Poisson weighting scheme was applied with a p factor of 0.04. The final agreement factors were R = 0.032, R' = 0.034, goodness-of-fit = 1.05.

Complex 3. *Crystal data.* C$_{51}$H$_{41}$O$_5$P$_3$PdW, M = 1117.1, triclinic, space group P$\bar{1}$, a = 11.521(2), b = 13.273(3), c = 15.879(2) Å, α = 104.83(1), β = 93.33(1), γ = 102.60(2)°, U = 2274.0 Å^3, Z = 2, D$_c$ = 1.63 g cm^{-3}, F(000) = 1104, μ = 31.2 cm^{-1}.

Data were collected using a crystal *ca.* 0.15 × 0.15 × 0.1 mm in the θ–2θ mode with Δθ = (0.8 + 0.35 tanθ)° and a maximum scan time of 1 min. A total of 5551 unique reflections were measured for 2 < θ < 22° and +h ± k ± l, and 3684 with $|F^2| > \sigma(F^2)$ were used in the refinement where $\sigma(F^2)$ = [σ^2(I) + (0.04I)^2]$^{\frac{1}{2}}$/Lp. There was no crystal decay. An absorption correction was made using DIFABS after isotropic refinement with maximum and minimum corrections of 1.16 and 0.76. The structure was solved by routine heavy-atom methods and non-hydrogen atoms refined anisotropically by block-diagonal least squares. Hydrogen atoms were omitted. The weighting scheme was w = 1/σ^2(F) and the final residuals were R = 0.048, R' = 0.055.

Complex 5. *Crystal data.* C$_{51}$H$_{41}$O$_5$P$_3$PdW·0.5CHCl$_3$, M = 1176.8, monoclinic, space group P2$_1$/n a = 12.578(2), b = 20.583(2), c = 18.645(3) Å, β = 94.18(1)°, U = 4814.2 Å^3, Z = 4, D$_c$ = 1.62 g cm^{-3}, F(000) = 2324, μ = 30.3 cm^{-1}.

Data were collected using a crystal *ca.* 0.4 × 0.2 × 0.1 mm in the θ–2θ mode with Δθ = (0.8 + 0.35 tanθ)° and a maximum scan time of 1 min. A total of 6422 unique reflections were measured for 2 < θ < 22° and +h + k ± l, and 4333 with $|F^2| > \sigma(F^2)$ were used in the refinement where $\sigma(F^2)$ = [σ^2(I) + (0.04I)^2]$^{\frac{1}{2}}$/Lp. There was no crystal decay. An absorption correction was made using DIFABS[49] after isotropic refinement with maximum and minimum corrections of 1.16 and 0.86. The structure was solved by routine heavy-atom methods and non-hydrogen atoms were refined anisotropically by block-diagonal least squares. Hydrogen atoms were omitted. The crystal contains a molecule of chloroform disordered about the inversion centre at $\frac{1}{2}$,0,0. The weighting scheme was w = 1/σ^2(F) and the final residuals were R = 0.036 and R' = 0.048.

Additional material available from the Cambridge Crystallo-graphic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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