An η^2 Transition State for the Insertion of [Pd(dppe)] Fragments into the Phosphorus–Carbon Bonds of Phosphiranepentacarbonyltungsten Complexes. Crystal and Molecular Structures of (2*R*,3*S*,4*R*)- and (2*R*,3*S*,4*S*)-[Pd(dppe)(CHPhCHPhPPh)-W(CO)$_5$], dppe = 1,2-bis(diphenylphosphanyl)ethane

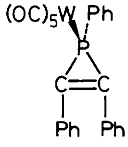
Duncan Carmichael,[a] Peter B. Hitchcock,[a] John F. Nixon,[a]* François Mathey,[b] and Louis Ricard[b]

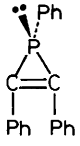
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.*

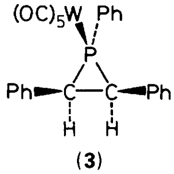
[b] *DCPH Ecole Polytechnique, 91128 Palaiseau, Cedex, France*

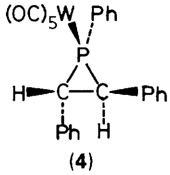
Evidence for a transition state involving η^2 co-ordination of a P–C bond to [Pd(dppe)] is obtained from an analysis of the insertion of [Pd(dppe)] fragments into (*E*)- and (*Z*)-[W(CO)$_5$(PPh–CHPh–CHPh)] complexes.

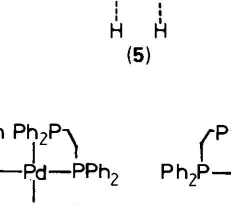
Phosphorus–carbon bonds of many phosphane-supported transition metal complexes are unstable under catalytic conditions and the area of metal-induced P–C cleavage reactions is receiving increased attention.[1] In recent papers we have demonstrated facile insertion of [M(PR$_3$)$_2$] (M = Pd, Pt, PR$_3$ = phosphane ligand) fragments into the strained P–C ring bonds of the phosphirene skeletons of (**1**) and (**2**),[2,3] and as these reactions suggest an opportunity to study the mechanism and stereochemistry of phosphorus–carbon bond ruptures under very mild conditions, we have now examined the interaction of [Pd(dppe)] fragments with the isomeric *P*-co-ordinated phosphirane complexes (*Z*)- and (*E*)-[W(CO)$_5$(PPh–CHPh–CHPh)], (**3**)† and (**4**) respectively.[4]

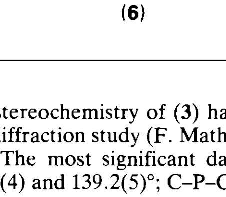

(**1**)

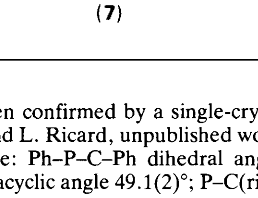

(**2**)


(**3**)


(**4**)


(**5**)


(**6**)


(**7**)

Room temperature reaction of [Pd(dppe)(C$_2$H$_4$)],[5] {prepared by *in situ* LiBEt$_3$H/tetrahydrofuran (THF) reduction of [PdCl$_2$(dppe)] in a stream of ethylene,[6]} with (**3**) yielded a single phosphapalladacyclobutane product (**5**), whilst insertion into (**4**) yielded (**6**).‡ *X*-Ray crystallographic studies§ establish the structures (2*R*,3*S*,4*R*)-[Pd(dppe)(CHPhCHPh-PPh)W(CO)$_5$] (**5**) and (2*R*,3*S*,4*S*)-[Pd(dppe)(CHPhCHPh-PPh)W(CO)$_5$] (**6**), (Figure 1)¶ and confirm that insertion proceeds with retention of the configuration of the parent phosphirane complexes. The puckered metallacyclic products

---

† The stereochemistry of (**3**) has been confirmed by a single-crystal *X*-ray diffraction study (F. Mathey and L. Ricard, unpublished work, 1989). The most significant data are: Ph–P–C–Ph dihedral angles −152.1(4) and 139.2(5)°; C–P–C intracyclic angle 49.1(2)°; P–C(ring) bond lengths 1.858(6) and 1.827(6) Å.

‡ The presence of a second phosphapalladacyclobutane (**7**) (*ca.* 3%) in the latter reaction is implied by the presence of a second high-field resonance in the ^{31}P{^{1}H} n.m.r. spectra of crude mixtures derived from [Pd(dppe)(C$_2$H$_4$)] and (**4**). Complex (**4**) has non-equivalent intracyclic P–C bonds and two discrete insertion products are therefore to be expected. Whilst we have no proof of the structure of (**7**), it seems likely to be (2*R*,3*R*,4*R*)-[Pd(dppe)(CHPhCHPhPPh)-W(CO)$_5$], which results from insertion of [Pd(dppe)] into the P–C bond having the *trans*-oriented phenyl groups. Importantly, its spectroscopic parameters [δ(P^X) −105.3, $^2J_{P(A)P(X)}$ 222, $^2J_{P(M)P(X)}$ 21 Hz] are inconsistent with those of (**5**).

§ *Spectroscopic data* (chemical shifts in p.p.m. relative to SiMe$_4$ or H$_3$PO$_4$ as appropriate; positive to high frequency of the reference; *J* in Hz): for (**5**), ν(CO) 2060s, 1962vw, 1919s, 1896m, 1883m cm^{-1}; ^{31}P{^{1}H} n.m.r., δ 39.7 (P^A), 36.0 (P^M), −119.6 (P^X); J_{pp}: $^2J_{AM}$, 24; $^2J_{MX}$, 26; $^2J_{AX}$, 235; $^1J_{WP(X)}$ 192; ^{1}H n.m.r. δ 5.63 (pseudo-t, $^2J_{PH}$ = $^3J_{HH}$ = 11.6), 3.78 (m, ΣJ_{PH} 32.3).

For (**6**), ν(CO) 2055sh, 1975w, 1909s, 1895s cm^{-1}; ^{31}P{^{1}H} n.m.r., δ 33.3 (P^A), 36.4 (P^M), −66.9 (P^X); J_{PP}: $^2J_{AM}$, 18; $^2J_{MX}$, 12; $^2J_{AX}$, 250; $^1J_{WP(X)}$ 208; ^{1}H n.m.r. δ 5.39 (pseudo-t, $^2J_{PH}$ = $^3J_{HH}$ = 12.4), 3.18 (m, ΣJ_{PH} 20.4).

¶ *Crystal data*: for (**5**), from CHCl$_3$/MeOH, CHCl$_3$ solvate, *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°, *U* = 4814.2 Å^3, *Z* = 4, D_c = 1.62 g cm^{-3}; monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 30.3 cm^{-1}. The structure of the air-stable crystal (*ca.* 0.4 × 0.2 × 0.1 mm) was solved by routine heavy-atom procedures and refined by full-matrix least-squares methods with non-hydrogen atoms anisotropic on an Enraf-Nonius CAD 4 diffractometer and DEC MicroVax computer. An absorption correction was made (max 1.16, min 0.86), but no correction for crystal decay was applied. Of 6422 reflections observed, 4333 with $|F^2| > \sigma(F^2)$ were used in the refinement, which converged at *R* = 0.036, R_w = 0.048.

For (**6**), from THF/MeOH, *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}, monochromated Mo-K_α radiation, μ = 31.2 cm^{-1}. Structure solution as for (**5**). 5551 reflections were collected from an air-stable orange crystal (0.15 × 0.15 × 0.1 mm), and 3684 were used in the refinement, which converged at *R* = 0.048, R_w = 0.055.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

differ principally in the disposition of the C(7) aryl group and there is evidence that the axial orientation in (**5**) causes considerable steric pressure on the palladium co-ordination sphere, which results in: (a) significantly increased Pd–P(1), W–P(1), P(1)–Pd–C(7), and Pd–P(1)–W bond lengths and angles when compared with those of (**6**), and (b) a short Pd–C(14) separation (2.74 Å). Although this suggests that (**6**) should be thermodynamically favoured, careful $^{31}P\{^1H\}$ n.m.r. examinations show it to be absent from crude reaction mixtures derived from $[Pd(dppe)(C_2H_4)]$ and (**3**).

Strict retention of configuration, together with the exclusive formation of a sterically disfavoured isomer from (**3**), implies that insertion of the [Pd(dppe)] fragment proceeds *via* a transition state involving η^2 co-ordination of the P–C bond to the metal centre[7] rather than through free radicals or charge-separated species, and is therefore in accord with current theories concerning the nature of the P–C bond breaking process.[1,8] Although the insertion reaction is clearly driven by unusually favourable energetics resulting from the low promotion potential and high radial extension of the σ(PC) LUMO,[9—11] it may have potential for the elucidation of the factors affecting P–C bond stability in more conventional phosphane ligands, as a variety of functional groups may be readily introduced at phosphorus[12] or carbon.[4,13]

We thank CNRS and SERC for financial support, and Johnson Matthey for a loan of palladium salts.

Received, 6th June 1989; Com. 9/02377A

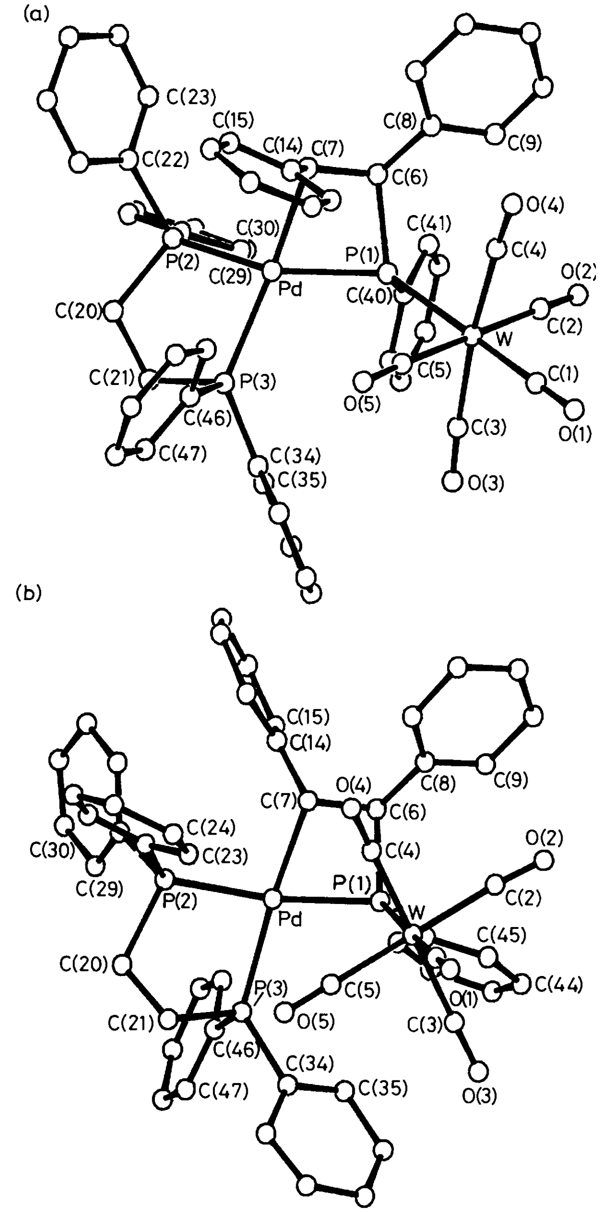


Figure 1. Molecular structures of (**5**) (a) and (**6**) (b). Selected bond lengths (Å) and angles (°): for (**5**): W–P(1), 2.589(2); Pd–P(1), 2.366(2); Pd–P(2), 2.310(2); Pd–P(3), 2.348(2); Pd–C(7), 2.131(8); P(1)–C(6), 1.894(8); P(1)–C(40), 1.850(8); C(6)–C(7), 1.517(12); W–P(1)–Pd, 133.04(9); Pd–P(1)–C(6), 82.3(3); Pd–C(7)–C(6), 100.1(5); Pd–C(7)–C(14), 96.6(5); P(1)–Pd–C(7), 71.5(2); P(1)–C(6)–C(7), 100.6(5); P(2)–Pd–P(3), 83.33(8). For (**6**): W–P(1), 2.556(3); Pd–P(1), 2.320(4); Pd–P(2), 2.337(4); Pd–P(3), 2.324(4); Pd–C(7), 2.135(13); P(1)–C(6), 1.872(12); P(1)–C(40), 1.860(13); C(6)–C(7), 1.54(2); W–P(1)–Pd, 115.8(1); Pd–P(1)–C(6), 84.1(5); Pd–C(7)–C(6), 99.3(8); Pd–C(7)–C(14), 119(1); P(1)–Pd–C(7), 68.9(4); P(1)–C(6)–C(7), 95.1(8); P(2)–Pd–P(3), 83.8(1).

References

1 P. E. Garrou, *Chem. Rev.*, 1985, **85**, 171.
2 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey, and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 1986, 762.
3 S. S. Al-Juaid, D. Carmichael, P. B. Hitchcock, S. Lochschmidt, A. Marinetti, F. Mathey, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1988, 1156.
4 A. Marinetti and F. Mathey, *Organometallics*, 1984, **3**, 456.
5 R. S. Paonessa, A. L. Prignano, and W. C. Trogler, *Organometallics*, 1985, **4**, 647.
6 M. K. Patel and A. Pidcock, to be published.
7 S. A. Maclaughlin, A. J. Carty, and N. J. Taylor, *Can. J. Chem.*, 1982, **60**, 87.
8 A. J. Carty, *Pure Appl. Chem.*, 1982, **54**, 113.
9 D. H. Aue, H. M. Webb, W. R. Davidson, M. Vidal, M. T. Bowers, H. Goldwhite, L. E. Vertal, J. E. Douglas, P. A. Kollman, and G. L. Kenyon, *J. Am. Chem. Soc.*, 1980, **102**, 5151.
10 D. Gonbeau and G. Pfister-Guillouzo, *Inorg. Chem.*, 1987, **26**, 1799.
11 K. D. Dobbs, J. E. Boggs, A. R. Barron, and A. H. Cowley, *J. Phys. Chem.*, 1988, **92**, 4886.
12 S. Holand and F. Mathey, *Organometallics*, 1988, **7**, 1796.
13 K. Lammertsma, P. Chand, S.-W. Yang, and J.-T. Hung, *Organometallics*, 1988, **7**, 1875.