Differences in the Interaction of 1,2,3-Triphenylphosphirene with Platinum(II) and Platinum(0) Complexes. Crystal and Molecular Structures of *cis*-[PtCl$_2$(PPhCPh=CPh)(PEt$_3$)] and *cis*-[PtI(PPhMeCPh=CPh)(PPh$_3$)]

Salih S. Al-Juaid,[a] Duncan Carmichael,[a] Peter B. Hitchcock,[a] Siegfried Lochschmidt,[b] Angela Marinetti,[b] François Mathey,[b]* and John F. Nixon[a]*

[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, U.K.*
[b] *Laboratoire CPMT, DCPH, Ecole Polytechnique, 91128 Palaiseau Cedex, France*

1,2,3-Triphenylphosphirene undergoes only η^1-co-ordination with Pt^{II} complexes whereas with Pt^0 centres insertion also occurs to yield phosphaplatinacyclobutene products.

Following initial reports of the preparation of 1,2,3-triphenylphosphirenetungsten pentacarbonyl (**1**)[1] and its decomplexation to yield the stable 1,2,3-triphenylphosphirene (**2**),[2] there has been considerable interest in the synthetic potential of (**2**) and its derivatives.[3] Mathey and co-workers have demonstrated that CO[4] and alkenes[5] insert into the pentacarbonyl-(phosphirene)tungsten skeleton under forcing conditions and have postulated the phosphametallacyclobutene ring system (**3**), generated transiently at high temperatures, as the key intermediate in the insertion process.[4,5] Whilst there appear to be no literature reports of stable species such as (**3**), the P-complexed metallacycles (**4**) have been prepared at the University of Sussex and a nickel analogue of (**4**) has been shown to be susceptible to insertion of CO.[7] Related palladium complexes are probably involved in the [Pd(PPh$_3$)$_4$]-mediated insertion of terminal alkynes into (**1**).[8]

A recent molecular orbital study[9] indicates that although the HOMO of phosphirene comprises a hybrid orbital

Table 1. Selected n.m.r. data.[a]

(**5**): δ^{31}P: -268.2, $^{1}J_{\mathrm{PtP}}$ 4285
(**6**): δ^{31}P$_A$: -124.9, $^{1}J_{\mathrm{PtP_A}}$ 3413
$\delta^{31}P_x$: -256.4, $^{1}J_{\mathrm{PtP_x}}$ 4477, $^{2}J_{\mathrm{P_AP_x}}$ 22
(**7**): δ^{31}P$_A$: -125.1, $^{1}J_{\mathrm{PtP_A}}$ 4222
δ^{31}P$_x$: -296.9, $^{1}J_{\mathrm{PtP_x}}$ 3927, $^{2}J_{\mathrm{P_AP_x}}$ 60
(**8**): δ^{31}P$_A$: -119.9, $^{1}J_{\mathrm{PtP_A}}$ 2184, $^{2}J_{\mathrm{P_AP_B}}$ 12, $^{2}J_{\mathrm{P_AP_x}}$ 69
δ^{31}P$_B$: -122.5, $^{1}J_{\mathrm{PtP_B}}$ 2212, $^{2}J_{\mathrm{P_AP_x}}$ 10
δ^{31}P$_x$: -256.1, $^{1}J_{\mathrm{PtP_x}}$ 693
(**9**): δ^{31}P$_A$: -126.5, $^{1}J_{\mathrm{PtP_A}}$ 2105, $^{2}J_{\mathrm{P_AP_x}}$ 9
δ^{31}P$_x$: -232.4, $^{1}J_{\mathrm{PtP_x}}$ 2879

[a] ^{31}P measurements at 32.4 MHz are referred to P(OMe)$_3$ as external standard; δ in p.p.m., positive being to high frequency of the reference, *J* in Hz.

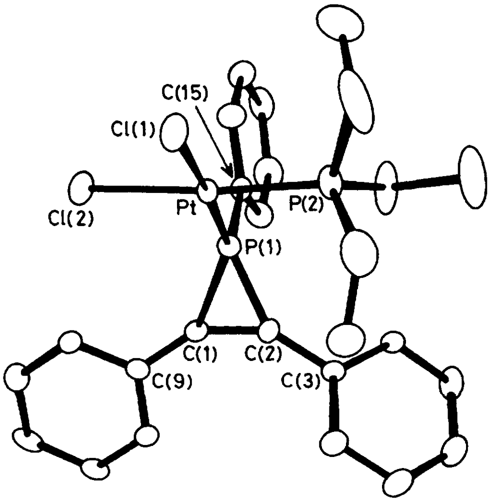


Figure 1. Molecular structure of [PtCl$_2$(PPhCPh=CPh)(PEt$_3$)] (**6**). Selected bond lengths (Å): Pt–P(1), 2.207(2); Pt–P(2), 2.217(3); Pt–Cl(1), 2.337(3); Pt–Cl(2), 2.370(3); P(1)–C(1), 1.776(9); P(1)–C(2), 1.782(9); C(1)–C(9), 1.429(13); C(2)–C(3), 1.457(12). Angles (°): Pt–P(1)–C(1), 125.7(3); Pt–P(1)–C(2); 130.3(3) Pt–P(1)–C(15), 116.1(3); C(1)–P(1)–C(2), 44.0(4); P(1)–C(1)–C(2), 68.3(6); P(1)–C(2)–C(1), 67.8(5); C(1)–P(1)–C(15), 111.7(4); C(2)–P(1)–C(15), 109.4(8); C(1)–C(2)–C(3), 144.7(9); C(2)–C(1)–C(9), 145.4(9).

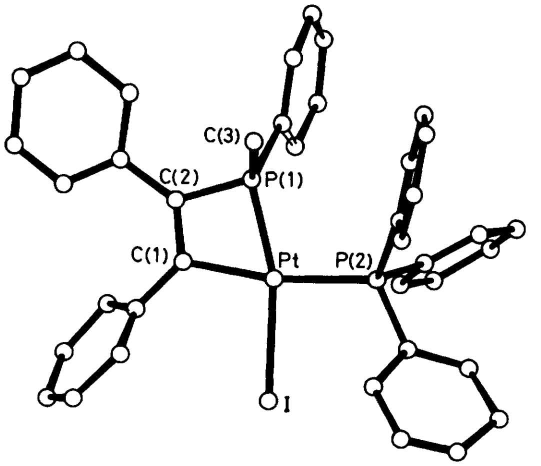
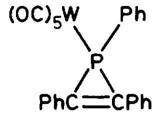


Figure 2. Structure of one molecule of [PtI(PPhMeCPh=CPh)(PPh$_3$)] (**9**). Selected bond lengths (Å): Pt–I, 2.645(1); Pt–P(1), 2.238(5); Pt–P(2), 2.310(4); Pt–C(1), 2.07(2); P(1)–C(2) 1.77(2); P(1)–C(3), 1.81(1) C(1)–(2), 1.36(2). Angles (°): I–Pt–P(1), 163.4(1); I–Pt–C(1), 96.1(5); P(1)–Pt–C(1), 67.7(5); Pt–P(1)–C(2), 86.6(6); Pt–C(1)–C(2), 106(1); P(1)–C(2)–C(1), 100(1).

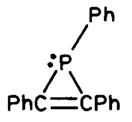
involving the phosphorus lone pair, the ring P–C bonds lie at high energy and might be likely to insert transition metal-ligand fragments, thereby providing access to analogues of the postulated intermediate (**3**). Since later transition metals readily activate strained rings,[10] we have investigated the differing reactivity of (**2**) towards Pt^{II} and Pt^0 metal centres.

Treatment of dichloromethane solutions of (**2**) with [PtCl$_2$(COD)] (COD=cyclo-octa-1,5-diene) or [PtCl$_2$(PEt$_3$)]$_2$ at room temperature does not lead to ring-opened products, but instead yields the *cis*-bis(phosphane)platinum (II) complexes (**5**) and (**6**), readily assigned as being η^1-ligated on the basis of the large magnitudes of their $^1J_{\text{PtP}}$ coupling constants.[11] Confirmation of the structure of (**6**) was established by a single-crystal *X*-ray diffraction study, (Figure 1).†

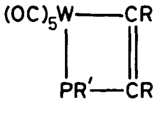
Comparison of (**6**) with free triphenylphosphirene (**2**)[2] reveals that co-ordination to the Pt^{II} centre results in (a) decreased pyramidality at phosphorus, (b) an increase in the intracyclic C(1)=C(2) bond length from 1.299(3) to 1.332(13) Å, and (c) a corresponding decrease in the mean intracyclic P–C bond lengths from 1.820(3) to 1.779(9) Å. The increased stability of the complexed phosphirene ring corresponds to the suppression of the destabilising interaction between the lone pair at P and the double bond, and has also been observed upon co-ordination of (**2**) to [W(CO)$_5$].[2,12]



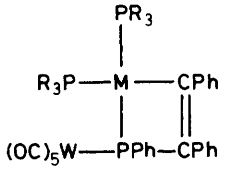
(1)



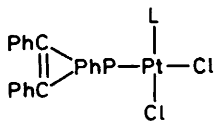
(2)



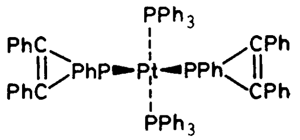
(3)



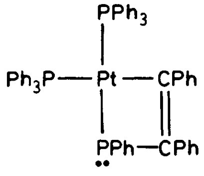
(4) (**a**) M = Pd, PR$_3$ = PEt$_3$
(**b**) M = Pt, PR$_3$ = PEt$_3$
(**c**) M = Pt, PR$_3$ = PPh$_3$
(**d**) M = Pt, PR$_3$ = $\frac{1}{2}$ dppe



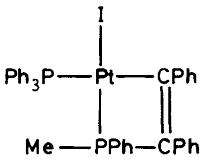
(5) L = η^1-PPhCPh=CPh
(6) L = PEt$_3$



(7)



(8)



(9)

Similarly, treatment of (**2**) with [Pt(PPh$_3$)$_2$C$_2$H$_4$] (tetrahydrofuran, −40 °C) proceeds smoothly with evolution of ethylene to yield a blood-red solution attributed to the η^1-complex (**7**) on the basis of the characteristic triplet P$_\text{A}$ and P$_\text{x}$ resonances in the ^{31}P{^{1}H} n.m.r. spectrum and the large magnitude of $^1J_{\text{PtP}_\text{x}}$ (3927 Hz), typical of tetrakis(phosphane)-platinum(0) species. {Compare [Pt(dppp)$_2$] = 3644 Hz,[13] [Pt(PMe$_2$Ph)$_4$] = 3805 Hz.[14]}. However, upon warming to room temperature, (**7**) readily undergoes insertion of [Pt(PPh$_3$)$_2$] into the phosphirene ring and is cleanly converted into the key phosphametallacyclobutene (**8**), which was isolated as a pale yellow powder from tetrahydrofuran–hexane. The most interesting spectroscopic aspect of this insertion is the dramatic decrease in $^1J_{\text{PtP}_\text{x}}$ associated with the high-field phosphorus resonance [from 3927 Hz in (**7**) to 693 Hz in (**8**)]. The very small coupling constant in (**8**) presumably reflects a high p-character in the PtP$_\text{x}$ hybrid orbital implying high s-electron character in the phosphorus lone pair.[15] Accordingly, (**8**) shows behaviour characteristic of a phosphane and treatment with iodomethane (tetrahydrofuran,

---

† *Crystal data* for (**6**): from CH$_2$Cl$_2$/Et$_2$O. C$_{26}$H$_{30}$Cl$_2$P$_2$Pt, M = 670.5, orthorhombic, space group $P2_12_12_1$, a = 10.063(1), b = 14.767(2), c = 18.292(2) Å, U = 2714.3 Å^3, Z = 4, D_c = 1.64 g cm^{-3}. The structure was solved by routine heavy-atom methods and refined by full-matrix least-squares with all non-hydrogen atoms anisotropic, giving R = 0.031 R' = 0.037. 2692 reflections were measured on an Enraf-Nonius CAD 4 diffractometer using Mo-K_α radiation, and 2426 with $|F^2| > \sigma(F^2)$ were used in the refinement.

Crystal data for (**9**): from tetrahydrofuran/Et$_2$O. C$_{39}$H$_{33}$IP$_2$Pt, M = 885.6, triclinic, space group $P\bar{1}$, a = 10.507(2), b = 15.033(2), c = 25.523(8) Å, α = 77.06(2), β = 87.77(2), γ = 70.29(2)°, U = 3695.5 Å^3, Z = 4, D_c = 1.59 g cm^{-3}. The structure was solved by heavy-atom methods and refined by block-diagonal least-squares methods with Pt, I, and P atoms anisotropic, giving R = 0.052 and R' = 0.081. 6878 reflections were measured on an Enraf-Nonius CAD 4 diffractometer using Mo-K_α radiation, and 5784 with $|F^2| > \sigma(F^2)$ were used in the refinement. Atomic co-ordinates, bond lengths and angles, and thermal parameters for both (**6**) and (**9**) have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

25°C) yields the unusual *cyclo*metallated phosphane complex [PtI(PPhMeCPh=CPh)PPh$_3$], (**9**).

A single-crystal *X*-ray diffraction study of (**9**) confirms the formulation and establishes the structure proposed for (**8**) (Figure 2). The unit cell of (**9**) includes two distinct [PtI(PPhMeCPh=CPh)(PPh$_3$)] moieties which differ only in the orientation of one of the triphenylphosphane ligands. In each molecule the atoms of the Pt–C(1)=C(2)–P(1) ring lie in a plane which also includes the I and P(2) atoms. Whilst the Pt–I bond length is typical of iodide *trans* to phosphanes in platinum(II) complexes[16] the Pt–P(1) and Pt–C(1) bonds are short and reflect the strain imposed by the planarity of the ring. Likewise the very low value for $^1J_{PtP_X}$ (2879 Hz) compares closely with the value observed for *cis*-[Pt(dppm)I$_2$] (2878 Hz).[17]

The contrasting reactivity of (**2**) towards Pt^0 and Pt^{II} fragments is particularly noteworthy, as earlier work indicates that the closely related[9] silirene ($\overline{\text{SiC=C}}$) ring system interacts with Pd^{II} centres *via* a two-step mechanism involving an initial reduction of the metal to the Pd^0 oxidation state and subsequent insertion reactions.[18] Whether the stability of (**5**) and (**6**) towards ring-opening reactions is determined by kinetic or thermodynamic considerations is presently under study.

We gratefully acknowledge the loan of platinum metal salts (Johnson Matthey) and the financial support of C.N.R.S., the S.E.R.C. (studentship to D. C.), and the Saudi Arabian government (studentship to S. S. Al-J.).

Received, 16th May, 1988; Com. 8/01932K

References

1 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.
2 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Chem. Soc., Chem. Commun.*, 1984, 45.
3 F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 275; *Pure Appl. Chem.*, 1987, **59**, 993.
4 A. Marinetti, J. Fischer, and F. Mathey, *J. Am. Chem. Soc.*, 1985, **107**, 5001.
5 J. Svara, A. Marinetti, and F. Mathey, *Organometallics*, 1986, **5**, 1161.
6 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey, and A. Pidcock, *J. Chem. Soc., Chem. Commun.*, 1986, 762.
7 D. Carmichael, P. B. Hitchcock, J. F. Nixon, F. Mathey, and A. Pidcock, *Phosphorus Sulfur*, 1987, **30**, 233.
8 A. Marinetti and F. Mathey, *Tetrahedron Lett.*, 1987, **28**, 5021.
9 D. Gonbeau and G. Pfister-Guillouzo, *Nouv. J. Chim.*, 1985, **9**, 71.
10 K. C. Bishop, *Chem. Rev.*, 1976, **76**, 461.
11 J. F. Nixon and A. Pidcock, *Annu. Rev. NMR Spectrosc.*, 1969, **2**, 345.
12 D. Gonbeau, G. Pfister-Guillouzo, A. Marinetti, and F. Mathey, *Inorg. Chem.*, 1985, **24**, 4133.
13 J. Chatt, R. Mason, and D. W. Meek, *J. Am. Chem. Soc.*, 1975, **97**, 3826.
14 B. E. Mann, A. Musco, *J. Chem. Soc., Dalton Trans.*, 1980, 776.
15 J. Chatt, P. B. Hitchcock, A. Pidcock, C. P. Warrens, and K. R. Dixon, *J. Chem. Soc., Dalton Trans.*, 1984, 2237.
16 N. J. Kermode, M. F. Lappert, B. W. Skelton, A. H. White, and J. Holton, *J. Chem. Soc., Chem. Commun.*, 1981, 698.
17 M. C. Grossel, J. R. Batson, R. P. Moulding, and K. R. Seddon, *J. Organomet. Chem.*, 1986, **304**, 391.
18 D. Seyferth, M. L. Shannon, S. C. Vick, and T. F. O. Lim, *Organometallics*, 1985, **4**, 57 and references therein.