Insertion Reactions of the $[\mathrm{RhCl(PPh_3)_2}]$ Fragment into a Phosphirene Ring, and Carbonylation of the resulting Rhodium(III) Complex. Crystal and Molecular Structures of $[\mathrm{RhCl(PPhCPh{=}CPh)(PPh_3)_2}]$, $[\mathrm{RhCl(PPhCPh{=}CPhCO)(PPh_3)_2}]$ and the Novel Dimeric Complex $[\{\mathrm{RhCl(PPhCPh{=}CPhCO)(PPh_3)}\}_2]$

Florence A. Ajulu,[a] Duncan Carmichael,[a] Peter B. Hitchcock,[a] François Mathey,[b] Mohamed F. Meidine,[a] John F. Nixon,*[a] Louis Ricard[b] and M. Louise Riley[a]

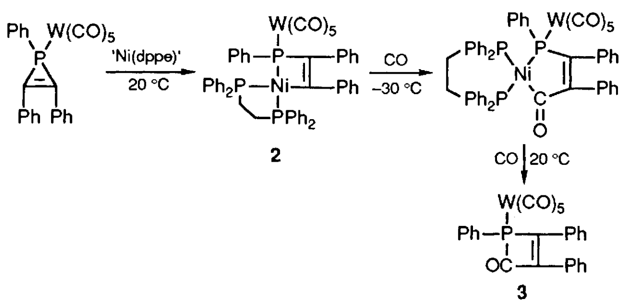
[a] *School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ, UK*
[b] *Laboratoire de Chimie du Phosphore et des Metaux de Transition, DCPH Ecole Polytechnique, 91128 Palaiseau Cedex, France*

The first example of insertion of the d^8 $\mathrm{Rh^I}$ fragment $[\mathrm{RhCl(PPh_3)_2}]$ into a phosphirene ring system results in a five-coordinate $\mathrm{Rh^{III}}$ complex, which undergoes insertion of carbon monoxide to give either monomeric $[\mathrm{RhCl(PPhCPh{=}CPhCO)(PPh_3)_2}]$ or dimeric $[\{\mathrm{RhCl(PPhCPhCO)(PPH_3)}\}_2]$, the structures of which have been elucidated by NMR spectroscopy and single-crystal X-ray diffraction studies.

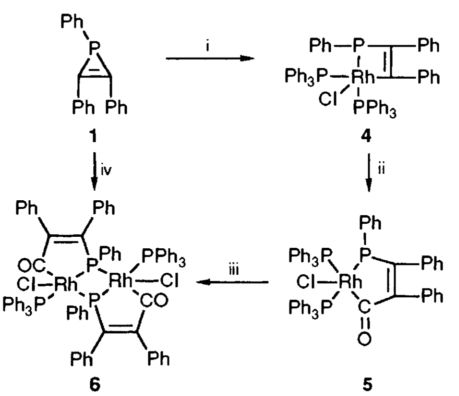
For some time we have been interested in the development of phosphirenes **1** as synthons for organophosphorus chemistry and, in recent papers,[1-3] have demonstrated the mild activation of free and complexed phosphirenes by insertion of d^{10} nickel, palladium and platinum centres into their P–C bonds. The synthetic potential of this approach is illustrated by the facile conversion of a *P*-coordinated phosphirene into the phosphorus analogue **3** of an unsaturated β lactam[4] by use of the nickel-inserted intermediate **2** (see Scheme 1).[5]

While these results were encouraging, our initial attempts to effect carbonylation of the free phosphirene ring with metals of the nickel triad were unsuccessful. In this paper we therefore present a preliminary report concerning the first functionalisation of phosphirenes by rhodium-containing centres, and demonstrate the reactivity of the activated product by insertion of carbon monoxide into the newly formed rhodium–carbon bond.

Triphenylphosphirene **1** reacts rapidly with the rhodium(I)



Scheme 1 dppe = $Ph_2PCH_2CH_2PPh_2$



Scheme 2 *Reagents and conditions*: i, $[RhCl(PPh_3)_3]$ in CH_2Cl_2, room temp.; ii, CO, CH_2Cl_2; iii, C_6H_6, reflux; iv, $[RhCl(CO)(PPh_3)_2]$, C_6H_6, reflux

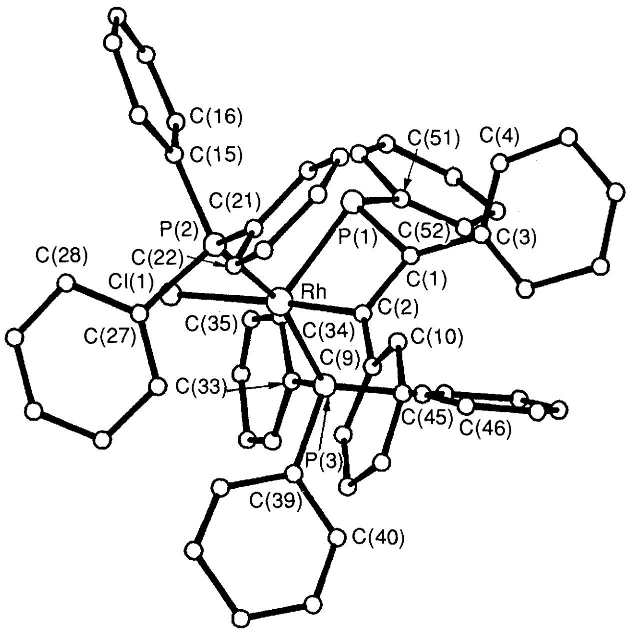


Fig. 1 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Rh–P(1), 2.295(9); Rh–P(2), 2.322(10); Rh–P(3), 2.402(10); Rh–Cl, 2.440(7); Rh–C(2), 1.99(2); P(1)–C(1), 1.83(3); C(1)–C(2), 1.38(4); P(1)–Rh–P(2), 89.8(3); P(1)–Rh–P(3), 104.7(3); P(2)–Rh–P(3), 165.5(3); Rh–P(1)–C(1), 83.9(9); P(1)–C(1)–C(2), 97(2); Rh–C(2)–C(1), 109(2), P(1)–Rh–C(2), 68.7(7).

complex $[RhCl(PPh_3)_3]$ in CH_2Cl_2 solution at room temperature to give the dark purple Rh^{III} complex $[\overline{RhCl(PPhCPh{=}}CPh)(PPh_3)_2]$ **4** in 80% yield. The structure of **4** in solution was established from an ABX (A, B = PPh_3, X

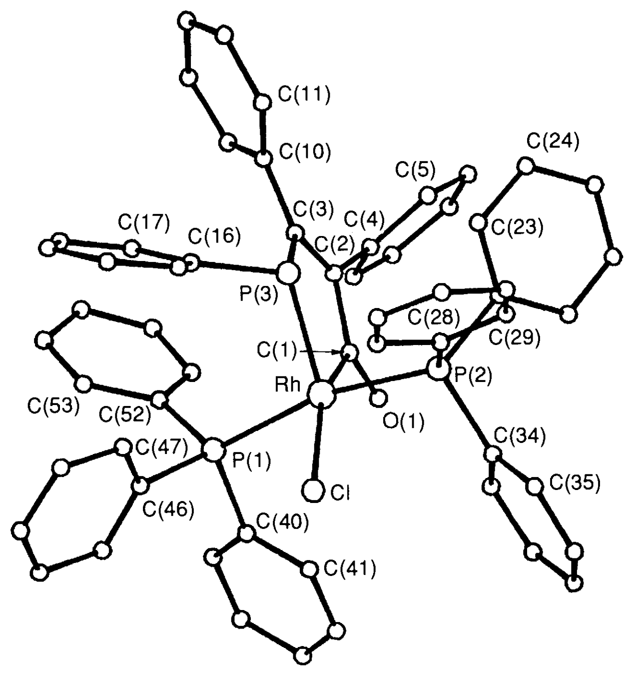


Fig. 2 Molecular structure of **5**. Selected bond lengths (Å) and angles (°): Rh–P(1), 2.368(2); Rh–P(2), 2.339(2); Rh–P(3), 2.269(2); Rh–Cl, 2.432(2); Rh–C(1), 1.993(7); P(3)–C(3), 1.824(7); C(1)–C(2), 1.485(9); C(2)–C(3), 1.340(9); O(1)–C(1), 1.219(8); P(1)–Rh–P(2), 166.29(6); P(1)–Rh–P(3), 104.53(6); P(2)–Rh–P(3), 89.16(6); Rh–P(3)–C(3), 102.0(2); P(3)–C(3)–C(2), 114.5(5); C(1)–C(2)–C(3), 116.5(6); Rh–C(1)–C(2), 112.6(5); P(3)–Rh–C(1), 82.0(2).

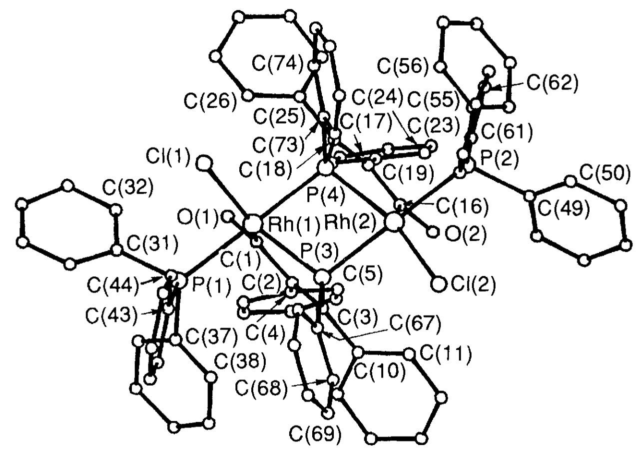


Fig. 3 Molecular structure of **6**. Selected bond lengths (Å) and angles (°): Rh(1)–P(1), 2.406(6); Rh(1)–P(3), 2.243(3); Rh(1)–P(4), 2.355(3); Rh(1)–Cl(1), 2.376(4); Rh(1)–C(1), 2.001(12); O(1)–C(1), 1.202(14); C(1)–C(2), 1.51(2); C(2)–C(3), 1.33(2); P(3)–C(3), 1.813(12); Rh(2)–P(2), 2.408(3); Rh(2)–P(3), 2.352(3); Rh(2)–P(4), 2.251(3); Rh(2)–Cl(2), 2.379(3); Rh(2)–C(16), 1.995(11); O(2)–C(16), 1.217(14); C(16)–C(17), 1.48(2); C(17)–C(18), 1.32(2); P(4)–C(18), 1.818(12); Rh(1)–P(3)–Rh(2), 103.6(1); Rh(1)–P(4)–Rh(2), 103.3(1); P(1)–Rh(1)–P(3), 103.8(1); P(1)–Rh(1)–P(4), 174.3(1); P(2)–Rh(2)–P(3), 174.6(1); P(2)–Rh(2)–P(4), 103.9(1): P(3)–Rh(1)–P(4), 76.2(1); P(3)–Rh(2)–P(4), 76.2(1); Rh(1)–P(4)–C(18), 109.4(4); Rh(2)–P(4)–C(18), 104.6(4); P(4)–Rh(2)–C(16), 79.6(3); P(4)–C(18)–C(17), 113.0(9); C(18)–C(17)–C(16), 117(1); Rh(2)–C(16)–C(17), 124.3(8); O(2)–C(16)–C(17), 123(1); Rh(1)–P(3)–C(3), 105.5(4); Rh(2)–P(3)–C(3), 111.0(4); P(3)–Rh(1)–C(1), 80.0(3); P(3)–C(3)–C(2), 112.5(9); C(3)–C(2)–C(1), 117(1); Rh(1)–C(1)–C(2), 123.1(8); O(1)–C(1)–C(2), 123(1).

$= \mathrm{P_{ring}}$) pattern in its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum† and confirmed for the solid state by a single-crystal X-ray diffraction study (Fig. 1).‡ The highly pyramidal geometry of the terminal phosphide must diminish any 4π lone pair—$\pi_{(\mathrm{C=C})}$ interaction in the metallacyclobutene, and presumably contributes to the stability of the complex.

Treatment of **4** with carbon monoxide in CH_2Cl_2 gave traces of *trans*-$[\mathrm{RhCl(CO)(PPh_3)_2}]$ and 80% of the dark-green crystalline $[\overline{\mathrm{RhCl(PPhCPh{=}CPhC}}\mathrm{O)(PPh_3)_2}]$ **5**,§ the formulation of which as a cyclometallated acyl complex was again confirmed by single-crystal X-ray diffraction‡ (Fig. 2). The insertion of CO into **4** is accompanied by a 111 ppm downfield shift of $\mathrm{P_X}$ and a doubling of the $^1J_{\mathrm{RhP(X)}}$ coupling, which requires an increased $\mathrm{P_X}$ s-electron density and suggests a better localised and more nucleophilic phosphide lone pair.[2,6] Consistently, when **5**, or a solution of $[\mathrm{RhCl(CO)(PPh_3)_2}]$ and triphenylphosphirene, is dissolved in refluxing benzene under an atmosphere of carbon monoxide for 4 h, the orange–red complex $[\{\overline{\mathrm{RhCl(PPhCPh{=}CPhC}}\mathrm{O)(PPh_3)}\}_2]$ **6** (80% yield) is formed by displacement of a triphenylphosphine ligand by the terminal phosphide. Its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum exhibits the [AA′BB′XX′] pattern (A,B = ^{31}P, X = ^{103}Rh, all I = 100% abundant) of a dimeric structure having only one triphenylphosphine ligand per rhodium atom, and a single-crystal X-ray diffraction study‡ confirms a dimeric structure, wherein both cyclometallated phosphide ligands serve as donors to each rhodium centre (Fig. 3).

It is not yet clear whether phosphide bridging facilitates or hinders further reactivity of the coordinated acetyl ligand, but it is already obvious that rhodium centres offer considerable scope for the activation and subsequent functionalisation of small phosphorus-containing rings. Studies of the insertion of small molecules into **4**, and possible pathways for reductive elimination from complexes such as **5**, are in progress.

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† *Spectroscopic data*: $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (chemical shifts in ppm relative to H_3PO_4; positive to high frequency of the reference, J in Hz): for **4**: $\delta\mathrm{P_A}$ 33.5, $\delta\mathrm{P_B}$ 29.9, $\delta\mathrm{P_X}$ 61.0, $^1J_{\mathrm{RhP(A)}}$ 119, $^1J_{\mathrm{RhP(B)}}$ 130, $^1J_{\mathrm{RhP(X)}}$ 45, $^2J_{\mathrm{P(A)P(B)}}$ 398, $^2J_{\mathrm{P(A)P(X)}}$ 21, $^2J_{\mathrm{P(B)P(X)}}$ 4.

For **5**: $\delta\mathrm{P_A}$ 23.1, $\delta\mathrm{P_B}$ 23.6, $\delta\mathrm{P_X}$ 171.7, $^1J_{\mathrm{RhP(A)}}$ 117, $^1J_{\mathrm{RhP(B)}}$ 122, $^1J_{\mathrm{RhP(X)}}$ 84, $^2J_{\mathrm{P(A)P(B)}}$ 370, $^2J_{\mathrm{P(A)P(X)}}$ 43, $^2J_{\mathrm{P(B)P(X)}}$ 9.

For **6**: $\delta\mathrm{P_A}$ 35.0, $\delta\mathrm{P_B}$ 21.3, $^1J_{\mathrm{RhP(A)}}$ 101, 81, $^1J_{\mathrm{RhP(B)}}$ 105, 0, $^2J_{\mathrm{P(A)P(A')}}$ −216, $^4J_{\mathrm{P(B)P(B')}}$ 0, $^2J_{\mathrm{P(A)P(B)}}$ 358, $^2J_{\mathrm{P(A)P(B')}}$ 10, $^2J_{\mathrm{P(A)P(X)}}$ 21, $^2J_{\mathrm{P(B)P(X)}}$ 4.

‡ *Crystallographic data*: For **4** (from C_7H_8–Et_2O). $C_{56}H_{45}ClP_3Rh\cdot CH_2Cl_2$. $M = 1034.2$. Monoclinic, space group $P2_1/n$, $a = 16.204(6)$, $b = 13.320(10)$, $c = 25.470(8)$ Å, $\beta = 104.80(3°)$, $U = 5314.9$ Å^3, $Z = 4$, $D_c = 1.29$ g cm^{-3}, monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 5.9$ cm^{-1}. 6822 reflections for $+h$, $+k$, $\pm l$ were collected from a purple crystal (*ca.* 0.3 × 0.2 × 0.2 mm) on an Enraf-Nonius CAD4 in θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ for $2 < \theta < 22°$, of which 2107 with $|F^2| > 3\sigma(F)^2$ were refined using heavy-atom methods on a microVax computer. A correction for a 36% loss of intensity of two standard reflections during the data collection was made, and refinement by full-matrix least-squares analysis with Rh, P and Cl atoms anisotropic converged at $R = 0.103$, $R_w = 0.134$.

For **5** (from CH_2Cl_2–Et_2O). $C_{57}H_{45}ClOP_3Rh\cdot C_4H_{10}O$. $M = 1051.4$. Monoclinic, space group $P2_1/n$, $a = 13.718(4)$, $b = 16.572(4)$, $c = 23.450(8)$ Å, $\beta = 106.90(3)°$, $U = 5100.5$ Å^3, $Z = 4$, $D_c = 1.37$ g cm^{-3}, monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 5.2$ cm^{-1}. 9306 reflections for $+h$, $+k$, $\pm l$ were collected from a green crystal (*ca.* 0.35 × 0.35 × 0.2 mm) on an Enraf-Nonius CAD4 in θ–2θ mode with $\Delta\theta = (0.8 + 0.35\tan\theta)°$ for $2 < \theta < 25°$ and a maximum scan time of one minute. No corrections for crystal decay or absorption were necessary, and 5594 having $|F^2| > 3\sigma(F)^2$ were processed using heavy-atom and full-matrix least-squares methods with non-hydrogen atoms anisotropic. Refinement converged at $R = 0.059$, $R_w = 0.075$.

For **6** (from C_7H_8). $C_{78}H_{120}Cl_2O_2P_4Rh_2\cdot 3C_7H_8$. $M = 1766.9$. Orthorhombic, space group $Pbca$, $a = 19.699(3)$, $b = 22.007(4)$, $c = 37.932(5)$ Å, $U = 16\,444$ Å^3, $Z = 8$, $D_c = 1.43$ g cm^{-3}, monochromated Mo-Kα radiation, $\lambda = 0.71069$ Å, $\mu = 5.9$ cm^{-1}. 15517 reflections for $+h$, $+k$, $+l$ with $2 < \theta < 25°$ were collected from a 0.1 × 0.1 × 0.05 mm air-stable orange crystal. 5981 having $|F^2| > 3\sigma(F)^2$ were used in the structure determination, which was solved by direct methods and refined to $R = 0.065$, $R_w = 0.077$ by full-matrix least-squares analysis with all non-hydrogen atoms anisotropic.

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

§ **5** is also obtained directly, in improved yield, through treatment of dichloromethane solutions of triphenylphosphirene **1** with *trans*-$[\mathrm{RhCl(CO)(PPh_3)_2}]$ at 40 °C.