Synthesis, Crystal Structure, and Reactivity of the (η^4-1,3-Diphosphacyclobutadiene)(η^5-1,2-dicarbaborane)rhodium Complex $[NEt_4][Rh(\eta^4-P_2C_2Bu^t_2)(\eta^5-C_2B_9H_{11})]$

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Tetrahydrofuran solutions of $K[Rh(PPh_3)_2(\eta^5-C_2B_9H_{11})]$ react with $Bu^tC{\equiv}P$ and NEt_4Cl to afford the salt $[NEt_4][Rh(\eta^4-Bu^t_2C_2P_2)(\eta^5-C_2B_9H_{11})]$, which with $[AuCl(PPh_3)]$ and $[Co(CO)_2(NCMe)(\eta^4-C_4Me_4)][PF_6]$ yields the compounds $[Rh(\eta^4-Bu^t_2C_2P_2ML_n)(\eta^5-C_2B_9H_{11})]$ [ML_n = $Au(PPh_3)$ or $Co(CO)_2(\eta^4-C_4Me_4)$]; all structurally identified by *X*-ray diffraction.

The cyclodimerisation of alkynes at transition metal centres to yield cyclobutadiene complexes has long been known,[1] and recent work has shown that phospha-alkynes can behave similarly forming η^4-1,3-diphosphacyclobutadiene compounds.[2] Related cyclodimerisation reactions of alkynes or phospha-alkynes involving carbametallaborane species are, as far as we are aware, unknown. We now report the cyclodimerisation of $Bu^tC{\equiv}P$ at a rhodium centre ligated by the $\eta^5-C_2B_9H_{11}$ group. The product obtained provides a bridge between phospha-alkyne and carbametallaborane chemistry.

Treatment of $K[Rh(PPh_3)_2(\eta^5-C_2B_9H_{11})]$[3] in THF (tetrahydrofuran) at room temperature with $Bu^tC{\equiv}P$, followed by addition of NEt_4Cl, gives in essentially quantitative yield the dark brown crystalline salt $[NEt_4][Rh(\eta^4-Bu^t_2C_2P_2)(\eta^5-C_2B_9H_{11})]$ (**1**),† the structure of which was established by *X*-ray diffraction.‡ In the anion (Figure 1) the rhodium atom is η^5-co-ordinated by the $C_2B_9H_{11}$ cage, as expected, but the metal is also ligated by an η^4-1,3-diphosphacyclobutadiene ring. Since the groups $\eta^5-C_2B_9H_{11}$ and $\eta-C_5R_5$ (R = H or Me) are isolobal, the anion of (**1**) is mapped with the recently reported compounds $[M(\eta^4-Bu^t_2C_2P_2)(\eta-C_5R_5)]$ (M = Co, Rh

† *Selected spectroscopic data* [the $^{31}P\{^1H\}$ shifts are relative to 85% H_3PO_4 (external)]. Compound (**1**) (brown), ^1H n.m.r. (CD_2Cl_2, room temperature), δ 0.97 (s, 18H, Bu^t), 1.32 (t, 12H, NCH_2Me, J_{HH} 7 Hz), 3.22 (q, 8H, NCH_2Me, J_{HH} 7 Hz) and 3.52 [s, br., 2H, $CH(C_2B_9H_{11})$]; $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, room temperature), δ 111.2 (t of d, Bu^tCP, J_{PC} 52 Hz, J_{RhC} 12 Hz), 53.2 (NCH_2Me), 39.9 [br., $CH(C_2B_9H_{11})$], 35.2 (t, CMe_3, J_{PC} 6 Hz), 31.4 (CMe_3), and 8.0 (NCH_2Me); $^{31}P\{^1H\}$ n.m.r. δ 61.5 (d, J_{RhP} 24 Hz). Compound (**3**) (yellow), $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, room temperature), δ 44.0 [br., $CH(C_2B_9H_{11})$], 35.8 (CMe_3), and 32.2 (CMe_3); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, −60 °C), δ 51.9 (s, PPh_3), 40.0 (d, $PCBu^t$, J_{PP} 213 Hz), and −21.3 (d, $PCBu^t$, J_{PP} 213 Hz). Compound (**4**) (yellow), ν_{CO}(max) 2023vs, 2040w(sh), and 2094w cm^{-1} (CH_2Cl_2); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, −60 °C), isomer (i), δ 69.1 (d, br., J_{PP} 28 Hz) and 42.5 (d, J_{PP} 28 Hz); isomer (ii), δ 92.1 (d, br., J_{PP} 30 Hz) and 37.8 (d, J_{PP} 30 Hz).

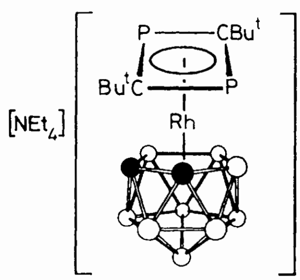
‡ *Crystal data* for (**1**); $C_{20}H_{49}B_9NP_2Rh$, M = 865.8, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 10.152(3), b = 12.205(4), c = 23.919(6) Å, U = 2965(1) Å^3, Z = 4, D_c = 1.35 g cm^{-3}, $F(000)$ = 1184, μ(Mo-K_α) = 6.8 cm^{-1}, R = 0.097 (R_w = 0.084) for 2033 absorption corrected intensities (298 K), θ–2θ scans, 2θ ≤ 50°, $F \geq 2\sigma(F)$, Mo-K_α ($\bar{\lambda}$ = 0.71069 Å). Data were collected on a Nicolet *P3m* diffractometer and the structure was solved by the usual heavy atom and Fourier methods, with refinement by full matrix least squares. (**3**); $C_{30}H_{44}AuB_9P_3Rh$, M = 894.9, monoclinic, space group $P2_1/a$ (non-standard, No. 14), a = 18.51(1), b = 10.363(4), c = 19.00(1) Å, β = 96.17(5)°, U = 3623(3) Å^3, Z = 4, D_c = 1.65 g cm^{-3}, $F(000)$ = 1704, μ(Mo-K_α) = 46.4 cm^{-1}, R = 0.043 (R_w = 0.046) for 3895 unique absorption corrected intensities, θ–2θ scans, 2θ ≤ 50°, $F \geq 5\sigma(F)$. (**4**); $C_{22}H_{41}B_9CoO_2P_2Rh$, M = 658.9, monoclinic, space group $P2_1/c$ (No. 14), a = 16.181(8), b = 10.361(5), c = 19.51(1) Å, β = 101.70(5)°, U = 3203(3) Å^3, Z = 4, D_c = 1.37 g cm^{-3}, $F(000)$ = 1344, μ(Mo-K_α) = 11.4 cm^{-1}, R = 0.13 (R_w = 0.11) for 1786 unique absorption corrected intensities, θ–2θ scans, 2θ ≤ 45°, $F \geq 3.5\sigma(F)$. Data collection and structure refinements for (**3**) and (**4**) were as for (**1**). The high R factor for (**4**) was due to limited and rather weak data obtained from the platelet (0.05 × 0.2 × 0.2 mm). 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.

or Ir) (**2**), obtained by treating the species $[M(C_2H_4)_2(\eta\text{-}C_5R_5)]$ with $Bu^tC{\equiv}P$.[4,5]

Complex (**1**) can be used as a precursor to new species in which a phosphorus atom of the phosphacyclobutadiene ring system co-ordinates to another metal centre. Thus (**1**) with $[AuCl(PPh_3)]$ in the presence of $TlBF_4$ affords the bimetallic complex $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**3**) (95%). Similarly, (**1**) with $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$[6] yields $[Rh\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**) (80%).†

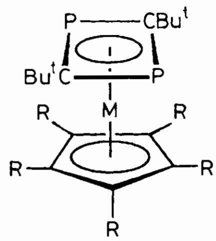
The structures of (**3**) and (**4**) were established by *X*-ray diffraction, and are shown in Figures 2 and 3, respectively.‡ In (**3**) there is a bond [2.269(3) Å] between the gold atom and a phosphorus atom of the C_2P_2 ring, a structural feature also found in (**4**) [Co–P 2.22(1) Å]. There are no rhodium–gold or rhodium–cobalt connectivities in these molecules. In (**3**) and (**4**), as in (**1**) the $\eta^4\text{-}C_2P_2$ rings are square and the atoms deviate little from planarity [mean deviation: ±0.023 (**1**), ±0.048 (**3**), and ±0.039 Å (**4**)]. In solution two isomers (*ca.* 4 : 1) of (**4**) are present, a feature revealed best by the $^{31}P\{^1H\}$ n.m.r. spectrum.† These isomers may arise through restricted rotation about the Co–P(2) bond, leading to different orientations of the $Co(CO)_2(\eta^4\text{-}C_4Me_4)$ fragment.

The molecule (**4**) is unique in containing both cyclobutadiene and diphosphacyclobutadiene ligands. Interestingly, treatment of (**2a**) with $[Co(C_2H_4)_2(\eta\text{-}C_5H_5)]$ gives successively the bi- and tri-metallic complexes $[Co\{\eta^4\text{-}Bu^t{}_2C_2P_2Co(C_2H_4)(\eta\text{-}C_5H_5)\}(\eta\text{-}C_5H_5)]$ (**5**) and $[Co\{\eta^4\text{-}Bu^t{}_2C_2P_2Co_2(C_2H_4)_2(\eta\text{-}C_5H_5)_2\}(\eta\text{-}C_5H_5)]$ (**6**).[5] The structure of (**5**) is akin to that of (**4**). No trimetallic species related to (**6**) was observed in our work, and if formed from the reagent $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ would be cationic in nature. Formulation of the species (**3**) and (**4**) with ylide type structures allows the rhodium centres in both compounds to



(**1**)

○BH ●CH



(**2a**) M = Co, R = H
(**2b**) M = Rh, R = H
(**2c**) M = Co, R = Me
(**2d**) M = Rh, R = Me
(**2e**) M = Ir, R = Me

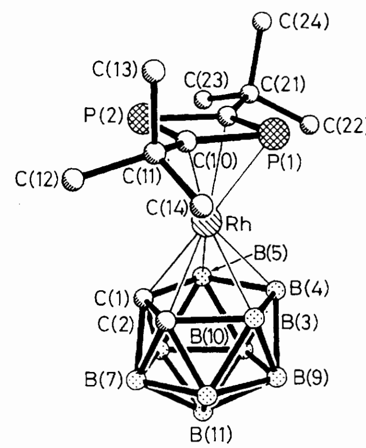
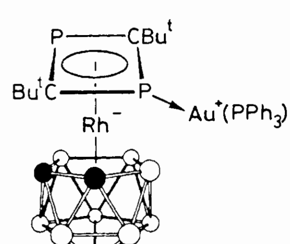
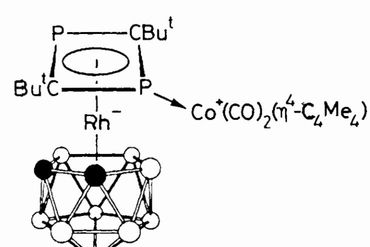


Figure 1. Molecular structure of the anion of $[NEt_4][Rh(\eta^4\text{-}Bu^t{}_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**1**). Dimensions: Rh–P(1) 2.334(6), Rh–P(2) 2.374(6), Rh–C(10) 2.21(2), Rh–C(20) 2.20(2), Rh–C(1) 2.17(2), Rh–C(2) 2.19(2), Rh–B(3) 2.21(2), Rh–B(4) 2.24(3), Rh–B(5) 2.23(3), P(1)–C(10) 1.78(2), P(1)–C(20) 1.80(2), P(2)–C(10) 1.77(2), P(2)–C(20) 1.79(2) Å.



(**3**)



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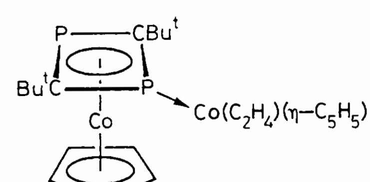
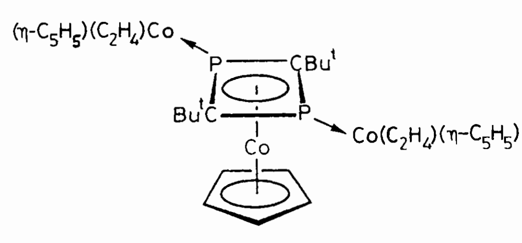


(**5**)



(**6**)

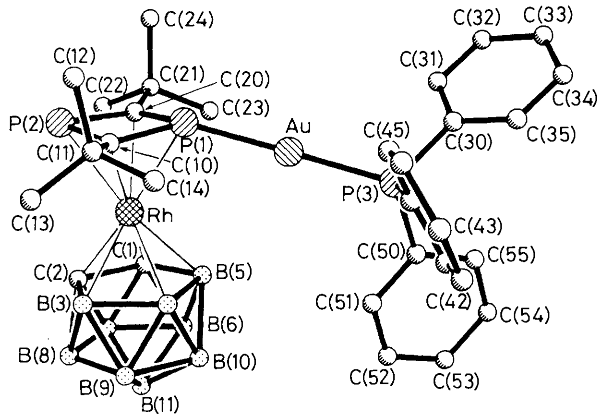


Figure 2. Molecular structure of $[Rh\{\eta^4\text{-}Bu^t_2C_2P_2Au(PPh_3)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**3**). Dimensions: Au–P(1) 2.269(3), Au–P(3) 2.281(3), Rh–P(1) 2.326(3), Rh–P(2) 2.368(3), Rh–C(10) 2.17(1), Rh–C(20) 2.21(1), Rh–C(1) 2.21(1), Rh–C(2) 2.17(1), Rh–B(3) 2.19(1), Rh–B(4) 2.21(1), Rh–B(5) 2.21(1), P(1)–C(10) 1.76(1), P(1)–C(20) 1.76(1), P(2)–C(10) 1.78(1), P(2)–C(20) 1.77(1) Å; P(3)–Au–P(1) 174.5(1), Au–P(1)–C(10) 131.0(3), Au–P(1)–C(20) 137.9(3), Au–P(1)–Rh 108.0(1)°.

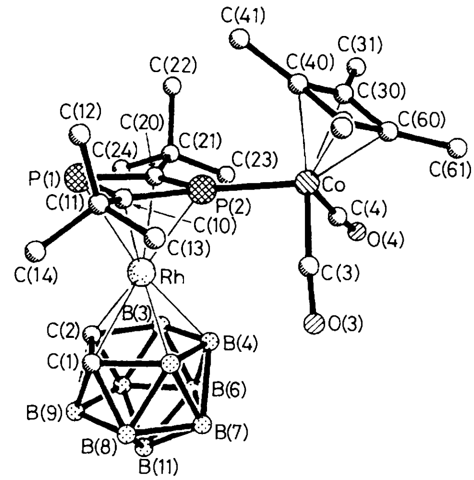


Figure 3. Molecular structure of $[Rh\{\eta^4\text{-}Bu^t_2C_2P_2Co(CO)_2(\eta^4\text{-}C_4Me_4)\}(\eta^5\text{-}C_2B_9H_{11})]$ (**4**). Dimensions: Co–P(2) 2.22(1), Rh–P(1) 2.40(1), Rh–P(2) 2.30(1), Rh–C(10) 2.16(3), Rh–C(20) 2.16(3), Rh–C(1) 2.21(3), Rh–C(2) 2.15(4), Rh–B(3) 2.21(4), Rh–B(4) 2.19(4), Rh–B(5) 2.19(4), P(1)–C(10) 1.69(4), P(1)–C(20) 1.77(3), P(2)–C(10) 1.78(4), P(2)–C(20) 1.73(3), Co–C(η^4–C_4Me_4) (mean) 2.01 Å; Co–P(2)–C(10) 142(1), Co–P(2)–C(20) 139(1), Co–P(2)–Rh 132.1(4)°.

acquire 18 electron valence shells, and the gold and cobalt atoms to have 14 and 18 electron configurations, respectively.

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