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

Helen F. Dare, Judith A. K. Howard, Massimino U. Pilotti, F. Gordon A. Stone, and Jürgen Szameitat

Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS, U.K.

Tetrahydrofuran solutions of $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$ react with $Bu^tC{\equiv}P$ and NEt_4Cl to afford the salt $[NEt_4][Rh(\eta^4\text{-}Bu^t_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$, which with $[AuCl(PPh_3)]$ and $[Co(CO)_2(NCMe)(\eta^4\text{-}C_4Me_4)][PF_6]$ yields the compounds $[Rh(\eta^4\text{-}Bu^t_2C_2P_2ML_n)(\eta^5\text{-}C_2B_9H_{11})]$ [ML_n = Au(PPh$_3$) or Co(CO)$_2$(η^4-C$_4$Me$_4$)]; 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 η^5-$C_2B_9H_{11}$ group. The product obtained provides a bridge between phospha-alkyne and carbametallaborane chemistry.

Treatment of $K[Rh(PPh_3)_2(\eta^5\text{-}C_2B_9H_{11})]$[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 $[NEt_4][Rh(\eta^4\text{-}Bu^t_2C_2P_2)(\eta^5\text{-}C_2B_9H_{11})]$ (**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 η^5-$C_2B_9H_{11}$ and η-C_5R_5 (R = H or Me) are isolobal, the anion of (**1**) is mapped with the recently reported compounds $[M(\eta^4\text{-}Bu^t_2C_2P_2)(\eta\text{-}C_5R_5)]$ (M = Co, Rh

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[†] *Selected spectroscopic data* [the $^{31}P\{^1H\}$ shifts are relative to 85% H_3PO_4 (external)]. Compound (**1**) (brown), ^{1}H n.m.r. (CD_2Cl_2, room temperature), δ 0.97 (s, 18H, Bu^t), 1.32 (t, 12H, NCH$_2$*Me*, J_{HH} 7 Hz), 3.22 (q, 8H, NC*H*$_2$Me, J_{HH} 7 Hz) and 3.52 [s, br., 2H, C*H*($C_2B_9H_{11}$)]; $^{13}C\{^1H\}$ n.m.r. (CD_2Cl_2, room temperature), δ 111.2 (t of d, Bu^t*C*P, J_{PC} 52 Hz, J_{RhC} 12 Hz), 53.2 (N*C*H$_2$Me), 39.9 [br., *C*H($C_2B_9H_{11}$)], 35.2 (t, *C*Me$_3$, J_{PC} 6 Hz), 31.4 (C*Me*$_3$), and 8.0 (NCH$_2$*Me*); $^{31}P\{^1H\}$ 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., *C*H($C_2B_9H_{11}$)], 35.8 (*C*Me$_3$), and 32.2 (C*Me*$_3$); $^{31}P\{^1H\}$ n.m.r. (CD_2Cl_2, −60 °C), δ 51.9 (s, PPh$_3$), 40.0 (d, *P*CBu^t, J_{PP} 213 Hz), and −21.3 (d, *P*CBu^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).

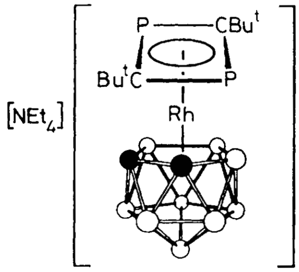
[‡] *Crystal data* for (**1**); $C_{20}H_{49}B_9NP_2Rh$, *M* = 865.8, orthorhombic, space group $P2_12_12_1$ (No. 19), *a* = 10.152(3), *b* = 12.205(4), *c* = 23.919(6) Å, *U* = 2965(1) Å^3, *Z* = 4, D_c = 1.35 g cm^{-3}, *F*(000) = 1184, μ(Mo-K_α) = 6.8 cm^{-1}, *R* = 0.097 (R_w = 0.084) for 2033 absorption corrected intensities (298 K), θ–2θ scans, 2θ ≤ 50°, $F \geqslant 2\sigma(F)$, Mo-K_α ($\bar{\lambda}$ = 0.71069 Å). Data were collected on a Nicolet *P*3*m* 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°, $F \geqslant 5\sigma(F)$. (**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°, $F \geqslant 3.5\sigma(F)$. 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 [$M(C_2H_4)_2(\eta$-$C_5R_5)$] 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 [$Rh\{\eta^4$-$Bu^t{}_2C_2P_2Au(PPh_3)\}(\eta^5$-$C_2B_9H_{11})$] (**3**) (95%). Similarly, (**1**) with [$Co(CO)_2(NCMe)(\eta^4$-$C_4Me_4)$][PF_6][6] yields [$Rh\{\eta^4$-$Bu^t{}_2C_2P_2Co(CO)_2(\eta^4$-$C_4Me_4)\}(\eta^5$-$C_2B_9H_{11})$] (**4**) (80%).†

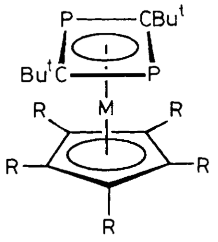
The structures of (**3**) and (**4**) were established by *X*-ray diffraction, and are shown in Figures 2 and 3, respectively.‡ In (**3**) there is a bond [2.269(3) Å] between the gold atom and a phosphorus atom of the C_2P_2 ring, a structural feature also found in (**4**) [Co–P 2.22(1) Å]. There are no rhodium–gold or rhodium–cobalt connectivities in these molecules. In (**3**) and (**4**), as in (**1**) the η^4-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 $Co(CO)_2(\eta^4$-$C_4Me_4)$ fragment.

The molecule (**4**) is unique in containing both cyclobutadiene and diphosphacyclobutadiene ligands. Interestingly, treatment of (**2a**) with [$Co(C_2H_4)_2(\eta$-$C_5H_5)$] gives successively the bi- and tri-metallic complexes [$Co\{\eta^4$-$Bu^t{}_2C_2P_2Co$-$(C_2H_4)(\eta$-$C_5H_5)\}(\eta$-$C_5H_5)$] (**5**) and [$Co\{\eta^4$-$Bu^t{}_2C_2P_2Co_2$-$(C_2H_4)_2(\eta$-$C_5H_5)_2\}(\eta$-$C_5H_5)$] (**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 [$Co(CO)_2(NCMe)(\eta^4$-$C_4Me_4)$][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

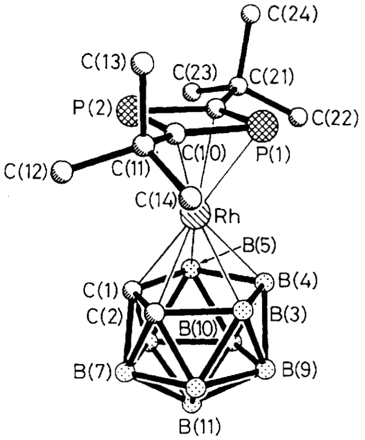
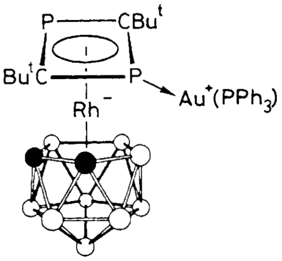
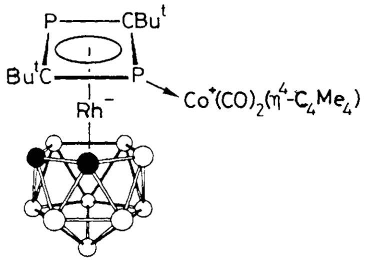


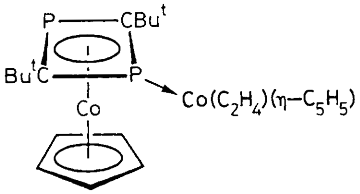
Figure 1. Molecular structure of the anion of [NEt_4][$Rh(\eta^4$-$Bu^t{}_2C_2P_2)(\eta^5$-$C_2B_9H_{11})$] (**1**). Dimensions: Rh–P(1) 2.334(6), Rh–P(2) 2.374(6), Rh–C(10) 2.21(2), Rh–C(20) 2.20(2), Rh–C(1) 2.17(2), Rh–C(2) 2.19(2), Rh–B(3) 2.21(2), Rh–B(4) 2.24(3), Rh–B(5) 2.23(3), P(1)–C(10) 1.78(2),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



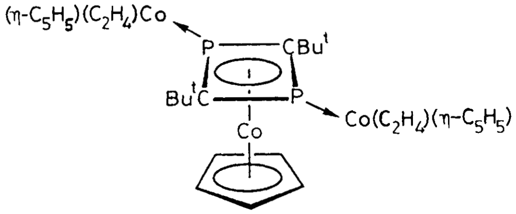
(**3**)



(**4**)



(**5**)



(**6**)

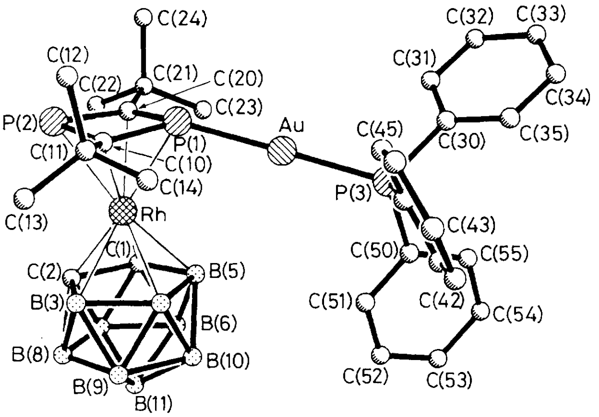


Figure 2. Molecular structure of $[\mathrm{Rh}\{\eta^4\text{-}\mathrm{Bu}^t{}_2\mathrm{C}_2\mathrm{P}_2\mathrm{Au}(\mathrm{PPh}_3)\}(\eta^5\text{-}\mathrm{C}_2\mathrm{B}_9\mathrm{H}_{11})]$ (**3**). Dimensions: Au–P(1) 2.269(3), Au–P(3) 2.281(3), Rh–P(1) 2.326(3), Rh–P(2) 2.368(3), Rh–C(10) 2.17(1), 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)°.

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

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References

1 'Comprehensive Organometallic Chemistry', eds. E. W. Abel, F. G. A. Stone, and G. Wilkinson, vol. 4, sect. 31.3.3; vol. 5, sect. 34.4.4; vol. 6, sect. 38.9, Pergamon, Oxford, 1982, and references cited therein.

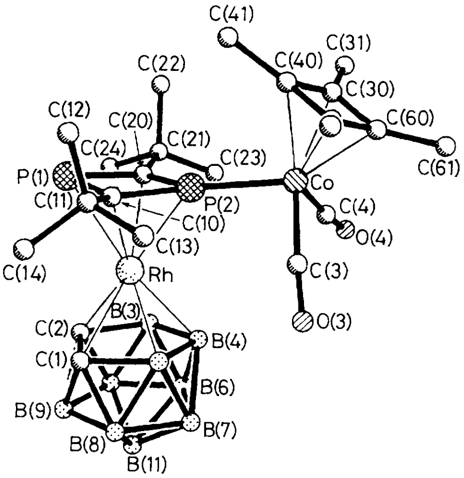

Figure 3. Molecular structure of $[\mathrm{Rh}\{\eta^4\text{-}\mathrm{Bu}^t{}_2\mathrm{C}_2\mathrm{P}_2\mathrm{Co}(\mathrm{CO})_2(\eta^4\text{-}\mathrm{C}_4\mathrm{Me}_4)\}(\eta^5\text{-}\mathrm{C}_2\mathrm{B}_9\mathrm{H}_{11})]$ (**4**). Dimensions: Co–P(2) 2.22(1), Rh–P(1) 2.40(1), Rh–P(2) 2.30(1), 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–$\mathrm{C}_4\mathrm{Me}_4$) (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)°.

2 J. F. Nixon, *Chem. Rev.*, 1988, **88**, 1327; M. Regitz and P. Binger, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1484.
3 J. A. Walker, C. B. Knobler, and M. F. Hawthorne, *Inorg. Chem.*, 1985, **24**, 2688.
4 P. B. Hitchcock, M. J. Maah, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1986, 737.
5 P. Binger, R. Milczarek, R. Mynott, M. Regitz, and W. Rösch, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 644; P. Binger, R. Milczarek, R. Mynott, C. Kruger, Y. H. Tsay, E. Raabe, and M. Regitz, *Chem. Ber.*, 1988, **121**, 637.
6 M. R. Cook, P. Härter, P. L. Pauson, and J. Šraga, *J. Chem. Soc., Dalton Trans.*, 1987, 2757.