First Example of Cyclodimerisation of a Phospha-alkyne to a 1,3-Diphosphacyclobutadiene. Syntheses of Complexes of the Type $[M(\eta^5\text{-}C_5R_5)\{\eta^4\text{-}(Bu^tCP)_2\}]$ R = H or Me; M = Co, Rh, or Ir): Crystal and Molecular Structure of η^5-Pentamethylcyclopentadienyl-2,4-di-t-butyl-1,3-diphosphacyclobutadienecobalt(I), $[Co(\eta^5\text{-}C_5Me_5)\{\eta^4\text{-}(Bu^tCP)_2\}]$

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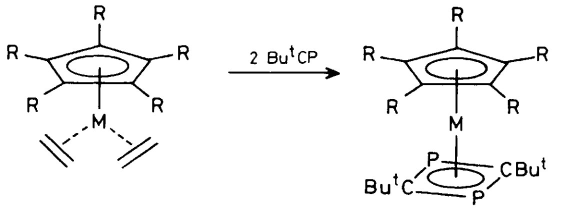
Displacement of ethylene from $[M(\eta^5\text{-}C_5R_5)(C_2H_4)_2]$, (R = H, M = Co or Rh; R = Me, M = Co, Rh, or Ir) by treatment with $Bu^tC\equiv P$ affords complexes containing the novel 2,4-di-t-butyl-1,3-diphosphacyclobutadiene ring.

In previous papers[1—7] we have described the versatility of the phospha-alkyne $Bu^tC\equiv P$ as a ligand in organotransition metal chemistry and have drawn attention to some similarities of its bonding characteristics with those of alkynes $RC\equiv CR$ and metal carbynes $L_nM\equiv CR$.[6] In view of the extensive studies of the interaction of alkynes with various cobalt(I) compounds to produce alkyne, cyclobutadiene, arene, metallacyclopentadiene, and related compounds,[8] we have studied the reaction of complexes of the type $[M(\eta^5\text{-}C_5R_5)(C_2H_4)_2]$ (R = H, M = Co or Rh; R = Me, M = Co, Rh, or Ir)[9—12] with $Bu^tC\equiv P$.



(**1**) R = H, M = Co
(**2**) R = H, M = Rh
(**3**) R = Me, M = Co
(**4**) R = Me, M = Rh
(**5**) R = Me, M = Ir

Reactions were carried out at room temperature in toluene solution to afford red-orange complexes (**1**)—(**5**)† of general formula $[M(\eta^5\text{-}C_5R_5)(Bu^tCP)_2]$. The $\eta^5\text{-}C_5Me_5$ complexes were the most reactive and reaction rates decrease in the order Co > Rh > Ir. Several possible structures (a)—(f) for complexes (**1**)—(**5**) are consistent with the observation of only one type of phosphorus in their ^{31}P n.m.r. spectra. The observation of a very low value for the $^1J_{RhP}$ coupling constant in both (**2**) (31.7 Hz) and (**4**) (29.3 Hz) rules out the η^1-bonding modes in (a) and (e) while (d) and (f) were considered unlikely in view of the relatively weak P–P bonds involved.

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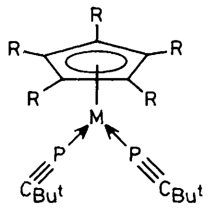
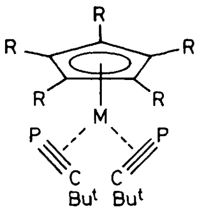
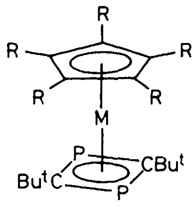
† (**1**) 62%, ^{31}P n.m.r. (toluene, rel. to trimethylphosphite) δ_P −101.0 p.p.m.; (**2**) 16%, ^{31}P n.m.r. δ_P −91.1 p.p.m., $^1J_{RhP}$ 31.7 Hz; (**3**) 95%, m.p. 92—94 °C (decomp.), M^+, *m/z* 394, ^1H n.m.r. ($CDCl_3$) δ 1.0 (s, 18H, Bu^t) and 2.05 (s, 15H, C_5Me_5), ^{31}P n.m.r. δ_P −113 p.p.m.; (**4**) 25%, ^1H n.m.r. δ 0.86 (s, 18H, Bu^t) and 2.17 (s, 15H, C_5Me_5), ^{31}P n.m.r. δ_P −101.4 p.p.m., $^1J_{RhP}$ 29.3 Hz; (**5**) 15%, ^1H n.m.r. δ 0.58 (s, 18H, Bu^t) and 1.90 (s, 15H, C_5Me_5), ^{31}P n.m.r. δ_P −108 p.p.m. All complexes are sufficiently stable in the solid state to allow brief handling in air. Mass spectral data for (**3**): *m/z* 394 (87%, M^+), 332 (32%, $M^+ - 2P$), 256 (100%, $M^+ - 2\,Bu^tC$), and 194 (75%, $M^+ - 2\,Bu^tCP$).



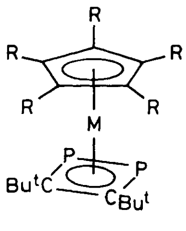
(a)



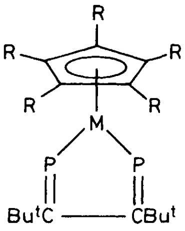
(b)



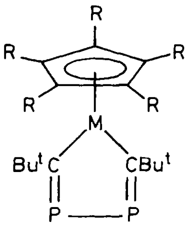
(c)



(d)



(e)



(f)

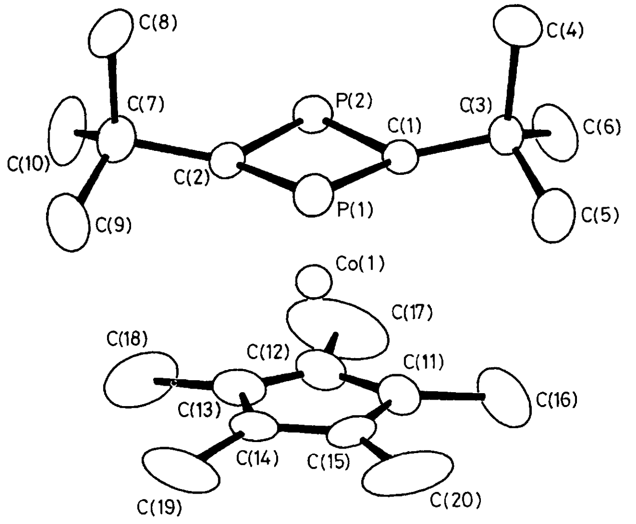
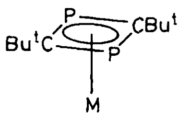
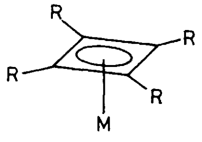


Figure 1. The molecular structure of $[Co(\eta^5\text{-}C_5Me_5)\{\eta^4\text{-}(Bu^tCP)_2\}]$. Some important dimensions are: P(1)–C(1) 1.80(1), P(1)–C(2) 1.79(1), P(2)–C(1) 1.82(1), P(2)–C(2) 1.80(1), Co(1)–P(1) 2.240(3), Co(1)–P(2) 2.244(4), Co(1)–C(1) 2.09(1), Co(1)–C(2) 2.08(1) Å; P(1)–C(1)–P(2) 98.0(5), P(1)–C(2)–P(2) 98.7(5), C(1)–P(1)–C(2) 82.0(5), C(1)–P(2)–C(2) 81.0(5)°. In the other independent molecule the comparable dimensions are: P–C 1.82(1), 1.81(1), 1.81(7), 1.79(1) Å, Co–P 2.247(3), 2.253(4) Å, Co–C 2.09(1), 2.07(1) Å; P–C–P 98.8(5), 97.5(5), C–P–C 81.2(5), 82.0(5)°.

A single crystal analysis‡ of (**3**) enabled a distinction to be made between (b) and (c) and established that a formally forbidden 2 + 2 cyclodimerisation of Bu^{t}CP has occurred to give the first known example of a 1,3-diphosphacyclobutadiene ring. The molecular structure of (**3**) is shown in Figure 1 and exhibits a number of interesting features.



(A)



(B)

The η^4-1,3-diphosphacyclobutadiene ring is essentially planar and all the P–C bond lengths are equivalent indicating that in the complexed form the 1,3-diphosphacyclobutadiene ring is a square rather than a rectangle. This is of interest since it parallels the known behaviour of co-ordinated cyclobutadienes[8,13] [*viz* structure (A) *cf.* (B)]. Interestingly the phosphorous–carbon bond length in (**3**) [1.80(1) Å] is as expected much longer than that of free Bu^{t}CP (1.54 Å) and significantly longer than both the P=C double bond length in phosphaalkenes R_2C=PR (1.69 Å) and phosphorus–carbon distances in phosphabenzenes (1.75 Å) in line with the anticipated bond orders.

The reactivity of the co-ordinated diphosphacyclobutadiene ring in (**3**) is under study.

We thank the S.E.R.C. for continuing financial support for the work and the University of Malaya, Malaysia, for a grant to M. J. M.

Received, 30th January 1986; Com. 134

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‡ *Crystal data:* $C_{20}H_{33}CoP_2$, M = 394.4, triclinic, space group $P\bar{1}$, a = 9.354(3), b = 12.875(6), c = 19.534(7) Å, α = 74.20(3), β = 78.08(3), γ = 89.95(3)°, Z = 4. The structure was solved by heavy atom methods and refined to R = 0.077 using 3702 reflections with $I > \sigma(I)$ measured on an Enraf-Nonius CAD4 diffractometer. The two independent molecules are essentially the same. 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, 1986.