First Example of a 1,2,4-Triphosphabuta-1,3-diene Complex: Synthesis and Crystal and Molecular Structure of [Co(η^5-$C_2R_2P_3$)(η^4-$C_2R_2HP_3$)] (R = Bu^t)

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Treatment of $CoCl_2$ with Li($C_2R_2P_3$) (R = Bu^t) in 1,2-dimethoxyethane yields the complex [Co(η^5-$C_2R_2P_3$)(η^4-$C_2R_2HP_3$)] containing a ligated 1,2,4-triphosphacyclopenta-1,3-diene ring system.

There is considerable current interest in the ligating behaviour of unsaturated organophosphorus ligands.[1] It has become increasingly apparent that formal replacement of a CH fragment by P or a CH_2 fragment by PR in organic compounds can lead to a variety of novel unsaturated organophosphorus compounds, many of which form complexes with transition metals. During the past few years the structural types (**a**)—(**h**) have been established (ML_n = transition metal and attendant ligands).[2—14]

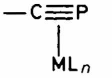
Very recently Mathey *et al.*[15] described the first example of an η^4-ligated 1-phosphabutadiene system (**i**) {ML_n = [W(CO)$_4$]} as its [W(CO)$_5$] adduct, formed *via* a coupling reaction of a vinyl carbene metal complex with the transient phosphinidene compound [W(CO)$_5$PPh]. We now describe the first example of a 1,2,4-triphosphabutadiene metal complex of type (**j**), which further extends the range of ligated unsaturated phosphorus ligands.

Treatment of Li($C_2R_2P_3$) (R = Bu^t) in 1,2-dimethoxyethane with $CoCl_2$ gave a low yield (*ca.* 5%) of the red diamagnetic complex [Co(η^5-$C_2R_2P_3$)(η^4-$C_2R_2HP_3$)] (**1**).† The $^{31}P\{^1H\}$ n.m.r. spectrum (Figure 1) exhibits two widely spaced ABX patterns for the two sets of three nonequivalent phosphorus nuclei in the two rings which have been fully analysed.‡ A single crystal *X*-ray structural determination reveals the molecular structure shown in Figure 2, indicating that the complex should be formulated as an (η^5-1,3,5-triphosphacyclopentadienyl)(η^4-1,2,4-triphosphacyclopentadiene)cobalt derivative.§

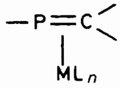
The complex (**1**) may arise from the intermediate paramagnetic [Co(η^5-$C_2Bu^t_2P_3$)$_2$] precursor by H abstraction from the solvent, since the yield is increased when the reaction is carried out in the presence of cyclopentadiene.

The η^5-1,3,5-triphosphacyclopentadienyl ring is planar as expected and the bond distances and bond angles are similar to those previously described for [Fe(η^5-$C_2Bu^t_2P_3$)$_2$][14] and [Fe(η^5-$C_2Bu^t_2P_3$)(η^5-C_5H_5)W(CO)$_5$].[16] The PPCP framework of the η^4-ligated 1,2,4-triphosphabutadiene fragment of the ($C_2Bu_2HP_3$) ring is also planar, and the C–P and P–P bond lengths (summarised in Figure 3) lie in the expected range for this unsaturated system.

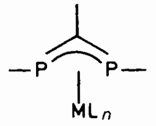
Interestingly the H atom attached to the unligated carbon atom of the η^4-($C_2Bu^t_2HP_3$) ring occupies an *endo*-position, but in contrast to analogous cyclopentadienylcyclopentadienecobalt complexes [Co(η^5-C_5H_5)(η^4-C_5H_5R)][17,18] it has



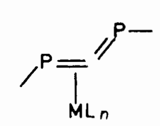
(**a**)



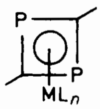
(**b**)



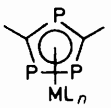
(**c**)



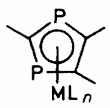
(**d**)



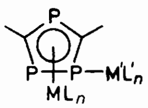
(**e**)



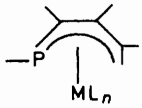
(**f**)



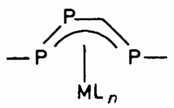
(**g**)



(**h**)



(**i**)



(**j**)

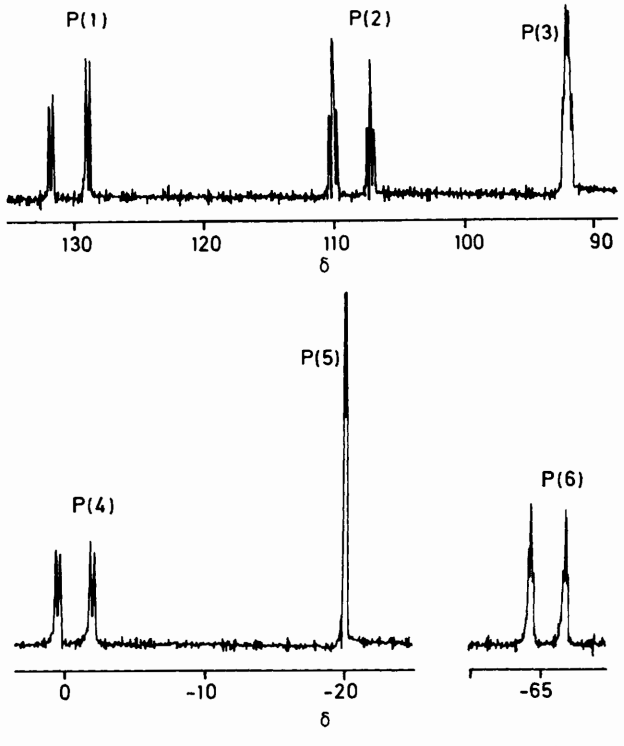


Figure 1. $^{31}P\{^1H\}$ N.m.r. spectrum of the complex (**1**).

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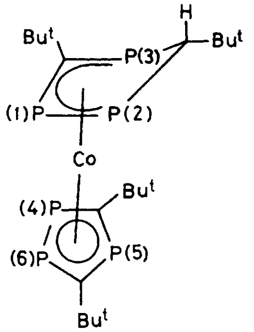
† *m/z* 522 (M^+, 40%) and 465 {[Co($C_2Bu^t_2P_3$)($C_2Bu^tHP_3$)]$^+$, 100%}.

‡ *Selected spectroscopic data:* ^{31}P δ (rel. H_3PO_4) P(1) +131.2, P(2) +109.5, P(3) +93.1, P(4) +0.2, P(5) −20.1, P(6) −64.7; $^1J_{P(1)P(2)}$ 419.7, $^2J_{P(1)P(3)}$ 41.6, $^2J_{P(2)P(3)}$ 40.2, $^1J_{P(4)P(6)}$ 360.6, $^2J_{P(5)P(6)}$ 24.5, $^2J_{P(4)P(6)}$ 24.5, $^2J_{P(2)P(4)}$ 39, $^2J_{P(3)P(6)}$ 24.2 Hz; ^{1}H δ 1.50 (Bu^t), 1.36 (Bu^t), 1.28 (Bu^t), 1.21 (Bu^t), and 0.8 (br., CH).

§ *Crystal data:* $C_{20}H_{37}CoP_6$, M = 522.3, triclinic, space group $P\bar{1}$, a = 10.489(10), b = 10.631(10), c = 12.573(8) Å α = 72.25(9), β = 89.94(8), γ = 79.65(9)°, U = 1311.4 Å^3, Z = 2, D_c = 1.32 g cm^{-3}, monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 10.2 cm^{-1}. The structure was solved by routine heavy-atom methods and refined by full-matrix least-squares with non-hydrogen atoms anisotropic using 2953 reflections with $I > \sigma(I)$ measured with an Enraf-Nonius CAD4 diffractometer. The hydrogen atom on C(3) was located on a difference map and refined isotropically. The final residuals were R = 0.088, R' = 0.107, with 248 parameters refined. The rather high R factor is a consequence of the weak diffraction from the crystal. 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.



(1)

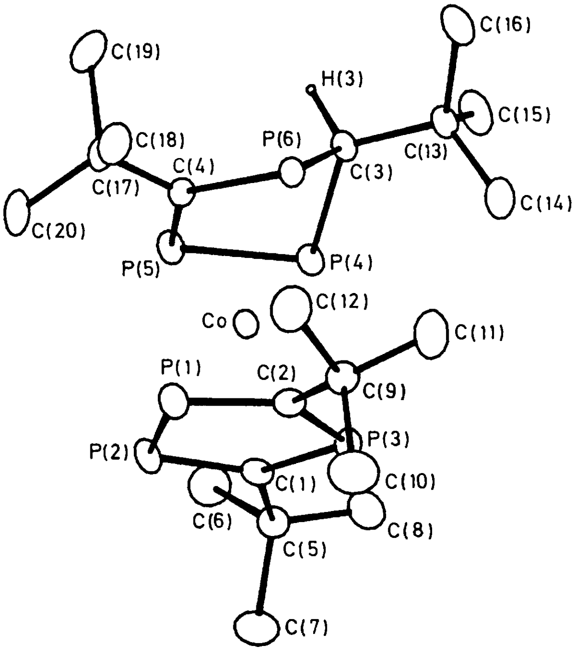


Figure 2. Molecular structure of complex (**1**).

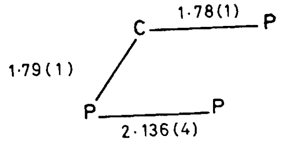


Figure 3. Bond lengths for the PPCP system in the complex (**1**).

not yet been possible to generate the $[Co(\eta^5\text{-}C_2Bu^t_2P_3)_2]^+$ cation {which would be isoelectronic with $[Fe(\eta^5\text{-}C_2Bu^t_2P_3)_2]$} by treatment of (**1**) with either CCl_4 or $Ph_3C^+BF_4^-$, presumably because of steric factors.

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