

Remarkable Carbonylation of a Co-ordinated Phospha-alkyne Bu^tC≡P to afford the Novel Phosphinidene Ligand Bu^tC(CO)P, Crystal and Molecular Structure of [Re₂(CO)₈Pt(dppe){Bu^tC(CO)P}] (dppe = 1,2-bisdiphenylphosphinoethane)

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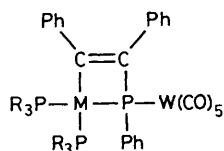
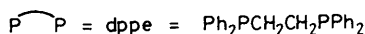
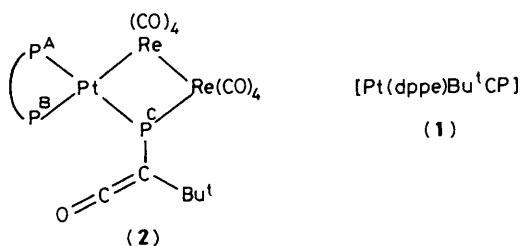
An unusual carbonylation of a co-ordinated phospha-alkyne to give a phosphinidene is reported.

In a series of papers¹⁻⁸ we have described the variety of bonding modes exhibited by the phospha-alkyne ligands RC≡P (R = Bu^t, adamantyl) in transition metal complexes. Previously we showed that the η²-bonding mode of the co-ordinated phospha-alkyne in [Pt(dppe)Bu^tCP] (1) changed on treatment with [Fe₂(CO)₉] to a μ³, η² ⊥ type in the complex [Pt(dppe)(Bu^tCP)Fe₂(CO)₆].²

We now report an unusual reaction in which the co-ordinated Bu^tCP in (1) is attacked by carbon monoxide to produce a complex containing the remarkable phosphinidene

moiety Bu^tC(CO)P. Thus treatment of (1) with [Re₂H₂(CO)₈] at room temperature gave a low yield (ca. 10%) of a red complex (2) among other products. The ³¹P{¹H} n.m.r. spectrum of (2) showed similarity to that we described recently⁹ for (3) indicating the presence of three types of phosphorus in a roughly square planar environment.†

A single crystal structure determination on (2) revealed the unusual molecular structure shown in Figure 1, in which the



(3)

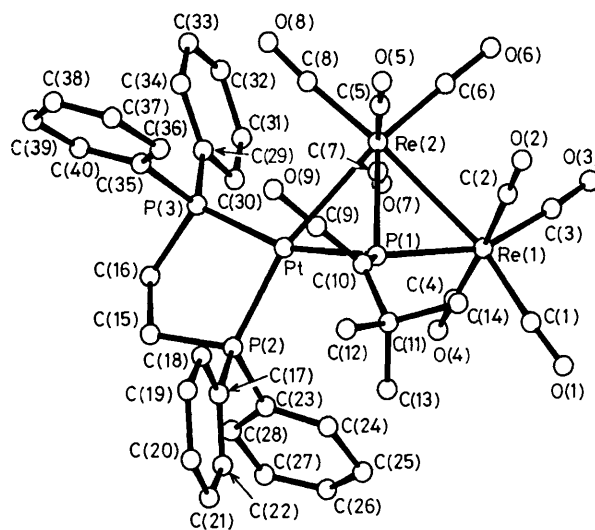


Figure 1

† ³¹P N.m.r. data for (2): δ P^A - 84.1, P^B - 93.0, P^C + 142.0 p.p.m.; J(PtP^A) 2710; J(PtP^B) 3590, J(PtP^C) 2120, J(P^AP^B) 0, J(P^AP^C) 267, J(P^BP^C) 23 Hz.

Bu[†]C(CO)P generated by CO attack at the C atom of Bu[†]CP acts as a bridge between platinum and one of the rhenium atoms.‡

As expected the P(1)–C(10) bond length [1.83(2) Å in (2)] is typical of a single bond and the P(1)C(10)C(11), C(9)C(10)C(11), and P(1)C(10)C(9) bond angles are close to 120°.

Although structures (2) and (3) appear to be related using the isolobal relationship $\text{Re}(\text{CO})_4 \leftrightarrow \text{CR}$ suggesting the presence of an Re=Re double bond in (2), the observed Re(1)–Re(2) distance [3.044(1) Å] is almost identical with the single bond length observed in $[\text{Re}_2(\text{CO})_{10}]^{10}$ of 3.041(1) Å. Furthermore it should be noted that whereas the environment around phosphorus in (2) is planar, in (3) it is approximately tetrahedral.⁹ A further interesting feature of the structure of (2) is the relatively short transannular P(1)–Re(2) distance [2.371(6) Å] compared with P(1)–Re(1) [2.453(6) Å].

The attack of carbon monoxide on a co-ordinated phosphoalkyne to generate the R(CO)P fragment is of interest since it may be the first step in the coupling of two phosphoalkynes

‡ *Crystal Data:* C₄₀H₃₃O₉P₃PtRe₂, *M* = 1318.1, monoclinic, space group *P*2₁/*c*, *a* = 14.356(4), *b* = 12.012(2), *c* = 25.570(6) Å, β = 94.01(2)°, *U* = 4398.7 Å³, *Z* = 4, *D_c* = 1.99 g cm⁻³. The structure was solved by heavy atom methods and refined to *R* = 0.060 using 3812 reflections with *I* > σ(*I*) measured on an Enraf-Nonius CAD4 diffractometer. 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.

RC≡P (R = adamantyl), via carbon monoxide which we observed recently⁷ in the formation of the ligand PCR(CO)PCR and further studies of this type of reaction are planned.

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