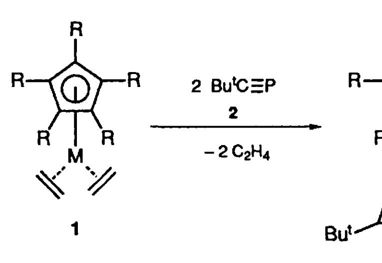
Bis(2,4-di-t-butyl-η^4-1,3-diphosphacyclobutadiene)nickel[1]

Thomas Wettling,[a] Gotthelf Wolmershäuser,[a] Paul Binger,[b] and Manfred Regitz*[a]

[a] *Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-6750 Kaiserslautern, FRG*
[b] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-4330 Mülheim a.d. Ruhr, FRG*

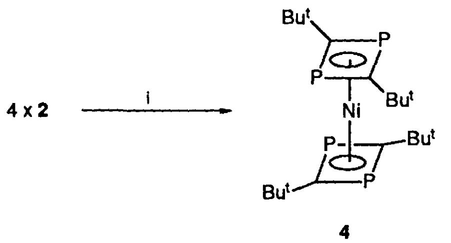
t-Butylphosphaacetylene **2** reacted with nickel acetylacetonate/n-butyllithium to furnish the title compound **4**, the structure of which has been elucidated by X-ray crystallography.

The pioneering work on the cyclotetramerisation of acetylene with nickel(II) cyanide or nickel(II) β-diketonates under pressure,[2] reactions which can also be realised in principle with nickel(0) compounds,[3] prompted the question as to whether or not phosphaalkynes[4] would exhibit similar behaviour. It is known that phosphaalkynes such as **2**[5] undergo cyclodimerisation with (η^5-cyclopentadienyl)bis(ethene)-cobalt, -rhodium, or -iridium complexes **1** to give products **3** in which λ^3-1,3-diphosphacyclobutadiene units are incorporated as η^4-ligands, Scheme 1.[6–8] Similar complexes with iron as the



R = H; M = Rh, Co
R = Me; M = Co, Rh, Ir

Scheme 1



Scheme 2 *Reagents and conditions*: i, Ni(acac)$_2$, 2 Bu^{n}Li, THF, −78 to +25 °C.

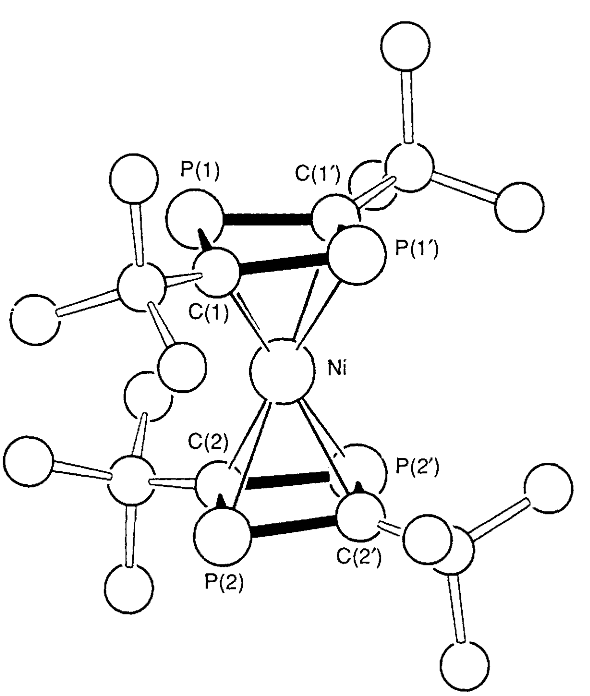


Fig. 1 Molecular structure of C$_{20}$H$_{36}$NiP$_4$, **4**. H atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ni–P(1) 2.252(2); Ni–P(2) 2.250(2); Ni–C(1) 2.063(7); Ni–C(2) 2.094(7); P(1)–C(1) 1.793(9); P(1)–C(1′) 1.806(8); P(2)–C(2) 1.800(9); P(2)–C(2′) 1.790(8); P(1)–C(1)–P(1′) 97.9(4); P(2)–C(2)–P(2′) 98.6(4); C(1)–P(1)–C(1′) 81.7(4); C(2)–P(2)–C(2′) 81.3(4).

central atom and the same dimeric ligands have also been prepared.[9,10] Furthermore the first results of the cyclotrimerisation of **2** have been reported.[8]

We now report on the first results of the cyclooligomerisation of **2** with nickel(0); the reaction gives rise to a compound containing four phosphaalkyne units. The product **4** is obtained in the form of orange–red crystals (from n-pentane at −78 °C, decomposition at 205 °C) when nickel acetylacetonate in tetrahydrofuran (THF) at −78 °C is reduced with n-butyllithium, followed by dropwise addition of compound **2**[5]; the mixture is then allowed to thaw by warming up to room temperature, concentrated, and the residue subjected to bulb-to-bulb sublimation at 250 °C (oven temperature) and 10^{-2} mbar (1 mbar = 10^2 Pa), Scheme 2.

Spectroscopic data and X-ray crystallography demonstrate that the product is bis(2,4-di-t-butyl-η^4-1,3-diphosphacyclobutadiene)nickel **4**.†‡ It thus represents the first metal complex containing two λ^3-1,3-diphosphacyclobutadiene ligands. To the best of our knowledge, only one comparable nickel(0) complex with tetraphenylcyclobutadiene units is known[11] but this was prepared in a completely different manner.

When the NMR signals of the carbon atoms of the four-membered rings as well as those of the phosphorus atoms of **4** are compared with those of complexes of the type **3**,[6–8] it is seen that the latter are markedly shifted to higher fields, whereas the coupling constants between the two nuclei in both types of complex are very similar.

The single crystal X-ray analysis (Fig. 1) shows that the 18e-complex **4** is a sandwich compound with crystallographic C_2 symmetry. The rotation axis is defined by the centres of the decks and the nickel atom. The t-butyl substituents of the two four-membered rings are arranged in an almost perfect staggered orientation.

Within the limits of error, all four C–P bond lengths are identical. Their average value amounts to 1.797 Å and is comparable with those found for similar sandwich and half-sandwich compounds containing a C$_2$P$_2$ layer.[7,8] The rhombus-like distortion of the C$_2$P$_2$ four-membered rings is also in accordance with previous results. Whereas the average value for the C–P–C′ angle is 81.5°, that of the P–C–P′ angle is 98.3°. The Ni–P distances (average value 2.251 Å) are in the expected range. However, the two Ni–C distances are slightly different [2.063(7) and 2.094(7) Å]. This is also reflected in the differing folding angles of the two four-membered rings. In the first case, the dihedral angle of the two CP$_2$ planes is 169.9° and in the second case 174.6°. With respect to the CP$_2$ planes the t-butyl groups are inclined by 14.2 and 10.2°, respectively away from the central atom.

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† *Spectroscopic data* for **4**, C$_{20}$H$_{36}$NiP$_4$: MS (70 eV), m/z 458 (M$^+$, 50%); ^{1}H NMR (C$_6$D$_6$) δ 1.28 (s); ^{13}C NMR (C$_6$D$_6$) δ 36.4 [t, $^2J_{C,P}$ 6.6 Hz, C(CH$_3$)$_3$], 33.0 [s, C(CH$_3$)$_3$], 135.8 (tt, $^1J_{C,P}$ 57.8 Hz, $^2J_{C\text{-}Ni\text{-}P}$ 4.5 Hz, C-ring); ^{31}P NMR (C$_6$D$_6$) δ 81.2 ppm.

‡ *Crystal data* for C$_{20}$H$_{36}$NiP$_4$: monoclinic, space group $C2/c$, a = 18.046(2), b = 8.883(2), c = 16.860(2) Å, β = 117.25(1)°, U = 2402.6(5) Å^3, Z = 4, D_c = 1.27 g cm^{-3}, μ = 10.07 cm^{-1}. A crystal (0.36 × 0.31 × 0.15 mm) was mounted on an Enraf-Nonius CAD-4 diffractometer, and 1966 reflections were measured at ambient temperature using Mo-Kα radiation (λ = 0.71073 Å), of which 1668 with $I > 3\sigma(I)$ were employed for the calculations. The structure was solved by direct methods (SHELXS 86). All non-hydrogen atoms were refined anisotropically, and a riding model starting from calculated positions was employed for the hydrogen atoms. 134 Parameters were refined with a weighting scheme [$w^{-1} = \sigma^2(F) + 0.0002\,F_o^2$]. The final values for R and R_w were 0.066 and 0.083, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to the Authors, Issue No. 1.

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