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Ligating similarities between the novel five-electron-donor η^4-$P_3C_2Bu^t_2(R)H$ ring system, ($R = CH(SiMe_3)_2$) and the η^5-cyclopentadienyl ring. Syntheses, crystal and molecular structures of $[Co_2(CO)_5(\mu$-$P_3C_2Bu^t_2CH(SiMe_3)_2)]$ and $[Co(CO)_2(\eta^4$-$P_3C_2Bu^t_2H(CH(SiMe_3)_2]$

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Abstract

Treatment of the 1,2,4-triphosphole, $P_3C_2Bu^t_2(CH(SiMe_3)_2)$, with $[Co_2(CO)_8]$ in THF under mild conditions affords the binuclear complex $[Co_2(CO)_5(\mu$-$P_3C_2Bu^t_2CH(SiMe_3)_2)]$, in which the ring acts as a six-electron donor. Under slightly more vigorous reaction conditions an H-transfer reaction occurs (presumably from the solvent) to afford the mononuclear compound $[Co(CO)_2(P_3C_2Bu^t_2H(CH(SiMe_3)_2)]$ containing an η^4-ligated five-electron-donor $P_3C_2Bu^t_2H(CH(SiMe_3)_2$ ring system. The molecular structures of both compounds have been determined by single-crystal X-ray diffraction studies. © 2000 Elsevier Science S.A. All rights reserved.

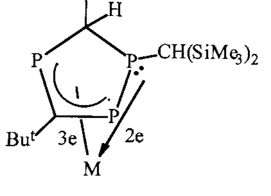
Keywords: Ruthenium; Cobalt; Triphosphole; Cyclopentadienyl

1. Introduction

Recently [1], we reported novel intramolecular H-transfer in the η-1,2,4-triphosphole ruthenium(0) complex $[Ru(\eta^4$-$C_8H_{12})(\mu$-$P_3C_2Bu^t_2(CH(SiMe_3)_2)]$ (**1**) to form $[Ru(\eta^5$-$C_8H_{11})(\eta^5$-$P_3C_2Bu^t_2H(CH(SiMe_3)_2)]$ (**2**) in the presence of PPh_3.

It seems likely that the hydrogen-transfer reaction from one ring to the other proceeds via the ruthenium centre, the first step presumably involving rearrangement of the η^4-ligated cycloocta-1,5-diene to the η^4-bonded cycloocta-1,3-diene isomer. The role of PPh_3 may be to accelerate the isomerisation step, possibly via the intermediacy of an η^2-monoalkene complex (see Scheme 1).

The η^4-bonding of the tri-phosphorus ring system, $P_3C_2Bu^t_2H(CH(SiMe_3)_2)$, to the metal centre in **2** can be considered as involving an η^3-1,3-diphospha-allyl component (three-electron-donor) which is augmented by an η^1-interaction (two-electron-donor) from the λ^3-P centre as shown below.



However, since all four atoms in the coordinated PPCP fragment of the $P_3C_2Bu^t_2H(CH(SiMe_3)_2$ ring in **2** are coplanar and they also lie parallel to the five carbon atoms of the η^5-ligated cyclooctadienyl ring, compound **2** can be also regarded as a pseudo-ruthenocene, containing both an η^5-bonded cyclo-octadienyl ring and the η^4-five-electron-donor $P_3C_2Bu^t_2H(CH(SiMe_3)_2$ ring, the latter having similar overall bonding characteristics to those of an η^5-cyclopentadienyl ligand. In this paper, we describe a further example of a mononuclear cobalt complex containing this type of η^4-ligated $P_3C_2Bu^t_2H$-

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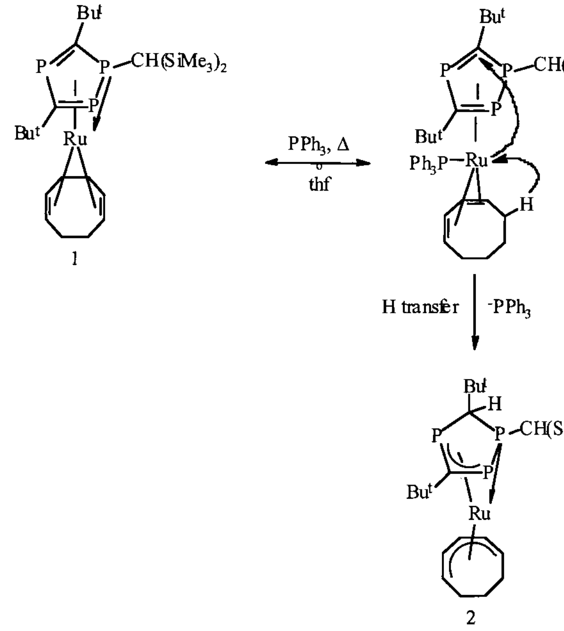
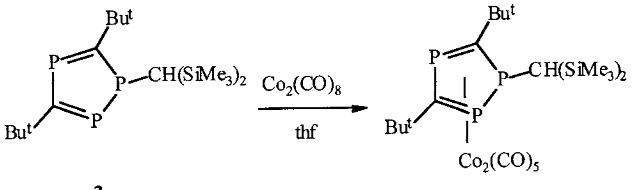


Scheme 1.

$(CH(SiMe_3)_2$ ring system which is formed from a precursor 1,2,4-triphosphole dicobalt complex.

2. Results and discussion

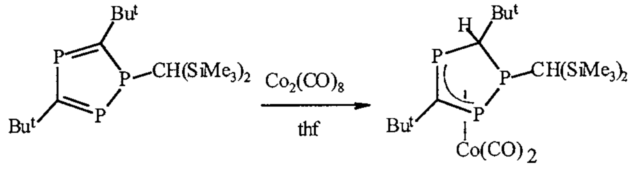
We find that, depending on the reaction conditions, the neutral triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ (**3**) [2] reacts with $[Co_2(CO)_8]$ in THF to give either the binuclear complex $[Co_2(CO)_5(\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2)]$ (**4**), in which the triphosphole acts as a six-electron donor to the two metal centres (similar to that which we previously reported [2]) in the compound $[Fe_2(CO)_6(\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2)]$ (**5**), or the mononuclear complex $[Co(CO)_2(P_3C_2Bu^t_2H(CH(SiMe_3)_2)]$ (**6**) in which the new triphospha-ring system, which has acquired an extra H atom (presumably from the solvent) acts as a five-electron donor. Complex **6** is thus structurally directly analogous to the long-known complex $[Co(CO)_2(\eta^5\text{-}C_5H_5)]$ and to monophospholyl complexes of the type $[Co(CO)_2(\eta^5\text{-}PC_4R_4)]$ [3–6].



3 **4**

Thus, treatment of **3** with $[Co_2(CO)_8]$ (in THF at room temperature for 19 h affords the brown complex $[Co_2(CO)_5(\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2)]$ (**4**) (40%), which has been fully spectroscopically characterised and its molecular structure, shown in Fig. 1, has been determined by a single-crystal X-ray diffraction study.

A similar reaction in which **3** and $[Co_2(CO)_8]$ were heated at 50°C for 3 h gave in addition to **4** (12.5%), the new red mononuclear complex $[Co(CO)_2(P_3C_2Bu^t_2H(CH(SiMe_3)_2)]$ (**6**) in 25% yield, which was also fully characterised spectroscopically and by a single-crystal X-ray analysis (Fig. 2).



3 **6**

The mass spectrum of compound **4** exhibits a parent ion at *m/e* 648 together with peaks corresponding to successive loss of five CO molecules and its infrared (IR) spectrum contains four terminal ν(CO) stretching bands at 2045, 2007, 1976 and 1971 cm^{-1} and one bridging band at 812 cm^{-1}. The $^{31}P\{^1H\}$-NMR spectrum of **4** showed the expected [AMX] pattern of lines; however, because of quadrupolar broadening by the two ^{59}Co nuclei, the small two-bond *J*(PP) coupling constants were not resolvable. The ^1H-NMR spectrum exhibited the expected resonances for the two inequivalent Me_3Si– groups and resonances for the two types of Bu^t group; however, the CH resonance was too broad to be seen.

A single-crystal X-ray study established the molecular structure of **4** in which the 1,2,4-triphosphole ring acts as a six-electron donor to give the optimum 18-valence-electron configuration for each cobalt atom.The Co(1)–Co(2) bond distance (2.590(2) Å) is similar to the value found in $[Co_2(CO)_8]$ (2.54 Å) and $[Fe_2(CO)_9]$ (2.523 Å) [7], but is significantly shorter in comparison with the Fe–Fe distance in the corresponding bridging triphosphole complex $[Fe_2(CO)_6(\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2)]$ (2.910(1) Å) (**5**) [2], presumably as a consequence of the presence of a bridging CO group in **4** which is absent in **5**. The ring geometry in **4** is considerably distorted from that of the parent triphosphole compound **3** [2] and all the bonds are longer. Bond length and bond angle data for **3**, **4** and **5** are listed in Tables 1 and 2.

The fact that the ring has expanded to accommodate the $[Co_2(CO)_5]$ fragment is surprising since this does not happen when the monophosphole, 1-*tert*-butyl-3,4-dimethylphosphole, is coordinated to a $[Mn_2(CO)_7]$ fragment [8], presumably because the smaller monophosphole ring is more strained.

The mass spectrum of **6** showed a parent ion at *m/e* 506 and peaks corresponding to the successive loss of two CO molecules. As expected, the IR spectrum in the ν(CO) stretching region is much simpler than that of **4**,

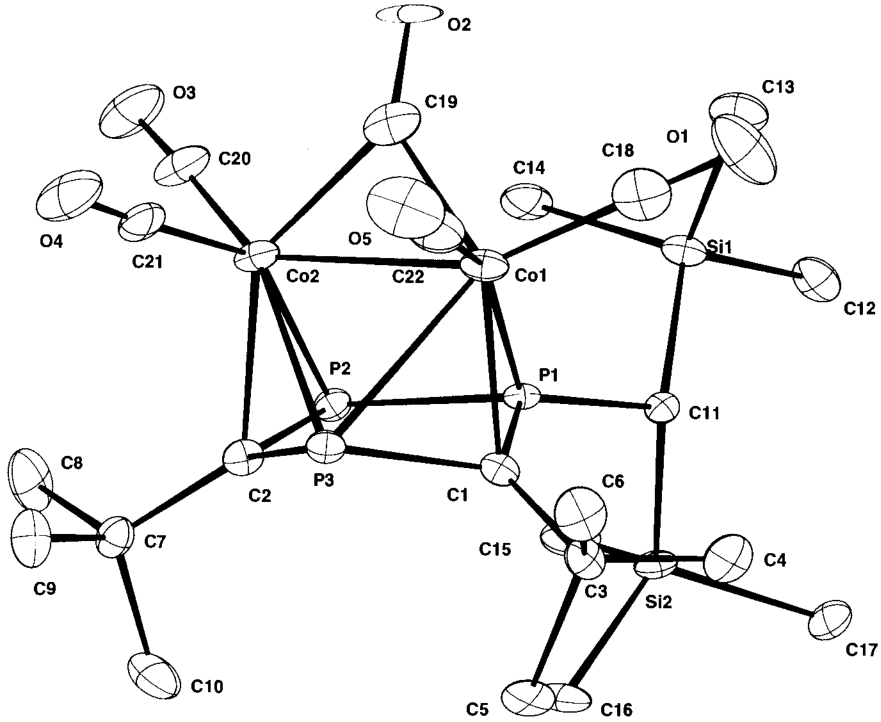


Fig. 1. Molecular structure of $[\mathrm{Co_2(CO)_5\{\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}}]$ (**4**) together with the atomic numbering scheme and selected bond lengths (Å) and bond angles (°). P(1)–P(2) = 2.194(3), P(1)–C(1) = 1.748(8), P(3)–C(1) = 1.806(8), P(3)–C(2) = 1.799(7), P(2)–C(2) = 1.743(8), P(1)–C(11) = 1.802(7), Co(1)–Co(2) = 2.590(2), Co(1)–P(1) = 2.192(2), Co(1)–P(3) = 2.458(3), Co(2)–P(2) = 2.320(3), Co(2)–P(3) = 2.499(3) Å; P(2)–P(1)–C(11) = 112.2(3), P(2)–P(1)–C(1) = 108.1(3), C(1)–P(1)–C(11) = 128.5(4), P(1)–P(2)–C(2) = 94.2(3), P(1)–P(2)–Co(2) = 85.9(10), C(2)–P(2)–Co(2) = 59.4(3), C(1)–P(3)–C(2) = 105.9(3), Co(1)–P(3)–Co(2) = 62.9(7), C(1)–P(3)–Co(1) = 56.6(3), C(2)–P(3)–Co(2) = 54.8(3), Co(2)–Co(1)–C(18) = 146.3(3), Co(1)–Co(2)–C(21) = 104.6(3)°.

exhibiting only two terminal ν(CO) bands at 2001 and 1954 $\mathrm{cm^{-1}}$, which are comparable to those reported for the fully aromatic η^5-2,5-diphenylphospholyl complex $[\mathrm{Co(CO)_2(\eta^5\text{-}PC_4Ph_2H_2)}]$ (2030, 1980 $\mathrm{cm^{-1}}$) [6]. The $^{31}\mathrm{P}\{^1\mathrm{H}\}$-NMR spectrum of **6** showed the expected [AMX] pattern of lines, which were much better resolved than in compound **4** and the small two bond J(PP) coupling constants (20.7 and 11.4 Hz, respectively) were both able to be determined. The molecular structure of **6**, obtained from a single-crystal X-ray diffraction study, is shown in Fig. 2 together with important bond length and bond angle data. Two views of the molecule shown in Fig. 2(a) and (b) reveal that the major structural features are (i) the $[\mathrm{Co(CO)_2}]$ fragment as expected interacts with only four of the five ring atoms, (ii) all four atoms of the ligated PCPP fragment are coplanar and (iii) the sum of the angles at the saturated P(2) atom is 343.3°.

3. Conclusions

On the basis of the results described above for the cobalt system, it is anticipated that a wide variety of phospha-organometallic metal complexes will exist containing the new five-electron four-centre donor (pseudo $\mathrm{C_5H_5}$ ring system) $\mathrm{P_3C_2Bu^t_2RH}$, (R = $\mathrm{(Me_3Si)_2CH}$). Indeed in unpublished work [9] we have also recently synthesised and fully structurally characterised two analogues of ‘ferrrocene’, namely $[\mathrm{Fe(P_3C_2Bu^t_2RH)_2}]$ and $[\mathrm{Fe(P_3C_2Bu^t_2RH)(\eta^5\text{-}P_3C_2Bu^t_2)}]$, which also show the five-electron four-centre bonding to the $\mathrm{P_3C_2Bu^t_2RH}$ ring, the latter complex resulting from the elimination of RH from one of the $\mathrm{P_3C_2Bu^t_2RH}$ rings of the former.

4. Experimental

Standard procedures for the manipulation of air-sensitive materials were employed. Unless otherwise stated, all manipulations were carried out at ambient temperature under an atmosphere of dry nitrogen gas using standard Schlenk, syringe and high-vacuum-line techniques, with glassware that had been flame-dried in vacuo prior to use. Solvents were dried, freshly distilled under a blanket of dinitrogen and degassed prior to use. IR spectra were recorded as Nujol mulls or in pentane solution on a Perkin–Elmer 1720 FTIR spectrometer and were calibrated relative to polystyrene. Mass spectra were recorded at the University of Sussex by Dr A. Abdul-Sada using a Fison Instruments-VG Autospec. Solution NMR spectra were recorded on

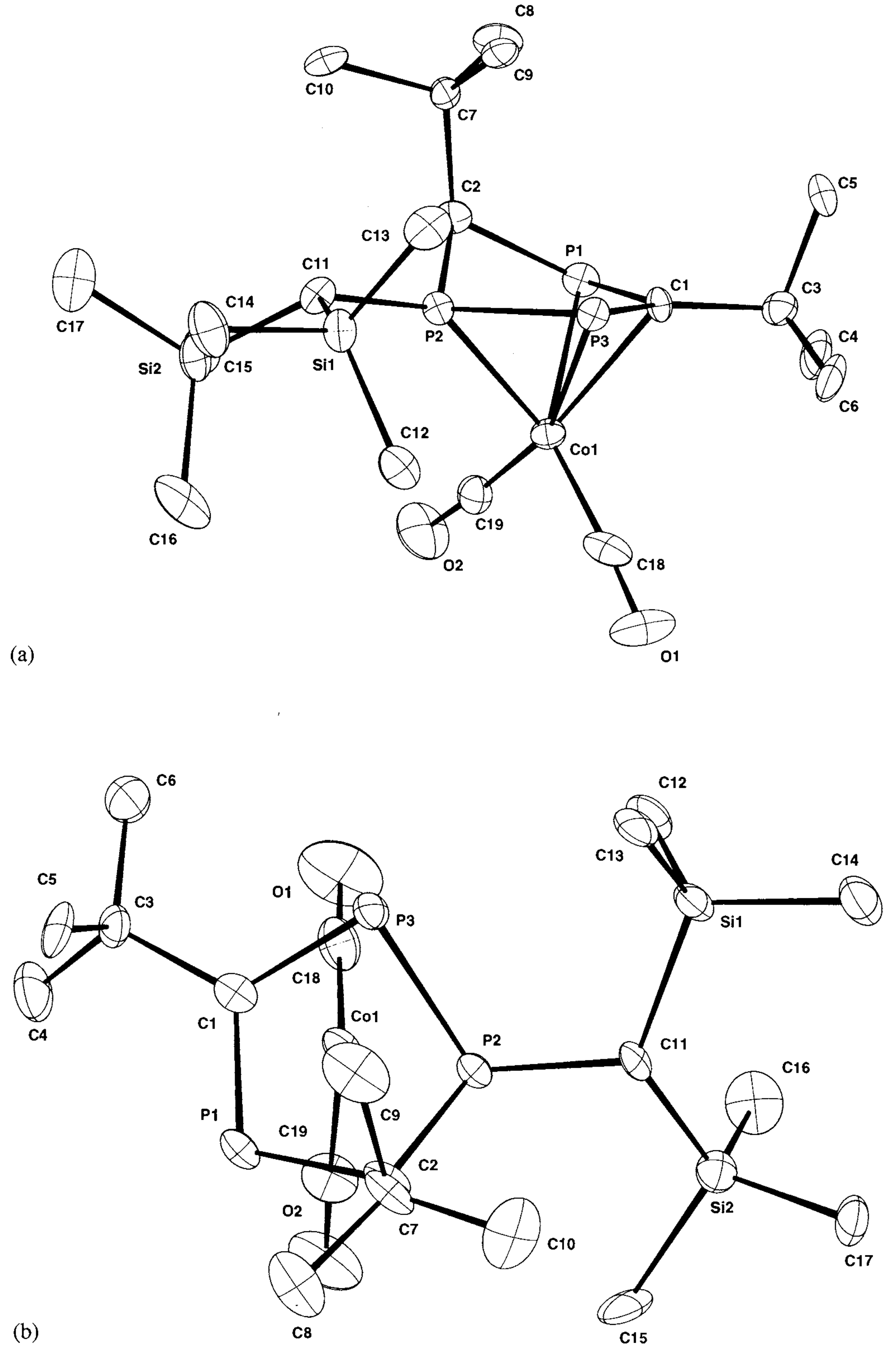
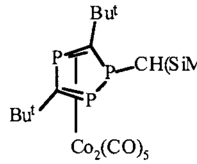


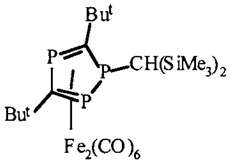
Fig. 2. Molecular structure of $[Co(CO)_2\{\mu\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ (**6**) together with the atomic numbering scheme and selected bond lengths (Å) and bond angles (°). P(2)–P(3) = 2.144(5), P(1)–C(1) = 1.762(12), P(3)–C(1) = 1.773(12), P(1)–C(2) = 1.885(11), P(2)–C(2) = 1.830(11), P(2)–C(11) = 1.817(11), Co–P(1) = 2.350(3), Co–P(2) = 2.219(3), Co–P(3) = 2.334(4), Co–C(1) = 2.084(12) Å; P(2)–P(3)–C(1) = 91.1(4), P(3)–C(1)–P(1) = 119.6(7), C(2)–P(2)–P(3) = 104.6(4), P(2)–C(2)–P(1) = 96.2(5)°.

Bruker ACP-250, DPX-300 or AMX-500 instruments at ambient probe temperature. Coupling constants (*J*) are given in Hz and chemical shift data (δ) in ppm relative to the residual proton chemical shift of the

Table 1
Selected bond lengths (Å) and bond angles (°) involving the two metals in complexes **4** and **5**



4



5

	4	5
Bond lengths		
M(1)–M(2)	2.590(2)	2.910(1)
M(1)–P(1)	2.192(2)	2.225(2)
M(1)–P(3)	2.458(3)	2.605(2)
M(1)–C(1)	2.101(8)	2.091(6)
M(2)–P(2)	2.320(3)	2.342(2)
M(2)–P(3)	2.499(3)	2.497(1)
M(2)–C(2)	2.074(8)	2.072(6)
Bond angles		
M(2)–M(1)–P(1)	79.61(8)	75.06(4)
M(2)–M(1)–P(3)	59.27(7)	53.51(3)
M(2)–M(1)–C(1)	94.20(2)	86.60(1)
P(2)–M(1)–P(3)	73.64(9)	72.00(5)
P(1)–M(1)–C(1)	48.00(2)	48.50(1)
P(3)–M(1)–C(1)	45.90(2)	43.50(1)
M(1)–M(2)–P(3)	59.27(7)	57.00(4)
M(1)–M(2)–C(2)	93.70(2)	91.40(1)
P(2)–M(2)–P(3)	77.20(9)	77.53(5)

deuterated solvent and P(OMe)$_3$ (141.0 ppm with respect to H_3PO_4 at 0.00 ppm). The triphosphole **3** was made according to literature procedures [2].

4.1. Synthesis of [Co$_2$(CO)$_5${P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}] (4)

A solution of [Co$_2$(CO)$_8$] (500 mg, 1.46 mmol) in THF (150 ml) and P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$ (250 mg, 0.64 mmol) in THF (10 ml) was stirred at room temperature for 19 h. Removal of solvent in vacuo afforded a brown residue which was extracted (petroleum ether 60–80°C) and on removal of solvent under reduced pressure gave a brown, oily solid. Chromatography (Kieselgel–petroleum ether 60–80°C) afforded [Co$_2$(CO)$_5${P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}] (**4**) (170 mg, 40%) (m.p. 151°C (dec.)). Found: C, 38.5; H, 5.8; $C_{22}H_{37}O_5P_3Co_2Si_2$ requires: C, 40.7; H, 5.7%.

^{31}P{^{1}H}-NMR (101.3 MHz, benzene-d_6, −70°C): δ −65.3 (d, P(A), $^1J_{P(A)P(X)}$ 392.6 Hz); δ −38.9 (s, P(Y)); δ 62.9 (d, P(X), $^1J_{P(X)P(A)}$ 392.6 Hz).

^{1}H-NMR (benzene-d_6, 25°C): δ 0.21 (s, 9H, Si(CH$_3$)$_3$); δ 0.60 (s, 9H, Si(CH$_3$)$_3$); δ 1.15 (s, 9H, C(CH$_3$)$_3$); δ 1.23 (s, 9H, C(CH$_3$)$_3$).

IR data: ν_{CO} (cm^{-1}): 2045 (s), 2007 (vs), 1996 (sh), 1971 (w), 1812 (s).

Mass spectrum (EI): m/z: 648 [M]$^+$ [Co$_2$(CO)$_5${P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]$^+$, 620 [Co$_2$(CO)$_4${P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]$^+$, 592 [Co$_2$(CO)$_3${P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]$^+$, 564 [Co$_2$(CO)$_2$ {P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]$^+$, 536 [Co$_2$(CO){P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$}]$^+$, 508 [Co$_2${P$_3$C$_2$Bu$^t_2$C(SiMe$_3$)$_2$}]$^+$, 390 [P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$]$^+$, 231 [P$_3$C$_2$Bu$^t_2$]$^+$, 73 [SiMe$_3$]$^+$.

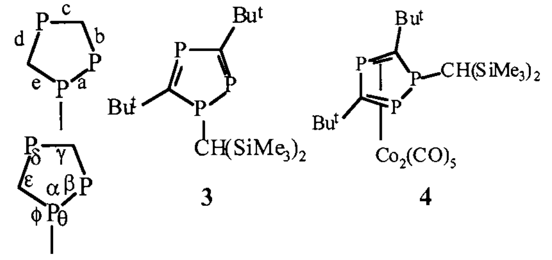
4.1.1. X-ray data for 4

Empirical formula: $C_{22}H_{37}Co_2O_5P_3Si_2$; $M = 648.5$; $T = 173(2)$ K; monoclinic $P2_1/n$ (no. 14), $a = 10.666(6)$, $b = 16.292(6)$, $c = 17.503(13)$ Å; $\beta = 99.77(6)$°; $V = 2997(3)$ Å^3; $Z = 4$; $D_{calc} = 1.44$ Mg m^{-3}; $F(000) = 1344$. Data were collected on a crystal of size 0.40 × 0.30 × 0.10 mm^3 using an Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71073$ Å. A total of 4180 independent reflections were collected, 2804 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The final R indices were $R_1 = 0.065$, $wR_2 = 0.143$ for $I > 2\sigma I$ and $R_1 = 0.109$, $wR_2 = 0.167$ for all data.

4.2. Synthesis of [Co(CO)$_2${P$_3$C$_2$HBu$^t_2$CH(SiMe$_3$)$_2$}] (6)

A solution of [Co$_2$(CO)$_8$] (755 mg, 2.20 mmol) in THF (30 ml) and P$_3$C$_2$Bu$^t_2$CH(SiMe$_3$)$_2$ (250 mg, 0.64 mmol) was heated at 50°C for 3 h. After removal of

Table 2
Selected bond lengths (Å) and bond angles (°) for the 1,2,4-triphosphole, **3**, and its [Co$_2$(CO)$_5$] complex, **4**



3 **4**

	3	4
Bond lengths		
a	2.098(1)	2.194(3)
b	1.718(4)	1.743(8)
c	1.763(4)	1.799(7)
d	1.720(3)	1.806(8)
e	1.734(4)	1.748(8)
Bond angles		
α	105.8(1)	108.1(3)
ϕ	121.2(2)	128.5(4)
θ	115.3(1)	112.2(3)
β	94.0(1)	94.2(3)
γ	123.1(2)	116.4(4)
δ	101.8(2)	105.9(3)
ε	113.9(2)	103.7(4)
$\alpha+\phi+\theta$	342.3	348.8

solvent in vacuo the residue was chromatographed (Kieselgel–hexane) to afford **5** as red crystals (110 mg, 12.5%) and **6** as dark-brown crystals (280 mg, 24.9%) after a further recrystallisation from hexane.

IR data: ν_{CO} (cm^{-1}): 2001 (vs), 1954 (s).

$^{31}P\{^1H\}$-NMR (121.4 MHz, benzene-d_6, 25°C): δ −63.8 (dd, P(A), $^1J_{P(A)P(M)}$ 420.3; $^2J_{P(A)P(X)}$ 21.3Hz); δ 5.7 (d, P(M) $^1J_{P(A)P(M)}$ 420.3); δ 49.1 (dd, P(X), $^2J_{P(A)P(X)}$ 20.7Hz) $^2J_{P(X)P(M)}$ 21.4 Hz).

Mass spectrum (EI): m/z: 506 $[M]^+$ $[Co(CO)_2\{P_3C_2Bu^t_2HCH(SiMe_3)_2\}]^+$, 478 $[Co(CO)\{P_3C_2Bu^t_2HCH(SiMe_3)_2\}]^+$, 450 $[Co\{P_3C_2Bu^t_2CH(SiMe_3)_2\}]^+$, 346 $[Co(CO)_2\{P_3C_2Bu^t_2\}]^+$.

4.2.1. *X-ray data for* **6**

Empirical formula: $C_{19}H_{38}CoO_2P_3Si_{2;}$ $M = 506.5$; $T = 173(2)$ K; triclinic $P1$ (no. 2), $a = 9.573(2)$, $b = 16.480(2)$, $c = 26.742(4)$ Å; $\alpha = 101.060(10)$, $\beta = 99.950(10)$, $\gamma = 91.420(10)°$; $V = 4070.9(3)$ Å^3; $Z = 6$; $D_{calc} = 1.24$ Mg m^{-3}; $F(000) = 1608$. Data were collected on a crystal of size $0.4 \times 0.3 \times 0.1$ mm^3 using an Enraf–Nonius CAD4 diffractometer, $\lambda = 0.71073$ Å. A total of 9958 independent reflections were collected, 5195 with $I > 2\sigma I$. The structure was solved by direct methods and refined using full-matrix least-squares on all F^2. The final R indices were $R_1 = 0.081$, $wR_2 = 0.157$ for $I > 2\sigma I$ and $R_1 = 0.173$, $wR_2 = 0.202$ for all data.

Acknowledgements

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References

[1] P.B. Hitchcock, J.F. Nixon, N. Sakarya, Chem. Commun. (Cambridge) (1996) 2751.
[2] V. Caliman, P.B. Hitchcock, J.F. Nixon., J. Chem. Soc. Chem. Commun. (1995) 1661.
[3] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998 and Refs. therein.
[4] F. Mathey, Coord. Chem. Rev. 137 (1994) 1.
[5] A.J.M. Caffyn, D. Carmichael, F. Mathey, L. Ricard, Organometallics 16 (1997) 2049.
[6] C. Carrier, H. Bonnard, F. Mathey, D. Neibecker, J. Organomet.Chem. 231 (1982) 361.
[7] F.A. Cotton, Prog. Inorg. Chem. 21 (1976) 1.
[8] J.M. Rosalky, B. Metz, F. Mathey, R. Weiss, Inorg. Chem. 16 (1977) 3307.
[9] V. Caliman, P.B. Hitchcock, C. Jones, J.F. Nixon, in preparation.