Synthesis and Structure of a Series of Unique Cobalt Phosphides†

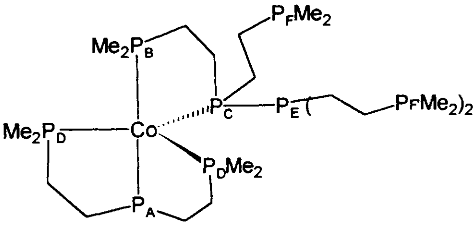
Peter G. Edwards,* Paul W. Read, Michael B. Hursthouse and K. M. Abdul Malik
School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, PO Box 912, Cardiff CF1 3TB, UK

The reaction of $CoCl_2$ and $[CoCl(PMe_3)_3]$ with the phosphidophosphine $LiP(CH_2CH_2PMe_2)_2$ afforded a unique class of cobalt phosphido complexes, revealing a new mode of reactivity for this ligand. The solid-state structure of the first monomeric cobalt phosphido complex, $[Co\{P(CH_2CH_2PMe_2)_2\}\{[P(CH_2CH_2PMe_2)_2]_2\}]$ **1** has been determined: monoclinic, space group $P2_1/c$, $a = 15.484(7)$, $b = 13.947(6)$, $c = 17.875(2)$ Å, $\beta = 108.54(2)°$. An analogue, $[Co\{P(CH_2CH_2PMe_2)_2\}(Me_2PCH_2CH_2PMe_2)]$ **2**, has been characterised by $^{31}P-\{^1H\}$ NMR spectroscopy. Complex **1** was shown to be fluxional in solution and further characterised by two-dimensional correlation $^{31}P-\{^1H\}$ NMR spectroscopy. The corresponding spectrum of **2** interestingly shows no $^2J(P-P)$ coupling *via* the cobalt centre.

Cobalt(I) phosphines have application to a number of catalytic systems, including the catalysis of polymerisation[1] and hydroformylation[2] reactions. Complexes that contain unco-ordinated donor atoms, for example oxygen or phosphorus, are of particular interest because of their potential ability to form bimetallic compounds and to stabilise co-ordinatively unsaturated intermediates formed during reaction cycles. As part of a study to investigate the properties of the potentially terdentate phosphido ligand $^-P(CH_2CH_2PMe_2)_2$, we report the reaction of a series of cobalt precursors with $LiP(CH_2CH_2PMe_2)_2$ in toluene–tetrahydrofuran (thf) at 193 K (Scheme 1). Compound **1** is novel as a co-ordination complex, containing both oxidation and reduction products. It also shows a unique type of behaviour for these types of ligand systems; since phosphides are excellent bridging ligands, **1** and **2** are the only examples of monomeric cobalt phosphido complexes. Only one transition-metal complex of $^-P(CH_2CH_2PMe_2)_2$ has been previously reported;[3a] and by comparison in the present circumstance, X-ray crystallography reveals unusual differences in the metal–phosphide ligand bonding.

$$\begin{tikzcd}
CoCl_2 \arrow[r, "(i)"] \arrow[d, "(ii)"'] & {[CoCl(PMe_3)_3]} \arrow[d, "(iii)"'] \\
1 & 2
\end{tikzcd}$$

Scheme 1 Reactions (*ii*) and (*iii*) performed in toluene–thf (80 : 20) at 193 K. (*i*) Na–Hg, PMe_3; (*ii*) $LiP(CH_2CH_2PMe_2)_2$; (*iii*) $LiP(CH_2CH_2PMe_2)_2$, dmpe



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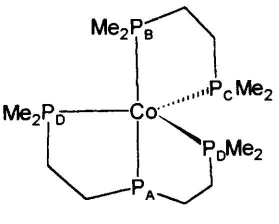

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Results and Discussion

$[Co\{P(CH_2CH_2PMe_2)_2\}\{[P(CH_2CH_2PMe_2)_2]_2\}]$ **1**.—The stoichiometric reaction of $CoCl_2$ with $LiP(CH_2CH_2PMe_2)_2$ in toluene affords yellow light petroleum-soluble crystals of **1** in moderate yield. Microanalysis confirms the formulation. The room-temperature $^{31}P-\{^1H\}$ NMR spectrum (Fig. 1) contains six resonances assignable on the basis of chemical shift and integration (Experimental section). Resonance A (δ 89.26) is attributed to the phosphido phosphorus. Some fine structure is associated with this peak, but coupling to other phosphorus atoms is negligible. Resonance B (δ 56.06) appears as a virtual quartet at room temperature, consistent with it being assigned to the axial tertiary phosphine on cobalt coupled to three equatorial tertiary phosphines, two of which are chemically equivalent. The $^2J(P-P)$ coupling constant is 34 Hz. This corresponds well to other literature *cis* coupling constants.[4] Resonance C (δ 45.74) is assigned to the co-ordinated P–P bonded equatorial phosphine. This resonance is very broad at room temperature ($\nu_{\frac{1}{2}}$ = 468 Hz) and is uninformative. Resonance D (δ 41.12) is assigned to the remaining two equatorial tertiary phosphines. The non-co-ordinated P–P bonded phosphorus is assigned to resonance E (δ −10.09) which appears as a doublet of multiplets at room temperature, where the separation of lines within each half is 21 Hz and the separation between each half is 197 Hz. These values correspond well with previously reported $^1J(P-P)$[5] and $^3J(P-P)$ coupling constants.[6] Resonance F (δ −47.54) is assigned to all

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

(three) unco-ordinated tertiary phosphines. In addition there is a small peak, G (δ −32.05), due to $(Me_2PCH_2CH_2)_2P-P(CH_2CH_2PMe_2)_2$ (oxidation product) contaminant and is assigned upon the basis of its chemical shift.[6] This contaminant will also give a resonance (δ −48.70)[6] obscured by F, resulting from tertiary PMe_2 groups. The two-dimensional correlation spectroscopy (COSY) $^{31}P-\{^1H\}$ NMR spectrum of **1** confirms the assignment described above (Fig. 2). From the off-diagonal couplings present it is clear that resonance C is assigned appropriately since it is coupled to both *cis* co-ordinated tertiary phosphines and to the non-co-ordinated P–P bonded phosphorus. This accounts for the broadness of the resonance.

A variable-temperature $^{31}P-\{^1H\}$ NMR study of complex **1** indicates that its solution structure is not rigid since the spectrum, which is well resolved at 193 K, broadens considerably as the temperature is raised to 373 K and all fine structure is lost in the linewidth of each of the resonances at the higher temperature. There is however no evidence of any process that exchanges co-ordinated for unco-ordinated phosphorus nuclei since there is no coalescence of resonances due to P_B and P_F or due to P_C and P_E. Fluxional behaviour is expected as there are no stereochemically rigid five-co-ordinate species known and an intramolecular site exchange may occur in **1** (*e.g. via* a Berry pseudo-rotation). Such an exchange mechanism does not require breaking of Co–P bonds; exchange between co-ordinated and unco-ordinated tertiary phosphines will be a higher-energy process and is not significant under the conditions of this study.

The crystal structure of complex **1** reveals that the solution and solid-state structures are consistent (Fig. 3). The co-ordination geometry around Co is approximately trigonal bipyramidal with the phosphido phosphorus and one chelate tertiary phosphine in the axial positions. An interesting feature, however, is that the longest metal–ligand bond is between metal and phosphido phosphorus, P(2) [2.297(1) Å, *ca.* 0.14 Å longer than the average metal–phosphine bond length]. This behaviour is anomalous; all other crystallographically characterised examples of this ligand in a non-bridging, chelating mode have shorter metal–phosphide bonds than metal–phosphine bonds.[3] That the phosphido phosphorus is pyramidal [as determined by the Co–P–C bond angles, average 104.4(2)°] is not surprising since as a two-electron anionic donor the cobalt attains an eighteen-electron valence configuration. The relative lengthening of this bond is also presumably not due to steric forces since the phosphido phosphorus is less encumbered than the terminal tertiary phosphine donors. There may be some steric influence on M–P bonding imposed by constraints of the chelate. Strain in the chelate rings is indicated by the relatively compressed P–C–C angles at C(3) [106.6(2)°] and C(6) [105.4(2)°]. However, should the cobalt to phosphido phosphorus bond be intrinsically stronger than the other Co–P bonds, this effect would

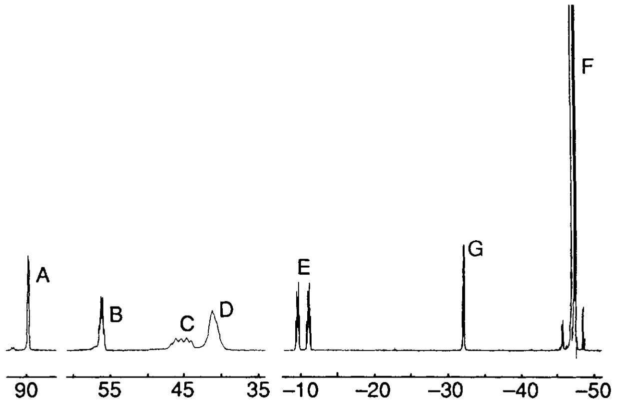

Fig. 1 Room-temperature $^{31}P-\{^1H\}$ NMR spectrum of complex **1**

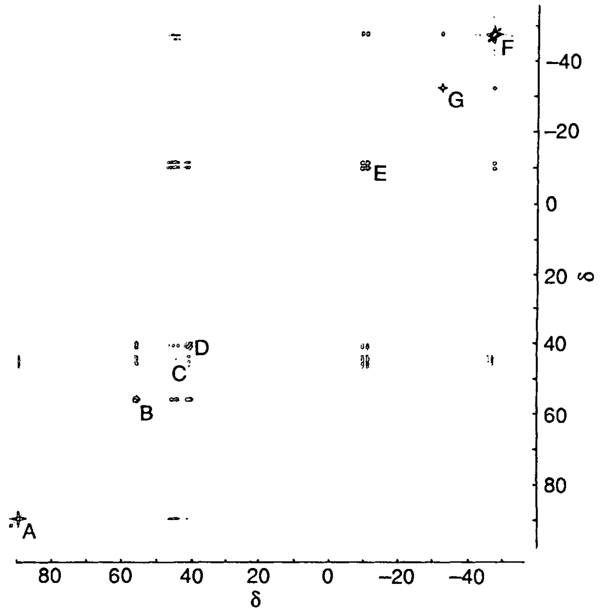

Fig. 2 Room-temperature two-dimensional COSY $^{31}P-\{^1H\}$ NMR spectrum of complex **1**

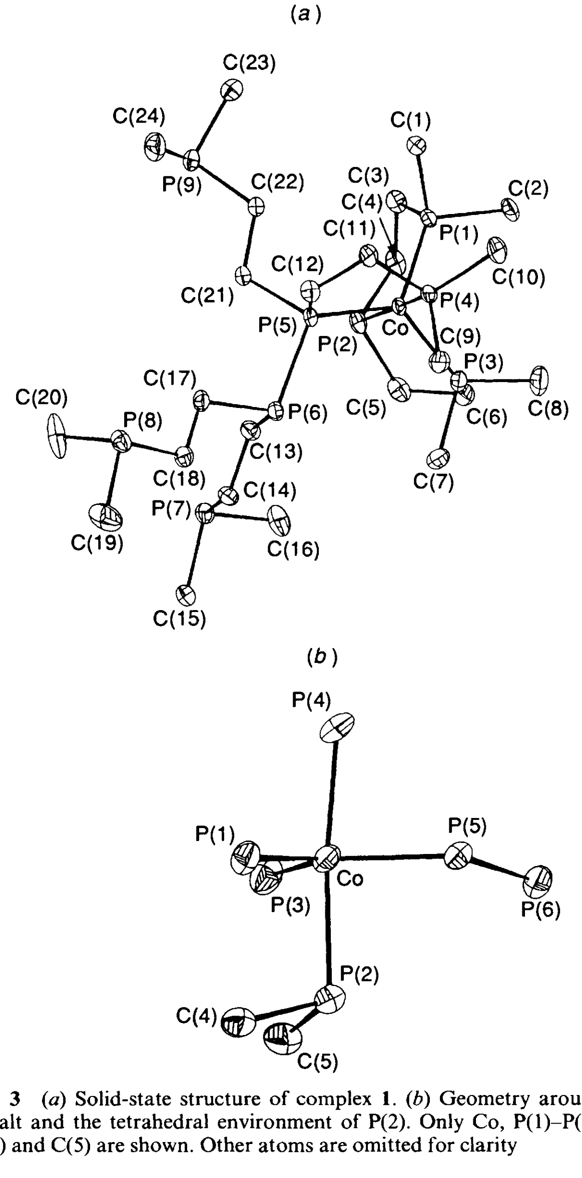

Fig. 3 (*a*) Solid-state structure of complex **1**. (*b*) Geometry around cobalt and the tetrahedral environment of P(2). Only Co, P(1)–P(6), C(4) and C(5) are shown. Other atoms are omitted for clarity

presumably be reversed [*i.e.* compression of angles at C(5) and C(4) instead]. Although the tertiary phosphorus donors in the chelate occupy equatorial sites, they are also more sterically encumbered and it is difficult to see that other steric forces would result in the observed difference in Co–P bond lengths. It is more likely that an electronic influence results in this closer contact between cobalt and the neutral tertiary phosphines. Presumably they are acting as better π acceptors than is the relatively electron-rich phosphido phosphorus. It is likely that the tertiary phosphines would be better σ donors than the secondary phosphido phosphorus, however this may be expected to be of less significance for low-oxidation-state electron-rich cobalt complexes such as **1**.

The Co atom is located slightly above the plane of the three equatorial phosphino phosphorus atoms, this presumably being due to the longer Co–P (phosphido) bond distorting the chelate-connected tertiary phosphorus atoms [P(1), P(3)] from their idealised position in a trigonal bipyramid and toward the phosphido phosphorus.

$[Co\{P(CH_2CH_2PMe_2)_2\}(dmpe)]$ **2**.—The reaction of $[CoCl(PMe_3)_3]$ with $Me_2PCH_2CH_2PMe_2$ (dmpe) and $LiP(CH_2CH_2PMe_2)_2$ in toluene affords an orange light petroleum-soluble complex **2** which can be crystallised in moderate yield. Microanalysis confirms the stoichiometry. The room-temperature $^{31}P-\{^1H\}$ NMR spectrum contains four resonances assignable on the basis of chemical shift and signal intensities (Fig. 4), and indicates that the solution structures of both **1** and **2** are similar with respect to the co-ordination environment of the cobalt centre. The phosphido phosphorus appears as a singlet at δ 94.55 (P_A) and the co-ordinated tertiary phosphines occur as a sharp doublet at δ 78.40 and two broad resonances at δ 71.17 and 27.15 in a ratio of 1:1:1:2 respectively. The presence of three resonances in the co-ordinated phosphine region of the spectrum indicates that the tertiary phosphines of the phosphide ligand are equivalent. The resonance at δ 78.40 is attributed to the axial tertiary phosphine from the dmpe ligand (P_B), *trans* to the phosphido phosphorus. The *cis* coupling constant is 40 Hz and this corresponds well with literature values.[4] The last two are assigned to P_C and P_D respectively.

In the two-dimensional COSY $^{31}P-\{^1H\}$ NMR spectrum of complex **2** (Fig. 5) an off-diagonal peak assignable to $^2J(P_B-P_C)$ or $^2J(P_B-P_D)$ is not observed indicating that these 90° couplings *via* the cobalt centre are small, as has been previously reported for other complexes.[7] An off-diagonal peak does however indicate the 120° ^2J coupling between P_C and P_D is significant and presumably gives rise to the broadness in the resonances due to P_C and P_D and the fine structure in the latter. The coupling in **2** observed in the peak at δ 78.40 is assigned to $^3J(P-P)$ (*via* the carbon backbone of the ligand). The resonances due to the equatorial phosphines are then broadened presumably due to the influence of three different, but small, $^2J(P-P)$ couplings.

It appears then that the chelating ability of the phosphido ligand inhibits oligomerisation of the cobalt complexes **1** and **2**. This feature may allow a more general access to monomeric transition-metal phosphido complexes that are otherwise uncommon for relatively electronegative metals. It is yet to be seen what resultant influences there may be on reactivity and other properties; such study is of interest and is being continued in this laboratory.

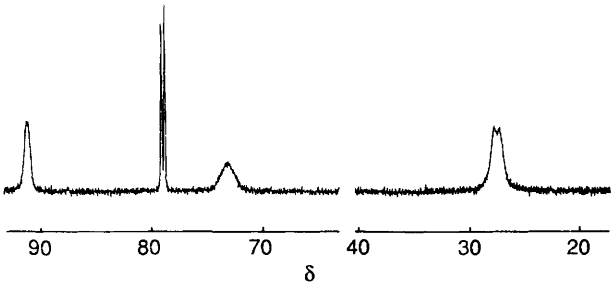

Fig. 4 Room-temperature $^{31}P-\{^1H\}$ NMR spectrum of complex **2**

Experimental

All manipulations were performed using a Vacuum Atmospheres HE-43-2 or Halco Engineering 140 FF glove-box, or standard Schlenk techniques under purified nitrogen. Unless otherwise stated all solvents were refluxed under nitrogen over sodium–benzophenone and were distilled immediately prior to use. Toluene was refluxed under nitrogen over sodium and distilled immediately prior to use. Perdeuterio solvents were refluxed over sodium (8 h) and distilled therefrom under nitrogen. Cobalt(II) chloride (Aldrich) was dried *in vacuo* [170 °C, 0.05 mmHg (*ca.* 6.65 Pa), 8 h] and $[CoCl(PMe_3)_3]$ was prepared following a literature route.[8]

Microanalyses were performed by C.H.N. Analysis, Leicester. The NMR spectra were recorded on a Bruker ACT 400 spectrometer (at the University of Warwick) operating at 162 MHz (^{31}P, in C_6D_6) and a JEOL FX90Q spectrometer operating at 36.23 MHz (variable-temperature ^{31}P in C_7D_8, $^{13}C-\{^1H\}$ and ^1H); ^{31}P referenced externally to 85% H_3PO_4 (δ 0), ^{13}C and ^1H to solvent carbons (C_6D_6, δ 128) or residual protons (C_6D_6, δ 7.15). The COSY-90 $^{31}P-^{31}P$ two-dimensional NMR spectroscopy was carried out on the Bruker ACT 400 instrument using the program COSY from the standard Bruker software. In the F2 dimension, 1024 data points were collected over 21 739 Hz, and in F1 256 data points over 10 870 Hz. Transformation was carried out with zero-filling to 512 points in F1, after application of Gaussian multiplication (line broadening = 200 Hz) applied to 0.2 of the time domain data in both dimensions. The 90° acquisition pulse length was 5 μs, protons were decoupled during acquisition, and a delay of 1.5 s was applied between acquisitions. Melting points were recorded in sealed glass capillaries and are uncorrected.

$[Co\{P(CH_2CH_2PMe_2)_2\}\{[P(CH_2CH_2PMe_2)_2]_2\}]$ **1**.—Cobalt(II) chloride (0.78 g, 6.01 mmol) was suspended in toluene (100 cm^3) with stirring and cooled (−80 °C), $LiP(CH_2CH_2PMe_2)_2$ (1.30 g, 6.02 mmol) in toluene–thf (5:1, 20 cm^3) was added slowly *via* syringe and the reaction mix allowed to warm to room temperature and stirred (12 h). Volatile materials were removed *in vacuo* and the brown residue washed with cold (−100 °C) light petroleum (2 × 10 cm^3, b.p. 40–60 °C).

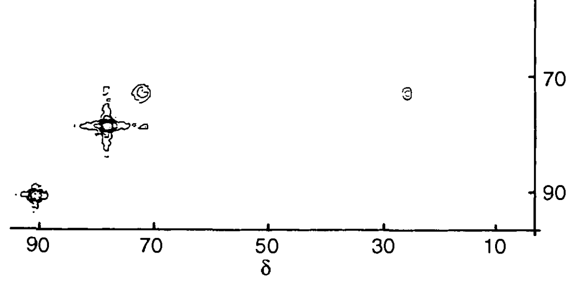

Fig. 5 Room-temperature two-dimensional COSY $^{31}P-\{^1H\}$ NMR spectrum of complex **2**

The residue was then extracted with light petroleum (3 × 40 cm^3) and filtered. Evaporation of the yellow filtrate to *ca.* 20 cm^3 and cooling (−20 °C, 4 h) afforded crude complex **1** (0.94 g, 1.37 mmol) in 23% yield. It may be crystallised from light petroleum as orange needles, m.p. 130–134 °C (Found: C, 41.3; H, 8.80. $C_{24}H_{60}CoP_9$ requires C, 42.0; H, 8.80%). IR (Nujol): 1734w, 1415w, 1287w, 1275w, 1262m, 1172w, 1163w, 1097w, 944s, 925s, 906s, 815w, 806m, 787w, 713s, 687s, 634s, 618w, 490m, 465w, 394s, 383s and 376s cm^{-1}. ^{31}P-{^1H} NMR: δ_P (162 MHz, C_6D_6) 89.26 (1P), 56.06 [1P, q, ^2J(P–P) 34], 45.74 (1P, br, $\nu_{\frac{1}{2}}$ 468), 41.12 (2P, br, $\nu_{\frac{1}{2}}$ 241 Hz), −10.09 [1P, dm, ^1J(P–P) 197, ^3J(P–P) 21 Hz] and −47.54 (3P, m). ^1H and ^{13}C NMR are broadened and uninformative.

Table 1 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Co	3116(1)	2222(1)	692(1)
P(1)	4259(1)	1295(1)	1207(1)
P(2)	3426(1)	2886(1)	1925(1)
P(3)	3457(1)	3590(1)	313(1)
P(4)	2687(1)	1572(1)	−466(1)
P(5)	1772(1)	1828(1)	717(1)
P(6)	690(1)	2947(1)	407(1)
P(7)	776(1)	5172(1)	2272(1)
P(8)	−2247(1)	2063(1)	−275(1)
P(9)	2033(1)	−379(1)	2620(1)
C(1)	4241(3)	−22(2)	1102(2)
C(2)	5319(2)	1539(3)	977(2)
C(3)	4700(3)	1421(3)	2294(2)
C(4)	4622(2)	2474(3)	2474(2)
C(5)	3717(3)	4170(3)	1798(2)
C(6)	4160(3)	4297(3)	1162(2)
C(7)	2540(3)	4456(3)	−137(2)
C(8)	4119(3)	3718(3)	−368(3)
C(9)	1957(3)	2263(3)	−1301(2)
C(10)	3467(3)	1043(3)	−933(2)
C(11)	1921(2)	575(2)	−451(2)
C(12)	1209(2)	955(2)	−102(2)
C(13)	999(2)	3621(2)	1353(2)
C(14)	426(2)	4525(2)	1324(2)
C(15)	8(3)	6198(3)	2009(2)
C(16)	1828(3)	5735(3)	2233(2)
C(17)	−368(2)	2321(3)	423(2)
C(18)	−1233(2)	2813(3)	−105(2)
C(19)	−3141(3)	2899(3)	−812(3)
C(20)	−2378(4)	2108(5)	697(3)
C(21)	1585(2)	1215(2)	1578(2)
C(22)	2205(2)	343(2)	1821(2)
C(23)	2980(4)	−1218(4)	2738(3)
C(24)	1088(3)	−1142(3)	2060(3)

[Co{P($CH_2CH_2PMe_2$)$_2$}(dmpe)] **2**.—The complex [CoCl(PMe_3)$_3$] (0.84 g, 2.60 mmol) was dissolved in toluene (80 cm^3) and cooled (−20 °C), dmpe (0.40 g, 2.60 mmol) was added *via* syringe and the mixture allowed to warm, with stirring, to room temperature. After stirring (10 min) the mixture was cooled (−80 °C) and LiP($CH_2CH_2PMe_2$)$_2$ (0.56 g, 2.60 mmol) in toluene–thf (5:1, 15 cm^3) added dropwise. The mixture was allowed to warm to room temperature and stirred (12 h). The solvents were removed *in vacuo* and the red residue washed with cold (−100 °C) light petroleum (2 × 10 cm^3). The residue was extracted into light petroleum (3 × 25 cm^3) and filtered. Concentration of the filtrate afforded red-orange crystals of complex **2** (0.43 g, 1.03 mmol) in moderate yield, m.p. 101–103 °C (Found: C, 40.3; H, 8.60. $C_{14}H_{36}CoP_5$ requires C, 40.2; H, 8.65%). IR (Nujol): 1421m, 1277w, 1261w, 1242m, 1172w, 1168w, 1090w, 927s, 909m, 819w, 800m, 789s, 721m, 687s, 638s, 629w, 477s, 431w, 397s, 388s and 369s cm^{-1}. ^{31}P-{^1H} NMR (162 MHz, C_6D_6): δ_P 94.55, 78.40 [d, ^3J(P–P) 40 Hz], 71.17 (br, $\nu_{\frac{1}{2}}$ 308) and 27.15 (br, $\nu_{\frac{1}{2}}$ 237 Hz). ^1H and ^{13}C NMR are broadened and uninformative.

X-Ray Crystallography.—Crystals of complex **1** suitable for X-ray work were grown from light petroleum and sealed under purified nitrogen in Lindemann capillaries.

Crystal data. $C_{24}H_{60}CoP_9$, M = 686.38, monoclinic, space group $P2_1/c$, a = 15.484(7), b = 13.947(6), c = 17.875(2) Å, β = 108.54(2)°, U = 3660(2) Å^3 (by least-squares refinement at 200 K of diffractometer angles for 250 reflections within θ = 2.5–29.7°, λ = 0.710 69 Å), Z = 4, D_c = 1.246 mg m^{-3}, F(000) = 1464, μ(Mo-Kα) = 0.876 mm^{-1}. Orange, air-sensitive needles. Crystal dimensions 0.15 × 0.08 × 0.05 mm.

Data collection and processing.[9] Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator using Mo-Kα radiation; 20 917 reflections measured (2.56 < θ < 29.7°; index ranges

Table 2 Bond lengths (Å) and angles (°) for non-hydrogen atoms in compound **1**

Co–P(1)	2.148(1)	Co–P(2)	2.297(1)	P(5)–P(6)	2.227(1)	P(6)–C(13)	1.858(3)
Co–P(3)	2.146(1)	Co–P(4)	2.162(1)	P(6)–C(17)	1.865(3)	P(7)–C(14)	1.842(3)
Co–P(5)	2.167(1)	P(1)–C(1)	1.846(3)	P(7)–C(15)	1.825(4)	P(7)–C(16)	1.829(5)
P(1)–C(2)	1.845(4)	P(1)–C(3)	1.853(3)	P(8)–C(18)	1.830(4)	P(8)–C(19)	1.832(4)
P(2)–C(4)	1.888(3)	P(2)–C(5)	1.879(4)	P(8)–C(20)	1.812(5)	P(9)–C(22)	1.835(3)
P(3)–C(6)	1.846(3)	P(3)–C(7)	1.843(4)	P(9)–C(23)	1.835(5)	P(9)–C(24)	1.829(5)
P(3)–C(8)	1.832(4)	P(4)–C(9)	1.833(3)	C(3)–C(4)	1.517(5)	C(5)–C(6)	1.513(6)
P(4)–C(10)	1.829(4)	P(4)–C(11)	1.833(4)	C(11)–C(12)	1.524(5)	C(13)–C(14)	1.533(4)
P(5)–C(12)	1.889(3)	P(5)–C(21)	1.863(3)	C(17)–C(18)	1.534(4)	C(21)–C(22)	1.524(4)
P(3)–Co–P(1)	114.73(5)	P(3)–Co–P(4)	95.91(4)	C(21)–P(5)–Co	122.4(1)	C(12)–P(5)–Co	110.9(1)
P(1)–Co–P(4)	96.81(4)	P(3)–Co–P(5)	124.50(4)	C(21)–P(5)–P(6)	103.0(1)	C(12)–P(5)–P(6)	97.7(1)
P(1)–Co–P(5)	120.29(4)	P(4)–Co–P(5)	84.71(4)	Co–P(5)–P(6)	117.9(1)	C(13)–P(6)–C(17)	101.3(2)
P(3)–Co–P(2)	86.95(4)	P(1)–Co–P(2)	86.51(4)	C(13)–P(6)–P(5)	100.0(1)	C(17)–P(6)–P(5)	105.2(1)
P(4)–Co–P(2)	174.22(4)	P(5)–Co–P(2)	89.53(4)	C(15)–P(7)–C(16)	99.8(2)	C(15)–P(7)–C(14)	99.8(2)
C(2)–P(1)–C(1)	98.5(2)	C(2)–P(1)–C(3)	99.1(2)	C(16)–P(7)–C(14)	100.4(2)	C(20)–P(8)–C(18)	99.9(2)
C(1)–P(1)–C(3)	100.9(2)	C(2)–P(1)–Co	117.6(1)	C(20)–P(8)–C(19)	100.6(3)	C(18)–P(8)–C(19)	100.9(2)
C(1)–P(1)–Co	124.9(1)	C(3)–P(1)–Co	111.8(1)	C(24)–P(9)–C(22)	100.5(2)	C(24)–P(9)–C(23)	99.4(3)
C(5)–P(2)–C(4)	96.9(2)	C(5)–P(2)–Co	104.7(1)	C(22)–P(9)–C(23)	97.5(2)	C(4)–C(3)–P(1)	106.6(2)
C(4)–P(2)–Co	104.3(1)	C(8)–P(3)–C(7)	99.3(2)	C(3)–C(4)–P(2)	108.4(2)	C(6)–C(5)–P(2)	112.7(2)
C(8)–P(3)–C(6)	100.7(2)	C(7)–P(3)–C(6)	100.3(2)	C(5)–C(6)–P(3)	105.4(2)	C(12)–C(11)–P(4)	107.3(2)
C(8)–P(3)–Co	122.8(2)	C(7)–P(3)–Co	119.2(1)	C(11)–C(12)–P(5)	109.0(2)	C(14)–C(13)–P(6)	114.0(2)
C(6)–P(3)–Co	110.9(1)	C(10)–P(4)–C(11)	103.0(2)	C(13)–C(14)–P(7)	112.0(2)	C(18)–C(17)–P(6)	112.4(2)
C(10)–P(4)–C(9)	99.6(2)	C(11)–P(4)–C(9)	100.2(2)	C(17)–C(18)–P(8)	112.4(2)	C(22)–C(21)–P(5)	110.7(2)
C(10)–P(4)–Co	124.0(1)	C(11)–P(4)–Co	107.9(1)	C(21)–C(22)–P(9)	115.2(2)		
C(9)–P(4)–Co	118.8(1)	C(21)–P(5)–C(12)	101.0(2)				

$-11 < h < 20$, $-17 < k < 18$, $-17 < l < 23$), 8473 unique (merging $R = 0.056$).

Structure analysis and refinement. The structure was solved by direct methods (SHELXS)[10] and refined by full-matrix least squares (SHELXL 93)[11] using all unique F_o^2 data corrected for Lorentz and polarisation factors (absorption effects were ignored). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in calculated positions with the U_{iso} values set at 1.2 times the U_{eq} of the parent carbons. The weighting scheme used was $w = 1/\sigma^2(F_o)^2$, which gave satisfactory agreement analyses. Final $R_1[=\Sigma(\Delta F)/\Sigma(F_o)]$ and wR_2 $[=\{\Sigma w[\Delta(F^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}]$ values were 0.0709 and 0.1242 respectively, for 319 parameters and all 8473 data [ρ_{min}, ρ_{max} -0.3504, 0.7092 e Å^{-3}, $(\Delta/\sigma)_{max}$ 0.90]. The corresponding R indices for 4726 data with $I > 2\sigma(I)$ are 0.039 and 0.095 respectively. Sources of scattering factor data are given in ref. 9. All calculations were performed on a 486DX2/66 personal computer. The fractional coordinates of the non-hydrogen atoms and selected bond lengths and angles are presented in Tables 1 and 2 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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