Crystal Structure and Dynamic Behaviour of $Ir_4(CO)_7(\mu\text{-}CO)_3[\mu\text{-}Ph_2P(CH_2)_4PPh_2]$

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Abstract

The title cluster compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 12.408(5)$, $b = 17.713(8)$, $c = 18.529(5)$ Å, $\beta = 90.80(3)°$ and $Z = 4$; R refined to 0.050 and R_w to 0.051 for 3556 reflections. Three edge-bridging COs define the basal face of an almost regular Ir_4 tetrahedron. The two Ir–P bonds are almost perpendicular to the basal plane. The asymmetry of the molecule is due to the aliphatic chain conformation. Contrary to related cluster compounds with a shorter aliphatic chain, the dynamic behaviour of the complex, as observed by ^{13}C and ^{31}P NMR, is not due to CO mobility but to rapid conformational changes in the aliphatic chain.

Introduction

A series of substituted derivatives of $Ir_4(CO)_{12}$ with uni- and bidentate phosphines have recently been reported [1]. They generally have CO ligands that either bridge two Ir atoms or are terminal. The bridging COs define the basal plane containing three Ir atoms of the metal core. Terminal COs are either apical if located on the fourth Ir atom, radial when located more or less in the basal plane, or axial if approximately perpendicular to the basal plane. CO site exchange is a common feature of these cluster compounds [2, 3]. One of the substituted derivatives, $Ir_4(CO)_7(\mu\text{-}CO)_3[\mu\text{-}Ph_2P(CH_2)_4PPh_2]$ (1) was previously reported to have a ground state structure with an axial P atom and a radial P atom on the basis of two widely different ^{31}P chemical shifts (−32.2 and −7.4 ppm at −95 °C in $(CD_3)_2CO$) [1]. Further NMR data of 1 (*vide infra*), however, were not in accord with such a ground state structure, and we now report a full structural characterization of 1 in the solid state and in solution.

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Experimental

Complex 1 was prepared according to the literature method [1], starting with $NEt_4[Ir_4(CO)_{11}Br]$ [4] enriched to c. 30% ^{13}C. The ^{13}C NMR spectra were recorded on a Bruker WH-360 (90.55 MHz) under atmospheric pressure. Chemical shifts are in ppm relative to Me_4Si. The COSY-90 ^{13}C NMR spectra [5] were obtained in CD_2Cl_2 at c. −80 °C with a sample of 1 enriched to c. 50% ^{13}CO. A total of 256 t_1 increments with 2-K transients were acquired. The spectral width was 6849.3 Hz in the F2 domain and 3424.7 Hz in the F1 domain. The spectra were zero filled to 2K × 2K and a shifted square sinus bell was applied to both domains prior to Fourier transformation. The ^{31}P NMR spectra were recorded on a Bruker CXP-200 (80.89 MHz) and a Bruker AM-400 (162.80 MHz). P chemical shifts are in ppm relative to external 85% H_3PO_4; high frequency displacements are positive. A Pt-100 Ω thermocouple [6] was used for temperature control. The programs EXCHANGE, EYRING-FIT and ANASPEC (ITERAT) [7] were used for the simulation of the variable temperature NMR spectra and for the calculation of activation parameters.

Crystal Structure Determination

The crystal data and details of the measurements are given in Table 1. The diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with Mo Kα radiation and reduced to F_o values. The metal atom positions were determined by direct methods [8], P atoms and the remaining light atoms by subsequent Fourier difference maps. The refinement was carried out by full-matrix least-squares calculations [9]. The thermal vibrations were treated anisotropically for the Ir and P atoms, and also for the C and O atoms of the CO groups. The C atoms of the aliphatic chain and of the phenyl groups were treated isotropically. Two single isotropic thermal parameters were refined for the H atoms (0.128 and 0.242 Å^2 for H(phenyl) and H(CH_2), respectively). The phenyl groups of the

TABLE 1. Crystal data and details of measurements for 1

Formula	$Ir_4C_{38}O_{10}P_2H_{28}$
Molar mass	1475.18
Crystal size (mm)	$0.10 \times 0.15 \times 0.11$
System	monoclinic
Space group	$P2_1/n$
a (Å)	12.408(5)
b (Å)	17.713(8)
c (Å)	18.529(5)
β (°)	90.80(3)
U (Å^3)	4072.2
Z	4
$F(000)$	2695
D_c (g cm^{-3})	2.4
λ (Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	126.730
Diffractometer	Enraf-Nonius CAD4
Scan mode	$\omega/2\theta$
θ-range (°)	2.5–25
ω-scan width (°)	1.6
Requested counting $\sigma(I)/I$	0.02
Prescan rate (min^{-1})	5
Prescan acceptance $\sigma(I)/I$	0.5
Maximum scan time (s)	90
Octants explored	$\pm h, +k, +l$
Measured reflections	7648
Unique observed reflections used in the refinement	3556
Absorption correction max. value	25%
R, R_w, S	0.050 0.051 1.04
K, g	0.965 0.002

Absorption correction was applied by azimuthal scanning of reflections at $\chi > 80$; $R_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma(F_o w^{1/2})$, where $w = k/[\sigma^2(F) + |g|F]$.

phosphine ligand were treated as rigid bodies (C–C 1.395 Å, C–C–C 120°) and the H atoms were added in calculated positions (C–H 1.08 Å) and refined 'riding' on their corresponding C atoms. The residual peaks were of c. 1.5 e/Å^3 in the vicinity of the metal atoms. The final atomic coordinates are listed in Table 2, and the thermal parameters in Table 3.

Crystal Structure of $Ir_4(CO)_7(\mu\text{-}CO)_3[\mu\text{-}Ph_2P(CH_2)_4PPh_2]$

The crystal consists of discrete molecular units separated by normal van der Waals interactions. The overall molecular geometry of **1** is shown in Fig. 1 together with the atomic labelling scheme. The four Ir atoms define an almost regular tetrahedron (Ir–Ir bond lengths range from 2.709(1) to 2.791(1) Å, average 2.731(1) Å) and three kinds of metal environments can be distinguished: the apical atom Ir(3) bears three terminal CO groups; one basal atom, Ir(4), bears two terminal and two edge-bridging COs, while Ir(1) and Ir(2) bear one terminal and two bridging COs and form an eight-membered ring with

TABLE 2. Fractional atomic coordinates

Atom	x	y	z
Ir(1)	0.48049(7)	0.13307(6)	0.26941(5)
Ir(2)	0.26659(7)	0.10265(6)	0.30377(5)
Ir(3)	0.42967(8)	0.07762(6)	0.40101(5)
Ir(4)	0.37158(8)	0.22060(6)	0.36574(5)
P(1)	0.5100(5)	0.1921(4)	0.1599(3)
P(2)	0.1321(5)	0.1503(4)	0.2278(3)
C(1)	0.5335(20)	0.2253(14)	0.3315(12)
O(1)	0.6120(13)	0.2594(10)	0.3448(10)
C(2)	0.3246(21)	0.3070(15)	0.3154(13)
O(2)	0.2946(17)	0.3558(11)	0.2853(11)
C(3)	0.3971(21)	0.2588(16)	0.4552(13)
O(3)	0.4161(20)	0.2827(15)	0.5089(14)
C(4)	0.2178(21)	0.1714(16)	0.3881(12)
O(4)	0.1504(14)	0.1812(12)	0.4275(10)
C(5)	0.1853(31)	0.0189(22)	0.3223(17)
O(5)	0.1460(23)	-0.0417(15)	0.3355(16)
C(6)	0.3772(16)	0.0474(17)	0.2345(12)
O(6)	0.3778(14)	-0.0088(10)	0.1992(9)
C(7)	0.6135(20)	0.0856(13)	0.2657(11)
O(7)	0.6957(15)	0.0599(13)	0.2661(12)
C(8)	0.5657(23)	0.1038(14)	0.4449(15)
O(8)	0.6405(17)	0.1216(15)	0.4737(12)
C(9)	0.4520(21)	-0.0235(18)	0.3728(12)
O(9)	0.4638(21)	-0.0859(13)	0.3604(12)
C(10)	0.3404(22)	0.0629(18)	0.4846(14)
O(10)	0.2943(21)	0.0573(18)	0.5361(13)
C(12)	0.7168(14)	0.2490(8)	0.1647(10)
C(13)	0.7930(14)	0.3052(8)	0.1787(10)
C(14)	0.7596(14)	0.3775(8)	0.1981(10)
C(15)	0.6500(14)	0.3936(8)	0.2034(10)
C(16)	0.5738(14)	0.3375(8)	0.1894(10)
C(11)	0.6072(14)	0.2651(8)	0.1700(10)
C(18)	0.5961(15)	0.1672(7)	0.0249(9)
C(19)	0.6386(15)	0.1238(7)	-0.0307(9)
C(20)	0.6507(15)	0.0461(7)	-0.0220(9)
C(21)	0.6203(15)	0.0116(7)	0.0423(9)
C(22)	0.5778(15)	0.0550(7)	0.0979(9)
C(17)	0.5657(15)	0.1328(7)	0.0892(9)
C(24)	0.1024(13)	0.0161(12)	0.1548(10)
C(25)	0.0468(13)	-0.0348(12)	0.1104(10)
C(26)	-0.0577(13)	-0.0182(12)	0.0866(10)
C(27)	-0.1066(13)	0.0492(12)	0.1072(10)
C(28)	-0.0511(13)	0.1001(12)	0.1516(10)
C(23)	0.0534(13)	0.0835(12)	0.1754(10)
C(30)	-0.0485(15)	0.1599(8)	0.3148(10)
C(31)	-0.1229(15)	0.1977(8)	0.3575(10)
C(32)	-0.1187(15)	0.2761(8)	0.3637(10)
C(33)	-0.0402(15)	0.3168(8)	0.3271(10)
C(34)	0.0342(15)	0.2790(8)	0.2844(10)
C(29)	0.0301(15)	0.2006(8)	0.2783(10)
C(35)	0.3945(17)	0.2372(14)	0.1137(14)
C(36)	0.3150(23)	0.1760(17)	0.0910(18)
C(37)	0.1963(26)	0.1906(26)	0.0856(18)
C(38)	0.1591(23)	0.2219(14)	0.1567(12)

the bidentate diphosphinobutane ligand. The two P atoms are both in axial sites on the basal face. The Ir–C and C–O distances for both terminal and

TABLE 3. Anisotropic thermal parameters (A^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ir(1)	0.027(1)	0.030(1)	0.027(1)	0.002(1)	0.003(1)	−0.002(1)
Ir(2)	0.024(1)	0.030(1)	0.031(1)	−0.004(1)	0.001(1)	0.001(1)
Ir(3)	0.034(1)	0.031(1)	0.025(1)	0.002(1)	−0.002(1)	0.002(1)
Ir(4)	0.036(1)	0.026(1)	0.035(1)	−0.005(1)	−0.002(1)	0.002(1)
P(1)	0.036(4)	0.050(4)	0.031(3)	0.011(3)	0.001(3)	−0.004(3)
P(2)	0.029(4)	0.039(4)	0.044(4)	−0.004(3)	−0.004(3)	0.001(3)
C(1)	0.042(15)	0.035(15)	0.025(12)	−0.004(11)	0.010(11)	0.002(13)
O(1)	0.029(10)	0.042(11)	0.071(13)	−0.013(9)	0.005(9)	−0.019(9)
C(2)	0.052(17)	0.020(15)	0.044(15)	0.004(12)	−0.030(12)	−0.003(12)
O(2)	0.081(15)	0.027(12)	0.081(15)	0.008(11)	−0.024(12)	−0.004(11)
C(3)	0.060(18)	0.068(20)	0.024(13)	−0.054(14)	0.010(12)	−0.039(15)
O(3)	0.088(18)	0.106(22)	0.088(18)	−0.025(16)	0.000(14)	−0.002(16)
C(4)	0.046(16)	0.060(19)	0.019(12)	−0.002(12)	−0.019(11)	0.018(14)
O(4)	0.045(11)	0.094(17)	0.047(11)	−0.021(11)	0.026(10)	−0.002(11)
C(5)	0.118(31)	0.088(28)	0.063(22)	−0.047(20)	0.060(22)	0.012(24)
O(5)	0.136(24)	0.073(18)	0.145(25)	0.011(17)	0.046(19)	−0.079(18)
C(6)	0.094(11)	0.085(22)	0.027(13)	0.015(14)	0.012(9)	0.017(13)
O(6)	0.062(13)	0.040(11)	0.043(10)	−0.022(9)	0.021(9)	−0.014(9)
C(7)	0.041(15)	0.032(15)	0.024(12)	0.005(10)	−0.010(10)	−0.010(12)
O(7)	0.028(11)	0.084(18)	0.110(18)	−0.004(14)	0.004(11)	0.022(11)
C(8)	0.058(19)	0.012(13)	0.064(18)	0.004(12)	−0.020(15)	−0.004(13)
O(8)	0.048(14)	0.113(22)	0.084(17)	0.014(14)	−0.026(12)	−0.022(14)
C(9)	0.048(16)	0.073(22)	0.015(12)	−0.022(13)	0.012(11)	−0.004(15)
O(9)	0.130(22)	0.053(15)	0.057(14)	−0.007(12)	0.024(13)	0.003(14)
C(10)	0.044(17)	0.082(24)	0.035(15)	−0.022(15)	−0.011(13)	0.018(16)
O(10)	0.099(20)	0.174(29)	0.074(17)	0.030(18)	0.061(16)	0.036(19)
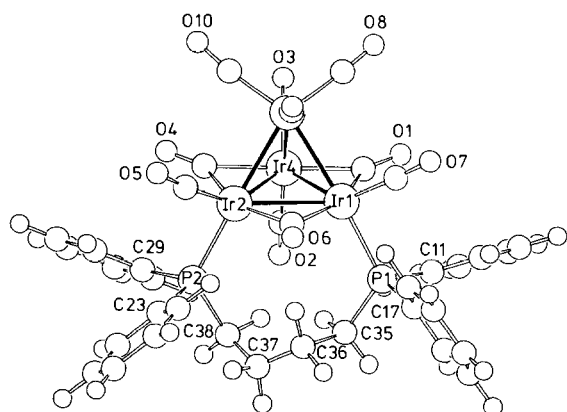
Fig. 1. Molecular structure of 1.

bridging ligands (average 1.87(3), 1.13(3), and 2.11(3), 1.16(3) Å, respectively) are in the range reported for other Ir clusters. As previously observed [10], the bridged Ir—Ir bonds around the basal plane are slightly longer (mean length 2.745(1) Å) than the unbridged ones (2.716(1) Å). The eight-membered ring formed by the Ir atoms and the P—(CH$_2$)$_4$—P chain has a twist conformation. The two Ir atoms and the P atoms are almost coplanar with a maximum deviation from the P(1)—Ir(1)—Ir(2)—P(2) mean plane of 0.05 Å. The P-bonded C atoms lie close to this plane (elevation 0.27 and 0.49 Å, respectively)

while the remaining part of the aliphatic chain is folded outwards from the basal Ir$_3$ plane in order to minimize repulsions with the neighbouring axial COs. Relevant bond distances and angles for 1 are reported in Table 4.

The pseudo m-symmetry (a mirror plane bisecting the bridged Ir—Ir bond and comprising Ir(3) and Ir(4)) is broken by the aliphatic chain conformation, so that the molecule is asymmetric in its crystal. The effect of the long aliphatic chain is clearly seen in the widening of the P—Ir—Ir—P system and in the value of the Ir—P—C angle (average 121(1)°) which is larger than in Ir$_4$(CO)$_{10}$[Me$_2$P(CH$_2$)$_2$PMe$_2$] (116(2)°) [1]. The P—C—C and C—C—C angles are also larger than expected for sp^3 atoms (112(1) and 115(3)°, respectively). These values suggest that the four-membered aliphatic chain leads to a rather tense steric situation. This is further supported by the observation that the Ir(1)—Ir(2) bond is the longest (2.791(1) Å) within the metal framework of 1, and is longer than the corresponding bond in the related species Ir$_4$(CO)$_{10}$[Me$_2$P(CH$_2$)$_2$PMe$_2$] (2.731(2) Å [1]) and Ir$_4$(CO)$_8$(Ph$_2$PCH=CHPPh$_2$)$_2$ (2.712(2) Å [11]) which both contain six-membered rings.

A comparable situation was observed in the series of diphosphino derivatives H$_4$Ru$_4$(CO)$_{10}$[Ph$_2$P-(CH$_2$)$_n$PPh$_2$] (n = 1, 2, 4) [12]. It was suggested that aliphatic chains longer than (CH$_2$)$_4$ could not be

TABLE 4. Bond distances (A) and relevant angles (°) with e.s.d.s in parentheses for [Ir$_4$(CO)$_7$(μ_2-CO)$_3$(Ph$_2$P–(CH$_2$)$_4$–PPh$_2$)]

Ir(1)–Ir(2)	2.791(1)
Ir(1)–Ir(4)	2.736(1)
Ir(2)–Ir(4)	2.709(1)
Ir(3)–Ir(1)	2.711(1)
Ir(3)–Ir(2)	2.727(1)
Ir(3)–Ir(4)	2.711(2)
Ir(1)–P(1)	2.316(6)
Ir(2)–P(2)	2.326(7)
P(1)–C(11)	1.78(2)
P(1)–C(17)	1.82(2)
P(2)–C(23)	1.81(2)
P(2)–C(29)	1.82(2)
P(1)–C(35)	1.84(2)
P(2)–C(38)	1.86(2)
C(35)–C(36)	1.52(2)
C(36)–C(37)	1.50(2)
C(37)–C(38)	1.51(2)
Ir(3)–C(8)	1.92(3)
C(8)–O(8)	1.11(3)
Ir(3)–C(9)	1.89(3)
C(9)–O(9)	1.14(3)
Ir(3)–C(10)	1.93(3)
C(10)–O(10)	1.12(3)
Ir(4)–C(2)	1.88(3)
C(2)–O(2)	1.09(3)
Ir(4)–C(3)	1.81(2)
C(3)–O(3)	1.11(3)
Ir(2)–C(5)	1.83(4)
C(5)–O(5)	1.21(4)
Ir(1)–C(7)	1.85(3)
C(7)–O(7)	1.12(3)
Ir(1)–C(1)	2.10(3)
Ir(4)–C(1)	2.11(2)
C(1)–O(1)	1.17(3)
Ir(4)–C(4)	2.14(3)
Ir(2)–C(4)	2.08(3)
C(4)–O(4)	1.13(3)
Ir(2)–C(6)	2.13(2)
Ir(1)–C(6)	2.08(3)
C(6)–O(6)	1.19(3)
Ir(1)P(1)C(11)	110.6(7)
Ir(1)P(1)C(17)	115.8(5)
Ir(1)P(1)C(35)	118.2(9)
Ir(2)P(2)C(23)	117.7(6)
Ir(2)P(2)C(29)	111.4(7)
Ir(2)P(2)C(38)	123(1)
P(1)C(35)C(36)	108(2)
P(2)C(38)C(37)	115(2)
C(35)C(36)C(37)	122(3)
C(36)C(37)C(38)	108(3)
Ir(1)C(1)O(1)	140(2)
Ir(1)C(7)O(7)	176(2)
Ir(1)C(6)O(6)	140(2)
Ir(2)C(6)O(6)	136(2)
Ir(2)C(5)O(5)	170(3)
Ir(2)C(4)O(4)	143(2)
Ir(4)C(4)O(4)	137(2)

(continued)

TABLE 4. *(continued)*

Ir(4)C(3)O(3)	178(2)
Ir(4)C(2)O(2)	178(2)
Ir(4)C(1)O(1)	139(2)
Ir(3)C(8)O(8)	175(3)
Ir(3)C(9)O(9)	175(2)
Ir(3)C(10)O(10)	175(3)

accommodated in a bidentate coordination mode by the diphosphino ligand, thus accounting for the observed dimerization of M$_4$ units via a diphosphino bridge. Similar behaviour can be expected for the Ir$_4$ species. Bridge-chelate isomerization should also be difficult to achieve for the same reasons.

Structure of 1 in Solution

In the ^{13}C NMR spectrum of a ^{13}C-enriched sample of 1 in CD$_2$Cl$_2$, all exchange processes are stopped at c. −80 °C. At this temperature, ten CO resonances are observed at δ 218.0 (a), 202.7 and 202.4 (b and b'), 173.1 (J(CP) 7.8 Hz) and 172.0 (J(CP) 8.1 Hz) (f and f'), 172.4 (d), 159.8 and 158.4 (c and e), and 156.6 (J(CP) 30 Hz) and 156.3 ppm (J(CH) 28 Hz) (g and g') (Scheme 1).
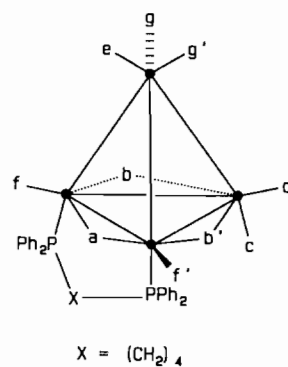
Scheme 1.

The three low field signals are clearly due to the edge-bridging COs, and the two highest field signals exhibit a ^{3}J(CP) typical of COs in a pseudo-*trans* position relative to a P atom [3]. The assignment of the other signals is based on COSY-90 spectra taken at −85 °C. A coupling is indeed observed between the bridging COs. Of the three signals appearing in the frequency range characteristic of radial COs, one is a singlet (d), whereas those at 173.1 and 172.0 ppm present a C–C coupling indicating a pseudo-*trans* relationship (f and f'). Analogous couplings have already been observed by Mann *et al.* [2] in Ir$_4$-(CO)$_{11}$(PEt$_3$). A pseudo-*trans* coupling is also observed between the signals at 159.8 and 158.4 ppm

which are therefore assigned to c and e. An ambiguity in the assignments exists within each of the four pairs of signals, but this is of no importance for the following discussion.

The following changes are observed upon raising the temperature from -80 to $-40\ ^{\circ}C$: (i) signals a, c, e and d do not broaden, (ii) bridging COs remain bridging, and b and b$'$ exchange, (iii) apical COs remain apical, and g and g$'$ exchange, and (iv) only two signals around 170 ppm exchange, namely f and f$'$.

The 2-D and variable temperature ^{13}C NMR are clearly incompatible with an axial—radial arrangement of the two P atoms as proposed previously [1], but are in agreement with a ground state structure in solution resembling that found in the crystal, e.g. with the two P atoms in axial positions. These results also indicate that the fluxionality of 1 is *not* due to CO mobility about the metal core. Therefore, it may be concluded that the asymmetry of 1 with respect to the plane containing a, c, d, e and two Ir atoms is due to an asymmetrical ground state conformation of the aliphatic chain, and that the exchanges observed upon raising the temperature are only due to flipping of the $(CH_2)_4$ chain between two equivalent conformations.

The $\{^1H\}^{13}C$ NMR spectrum of 1 in CD_2Cl_2 at $-80\ ^{\circ}C$ indeed shows four resonances in the aliphatic carbon region at δ 28.8 (d, 32 Hz), 27.4 (d, 23 Hz), 22.3 (d, 11 Hz) and 16.8 ppm (d $\approx$ 3 Hz). Upon raising the temperature, these signals coalesce pairwise, giving two apparent doublets at room temperature. Due to prohibitive acquisition times for the CH_2 signals, the rate constants k of this dynamic process were evaluated from line-shape analysis [7] of the variable temperature ^{13}C NMR spectra for the (f $\leftrightarrow$ f$'$) exchange using the following Kubo-Sack matrix elements [13]: $(1,1) = (2,2) = (3,3) = (4,4) = -k$; $(1,3) = (1,4) = (2,3) = (2,4) = (3,1) = (3,2) = (4,1) = (4,2) = k/2$.

A second series of rate constant measurements were obtained from the variable temperature $\{^1H\}^{31}P$

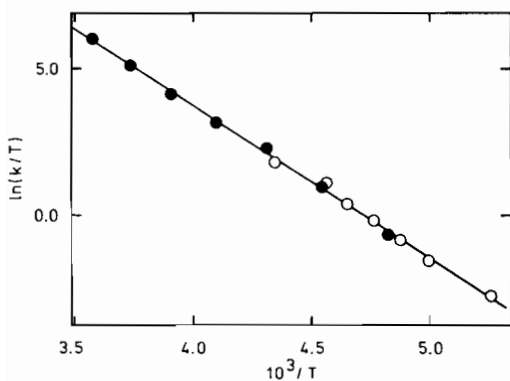NMR spectra of 1 in CD_2Cl_2. The two signals (δ -5.5 and -31.0 ppm) of the blocked spectrum at $-82\ ^{\circ}C$ coalesce at $c.\ -29\ ^{\circ}C$, and the rate constants of the two-site exchange were also evaluated by line shape analysis. The combined Eyring plot of the ^{13}C and ^{31}P NMR results (Fig. 2) shows a good agreement between the two sets of measurements, and a value of 41.5 ± 0.8 kJ/mol at 25 $^{\circ}C$ was obtained for the free enthalpy of activation of the chain flipping process.

A similar cluster compound, $Co_4(CO)_{10}[\mu\text{-}Ph_2P(CH_2)_4PPh_2]$ has been reported by Aime *et al.* [14] and an axial—radial arrangement of the P atoms has been proposed on the basis of the ^{31}P NMR spectra. However, the ^{13}C NMR spectrum was not measured and would presumably show the same characteristics to that of 1.

Supplementary Material

Lists of observed and calculated structure factors of atomic coordinates for H atoms, of thermal parameters, and of variable temperature ^{13}C and ^{31}P NMR data are available from R. Roulet.

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Fig. 2. Eyring plot of the rate of chain flipping in 1 as measured by ^{31}P NMR ($\bullet$) and by ^{13}C NMR ($\circ$).

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