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A seven-bond coupling, $^7J(PP)$ or through space coupling in the azine diphosphine Z,Z-$PPh_2CH_2C(Bu^t){=}N{-}N{=}(Bu^t)CCH_2PPh_2$: crystal structure of Z,Z-$P({=}O)Ph_2CH_2(Bu^t){=}N{-}N{=}(Bu^t)$-$CCH_2P({=}O)Ph_2$

Sarath D. Perera, Bernard L. Shaw*, Mark Thornton-Pett and Jonathan D. Vessey
School of Chemistry, Leeds University, Leeds LS2 9JT (UK)

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Abstract

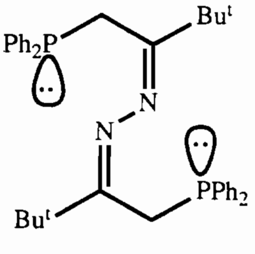
Analysis of the $^{13}C\{^1H\}$ NMR spectrum of Z,Z-$PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$ (**1**) gives second order patterns for the C_{ipso}, C_{ortho}, C_{meta}, PCH_2 and C=N carbons caused by a non-zero seven-bond coupling, $^7J(PP)$. Simulation of the spectra gives $^7J(PP) = 4.8$ Hz. The corresponding diphosphine dioxide **2** gives first order $^{13}C\{^1H\}$ spectra, i.e. $^7J(PP) \sim 0$ Hz. Possible explanations for this unusually large value of $^7J(PP)$ are discussed. Crystals of **2** are orthorhombic, space group *Pbca*, with $a = 1592.2(3)$, $b = 1196.1(2)$, $c = 1663.0(3)$ pm and $Z = 4$; final R factor 0.0381 for 1780 observed reflections.

Introduction

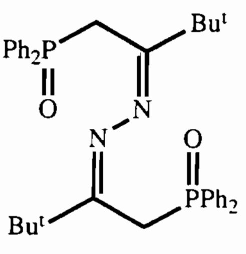
In a previous paper [1] we described the new azine diphosphine $PPh_2CH_2C(Bu^t){=}N{-}N{=}C(Bu^t)CH_2PPh_2$, which was shown to have the Z,Z configuration by X-ray crystallography. When this azine diphosphine **1** was treated with $[M(CO)_4$ (norbornadiene)] (M = Cr, Mo, W) the norbornadiene was displaced to give $[M(CO)_4\{PPh_2CH_2C(Bu^t){=}N{-}N{=}(Bu^t)CCH_2PPh_2\}]$ in which azine diphosphine is bonded in the E,Z configuration giving a nine-membered ring. These tetracarbonyl complexes were thermally unstable and when heated in benzene to *c.* 75 °C, the corresponding tricarbonyl complexes *fac*-$[M(CO)_3\{PPh_2CH_2C(Bu^t){=}N{-}N{=}(Bu^t)CCH_2PPh_2\}]$ were formed with the E,Z-azine diphosphine acting as a tridentate ligand.

Experimental

The general methods and instrumentation used were the same as those reported in recent papers from this laboratory [2]. The $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker AM-400 spectrometer; for **1** the digitisation was increased to *c.* 0.05 Hz/pt by recording the spectrum one resonance at a time. The spectra were simulated using standard Bruker software (PANIC programme). The diphosphine **1** and the corresponding dioxide **2** were prepared as described previously [1].



1



2

Single crystal X-ray diffraction analysis of 2

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω/θ scan mode using graphite monochromated Mo Kα radiation. The data-set was corrected for absorption semi-empirically using azimuthal psi scans.

The structure was determined by direct methods using SHELXS-86 [3] and was refined by full-matrix least-squares using the SHELX76 program system [4]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The phenyl groups were treated as rigid bodies with idealised hexagonal symmetry (C–C = 139.5 pm). All hydrogen atoms were included in calculated positions (C–H = 96 pm) and were refined with an overall isotropic thermal parameter. The weight-

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*Author to whom correspondence should be addressed.

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ing scheme $w = [\sigma^2(F_o) + 0.0003(F_o)^2]^{-1}$ was used. For final non-hydrogen atomic coordinates see Table 3.

Crystal data
$C_{36}H_{42}N_2O_2P_2$, $M = 596.69$, orthorhombic, space group *Pbca*, $a = 1592.2(3)$, $b = 1196.1(2)$, $c = 1663.0(3)$ pm, $U = 3.1671(11)$ nm^3, $Z = 4$, $D_x = 1.25$ Mg m^{-3}, λ(Mo Kα) = 71.069 pm, $\mu = 1.32$ cm^{-1}, $F(000) = 1272$.

Data collection
$4.0 < 2\theta < 50.0°$, 3169 data collected, 1780 with $I > 2.0\ \sigma(I)$ considered observed, $T = 80$ K.

Structure refinement
Number of parameters = 176, $R = 0.0381$, $R_w = 0.0390$.

Results and discussion

We have now studied the $^{13}C\{^1H\}$ NMR spectrum of this unusual diphosphine in more detail than previously and find that some of the carbons of the phenyl rings, namely the *ipso*-, *ortho*- and *meta*-carbons, together with the resonances of the PCH_2 and C=N carbons, give second order resonance patterns, which indicate a phosphorus–phosphorus coupling of a few hertz. The actual patterns are given in Fig. 1. We have calculated the patterns for these carbons using the measured values of J(PC) and various values of J(PP). The best agreement between the observed and simulated (calculated) patterns is for J(PP) = 4.8 Hz; as can be seen from Fig. 1, the agreement between the observed and simulated spectra is very good. The calculated spectra using other values of ^7J(PP), e.g. 4.6 or 5.0 Hz, agree less with the observed spectra than does that using ^7J(PP) = 4.8 Hz.

In view of the unusually large long range coupling in **1** we have examined the $^{13}C\{^1H\}$ NMR spectra of the corresponding diphosphine dioxide **2** (see Table 1). None of the ^{13}C resonances showed second order features, indicating that ^7J(PP) is approximately zero. We have also determined the crystal structure of this diphosphine dioxide **2** by X-ray diffraction and established that it also has the *Z*,*Z* configuration (Fig. 2, see below).

The value of 4.8 Hz for ^7J(PP) is ostensibly that of a seven-bond coupling constant. In the extensive studies of Colquhoun and McFarlane [5] on diphosphines of type Ph_2PXPPh_2 with X = a variety of bridging groups including $-(CH_2)_x-$ ($x = 1$–3), *cis* and *trans* –CH=CH–, –C≡C– etc., the values of J(PP) were measured by triple resonance experiments, e.g. for the ditertiary phosphines of type $Ph_2P(CH_2)_xPPh_2$ $^2J(PP) = +125$ Hz ($x = 1$), $^3J(PP) = +33.6$ Hz ($x = 2$) and $^4J(PP) = 1.0$ Hz ($x = 3$). Other workers have observed zero coupling constants for ^4J(PP) [6] and ^6J(PP) [7].

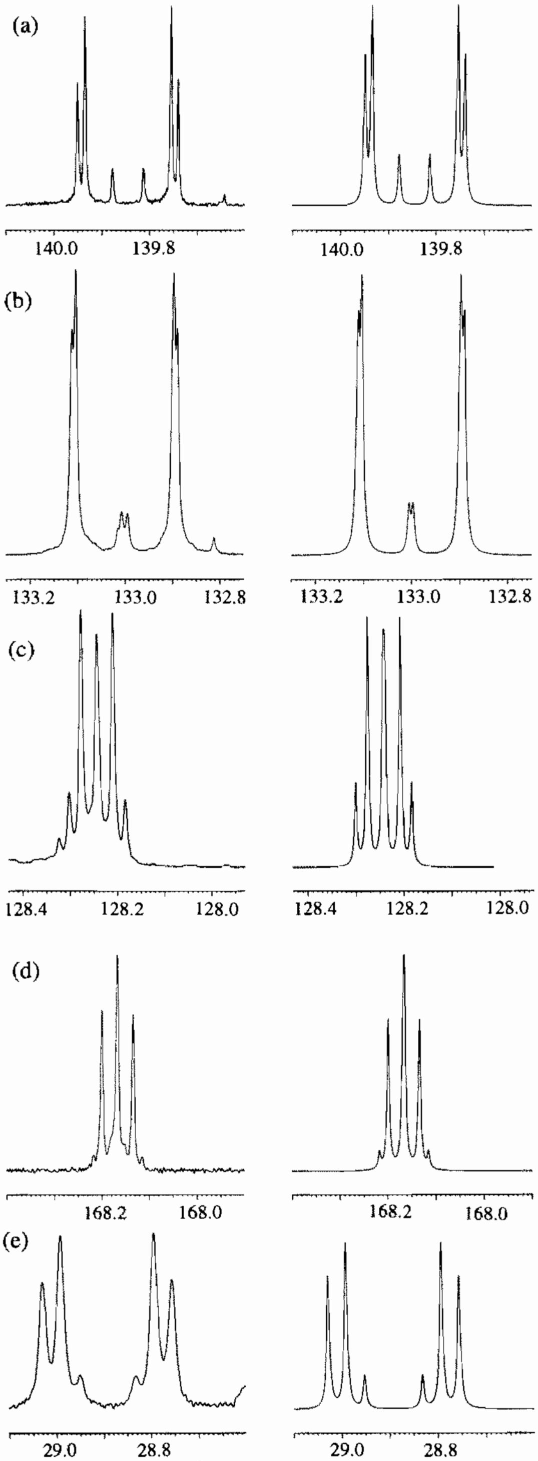

Fig. 1. Observed (left) and simulated (right) portions of the $^{13}C\{^1H\}$ NMR spectrum of **1** in $CDCl_3$ at 100.6 MHz. (a) C_{ipso}; (b) C_{ortho}; (c) C_{meta}; (d) C=N; (e) PCH_2.

Appreciable coupling constants ^7J(HH) and ^7J(FF) have been observed in fully conjugated systems, e.g. styrene [8] and fluorostyrenes [9]. A value of ^7J(PP) of 0.3 Hz has been reported for

TABLE 1. $^{13}C\{^1H\}$ NMR data[a]

Compound	δ_c (ppm)	$\Delta\delta$ (ppb)	^nJ (Hz)	$^{n'}J$ (Hz)	Assignment
1	168.1	2.4	5.0 ($n=2$)	1.6 ($n'=5$)	C=N
	139.8	22.9	18.2 ($n=1$)	−0.2 ($n'=8$)	C_{ipso}
	133.0	4.3	20.4 ($n=2$)	0.3 ($n'=9$)	C_{ortho}
	128.5				C_{para}
	128.3	1.9	6.7 ($n=3$)	0.0 ($n'=10$)	C_{meta}
	38.4				$\mathit{C}\mathrm{Me}_3$
	28.8	40.8	22.5 ($n=1$)	−2.6 ($n'=6$)	CH_2
	28.3				$\mathrm{C}\mathit{Me}_3$
2	167.4		8.7 ($n=2$)	2.3 ($n'=5$)	C=N
	134.8		100.1 ($n=1$)		C_{ipso}
	131.2		3.0 ($n=4$)		C_{para}
	130.5		9.5 ($n=2$)		C_{ortho}
	128.2		11.9 ($n=3$)		C_{meta}
	38.4				$\mathit{C}\mathrm{Me}_3$
	32.0		62.9 ($n=1$)		CH_2
	28.3				$\mathrm{C}\mathit{Me}_3$

[a] Recorded in 100.6 MHz in $CDCl_3$; $\Delta\delta = |\delta(^{13}CP - \delta(^{12}CP)|$; n is the order of the coupling to the proximate phosphorus and n' the order of the coupling to the more remote phosphorus.

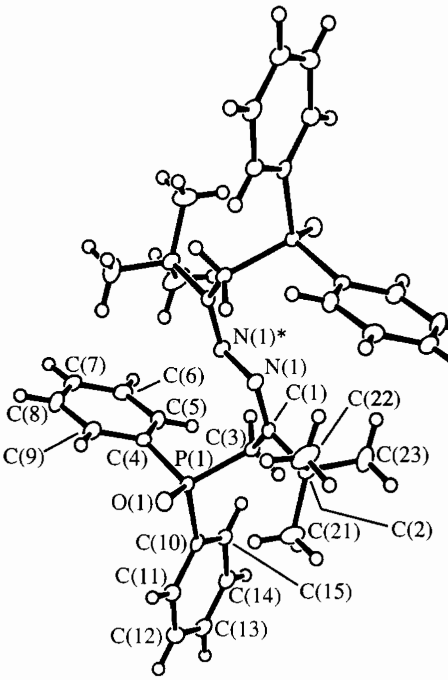

Fig. 2. ORTEP [13] representation of the crystal structure of 2.

TABLE 2. Bond lengths (pm) and angles (°) for compound 2 with e.s.d.s in parentheses

O(1)–P(1)	148.5(3)	C(3)–P(1)	182.6(5)
C(4)–P(1)	180.8(3)	C(10)–P(1)	181.3(3)
C(1)–N(1)	128.4(4)	N(1)–N(1*)	142.8(5)
C(2)–C(1)	153.1(6)	C(3)–C(1)	151.5(5)
C(21)–C(2)	153.0(6)	C(22)–C(2)	152.5(6)
C(23)–C(2)	153.4(6)		
C(3)–P(1)–O(1)	115.0(2)	C(4)–P(1)–O(1)	112.5(2)
C(4)–P(1)–C(3)	107.3(2)	C(10)–P(1)–O(1)	112.7(2)
C(10)–P(1)–C(3)	105.0(2)	C(10)–P(1)–C(4)	103.6(2)
C(1)–N(1)–N(1*)	112.8(3)		
C(2)–C(1)–N(1)	117.6(3)	C(3)–C(1)–N(1)	124.1(3)
C(3)–C(1)–C(2)	118.2(3)		
C(21)–C(2)–C(1)	111.8(3)	C(22)–C(2)–C(1)	110.8(3)
C(22)–C(2)–C(21)	108.7(4)	C(23)–C(2)–C(1)	106.8(3)
C(23)–C(2)–C(21)	109.1(3)	C(23)–C(2)–C(22)	109.6(3)
C(1)–C(3)–P(1)	112.2(3)	C(5)–C(4)–P(1)	121.6(2)
C(9)–C(4)–P(1)	118.1(2)	C(11)–C(10)–P(1)	117.9(2)
C(15)–C(10)–P(1)	121.9(2)		

N(1*) is related to N(1) by the symmetry operator (−x, −y, 1.0−z).

$(^i\mathrm{Pr})_2\mathrm{PCH_2P}(^i\mathrm{Pr})(\mathrm{CH_2CH_2P}(^i\mathrm{Pr})\mathrm{CH_2P}(^i\mathrm{Pr})_2$ [10] but we are unable to find in the literature other values of ^7J(PP).

The relatively large value for the ^7J(PP) in 1 may well be due to conformational control of the PPh_2 groups by the tertiary butyl groups: the crystal structure of 1 shows the phosphine phenyl groups to be almost eclipsed with respect to the CH_2 hydrogens (dihedral angle C(15)–P(8)–C(7)–H is 14.7(3)°), an orientation also observed in the structure of 2. Long-range coupling to P^{III} nuclei (but not P^V nuclei) is known to be particularly dependent upon the dihedral angles between bonds and the P^{III} lone pair [11], and it may be that the conformation of the PPh_2 groups imposed by the tertiary butyl groups fortuitously aligns the P^{III} lone pairs for good transmission of the coupling through the backbone. An alternative explanation involves a direct interaction between the phosphorus and the π-system of the azine backbone: since the coupling is only observed for the diphosphine 1 and not for the corresponding dioxide 2, this implies that the interaction involves the phosphorus lone pair. Furthermore, it is

TABLE 3. Atom coordinates ($\times 10^4$) for compound **2** with e.s.d.s in parentheses

	x	*y*	*z*
P(1)	720.6(4)	1130.1(6)	6763.6(4)
O(1)	670(1)	2233(2)	6355(1)
N(1)	−382(1)	311(2)	5028(1)
C(1)	−595(2)	520(2)	5757(2)
C(2)	−1424(2)	1141(3)	5895(2)
C(21)	−1369(2)	1950(3)	6606(2)
C(22)	−1676(2)	1797(3)	5147(2)
C(23)	−2091(2)	249(3)	6077(2)
C(3)	−103(2)	139(2)	6487(2)
C(4)	1717(1)	443(1)	6599(1)
C(5)	1886(1)	−614(1)	6915(1)
C(6)	2688(1)	−1072(1)	6843(1)
C(7)	3321(1)	−474(1)	6454(1)
C(8)	3152(1)	583(1)	6138(1)
C(9)	2350(1)	1041(1)	6211(1)
C(10)	656(1)	1244(1)	7849(1)
C(11)	781(1)	2294(1)	8194(1)
C(12)	800(1)	2408(1)	9028(1)
C(13)	695(1)	1472(1)	9518(1)
C(14)	570(1)	422(1)	9174(1)
C(15)	550(1)	308(1)	8339(1)

also possible that in some way a direct phosphorus–phosphorus lone pair interaction is contributing towards coupling. It has been shown that the radical cation $Ph_2PCH_2CH_2PPh_2{}^+$ has two equivalent phosphorus nuclei and that the diphosphine is in the *cisoid* fashion with the lone pair and singly occupied orbitals on the phosphoruses interacting [12]. As mentioned above, ^3J(PP) in $Ph_2PCH_2CH_2PPh_2$ is 33.6 Hz, but in *cis*-$Ph_2PCH{=}CHPPh_2$ ^3J(PP) is 105.5 Hz whereas in *trans*-$Ph_2PCH{=}CHPPh_2$ it is only 13.4 Hz. It is therefore possible that the lone pairs on phosphorus are interacting directly in *cis*-$PPh_2CH{=}CHPPh_2$ to give the large value of ^3J(PP).

Crystal structure of Z,Z-$Ph_2P(=O)CH_2C(Bu^t)=N{-}N=C(Bu^t)CH_2P(=O)Ph_2$ *(2)*

The crystal structure of the azine diphosphine dioxide **2** is shown in Fig. 2, with selected bond lengths and angles in Table 2 and atom coordinates in Table 3. The crystal structure of **2** shows that the arrangement around both C=N bonds is *Z*. The bond lengths of the backbone are very similar to those reported for the corresponding diphosphine **1** [1] except that the bond lengths between phosphorus and carbon are slightly less in **2** than in **1**, as would be expected.

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