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Crystal structure, and variable temperature proton and carbon-13 NMR spectra of the 9-membered ring complex $[Cr(CO)_4\{E,Z\text{-}PPh_2CH_2C(^tBu){=}N{-}N{=}C(^tBu)CH_2PPh_2\}]$ *

Sarath D. Perera, Bernard L. Shaw, Mark Thornton-Pett and Jonathan D. Vessey

School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)

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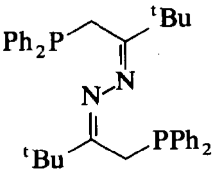
Abstract

Treatment of $[Cr(CO)_4(nbd)]$ (nbd = norbornadiene) with $Z,Z\text{-}PPh_2CH_2C(^tBu){=}N{-}N{=}C(^tBu)CH_2PPh_2$ gave the title compound **2b**, the structure of which was determined by a single crystal X-ray diffraction study. The proton NMR spectrum of **2b** at 308 K and 400 MHz showed that for each of the methylene groups the protons are equivalent, but the spectrum is temperature dependent and at 188 K the slow exchange limiting spectrum is obtained, with all methylene hydrogens chemically non-equivalent; corresponding changes were observed in the $^{13}C\text{-}\{^1H\}$ NMR spectrum. The behaviour is due to the fluxionality of the 9-membered ring.

In a previous paper [1] we described the azine diphosphine $Z,Z\text{-}PPh_2CH_2C(^tBu){=}N{-}N{=}C(^tBu)CH_2PPh_2$ (**1**). This diphosphine cannot chelate through both phosphorus atoms because of the Z,Z-configuration, but we found that under relatively mild conditions it can isomerise around one of the C=N bonds and the resulting E,Z-isomer can then act as a chelating ligand; for example, we reported that it reacted with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) at 20°C to give a tetracarbonyl complex, which we formulated as having a 9-membered chelate ring, **2a**. The corresponding chromium **2b** or tungsten **2c** complexes were also made but a higher temperature (60°C) was required to displace nbd from the tetracarbonyls. The assignment of **2b** and **2c** as tetracarbonyl complexes was based on the observation of three sets of resonances in a 2 : 1 : 1 intensity ratio in the carbonyl region of the $^{13}C\text{-}\{^1H\}$ NMR spectra. All the tetracarbonyl complexes **2a**–**2c** were found to be thermally unstable with respect to loss of a carbonyl ligand to give the corresponding tricarbonyl complexes. For the molybdenum complex **2a** the conversion into the tricarbonyl complex was rapid at ambient temperature, although for **2b** and **2c** more forcing conditions were required [1].



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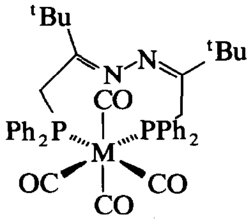

	M
2a	Mo
2b	Cr
2c	W

Nine-membered chelate rings are rare; for example, attempts to prepare complexes of $Ph_2P(CH_2)_6PPh_2$ in which the diphosphine acts as a chelating ligand gave only binuclear or polynuclear complexes with the diphosphine bridging two metal atoms [2].

We have now obtained crystals of the chromium complex **2b** suitable for a crystal structure determination. The X-ray diffraction study showed that two molecules are present in the asymmetric unit, and these are depicted in Fig. 1 (molecule 1 and molecule 2), with selected bond lengths and angles in Table 1 and atom coordinates in Table 2. The bond lengths and bond angles in these two molecules are very similar, and the main difference is the rotational position of the tert-butyl groups. The structure confirms our previous formulation of a 9-membered chelate ring with the

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Correspondence to: Professor B.L. Shaw.

* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday.

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TABLE 1. Selected bond lengths (pm) and angles (°) for **2b** with estimated standard deviations (e.s.d.'s) in parentheses

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
P(1)-Cr(1)	241.2(5)	239.8(5)	P(2)-Cr(1)	244.7(5)	243.3(5)
C(8)-Cr(1)	182.6(14)	178.1(16)	C(11)-Cr(1)	183.0(13)	183.2(13)
C(9)-Cr(1)	190.5(15)	185.1(15)	C(10)-Cr(1)	188.2(12)	191.4(15)
C(3)-C(2)	150.4(18)	150.6(19)	C(7)-C(6)	153.0(18)	152.8(21)
C(31)-C(3)	152.2(19)	153.9(19)	C(61)-C(6)	154.5(20)	153.7(21)
N(4)-C(3)	132.9(16)	130.5(16)	C(6)-N(5)	131.6(16)	129.8(16)
N(5)-N(4)	142.0(15)	141.1(17)			
P(2)-Cr(1)-P(1)	98.3(2)	98.3(2)			
C(8)-Cr(1)-P(1)	88.8(4)	89.5(5)	C(11)-Cr(1)-P(2)	85.2(5)	85.5(5)
C(9)-Cr(1)-P(1)	88.3(5)	89.2(5)	C(9)-Cr(1)-P(2)	97.2(5)	94.1(5)
C(10)-Cr(1)-P(1)	92.0(4)	91.9(5)	C(10)-Cr(1)-P(2)	93.4(4)	92.8(5)
C(11)-Cr(1)-P(1)	175.6(4)	176.2(4)	C(8)-Cr(1)-P(2)	172.9(3)	172.0(4)
C(9)-Cr(1)-C(8)	83.1(7)	87.9(8)	C(11)-Cr(1)-C(9)	88.6(6)	90.0(6)
C(11)-Cr(1)-C(8)	87.8(6)	86.7(6)	C(10)-Cr(1)-C(8)	86.2(6)	84.9(7)
C(10)-Cr(1)-C(9)	169.3(5)	172.7(6)	C(11)-Cr(1)-C(10)	90.4(6)	88.4(6)
C(2)-P(1)-Cr(1)	116.4(5)	117.1(5)	C(7)-P(2)-Cr(1)	128.2(5)	127.0(5)
C(3)-C(2)-P(1)	114.3(9)	115.2(10)	C(6)-C(7)-P(2)	118.8(9)	121.1(10)
C(2)-C(3)-N(4)	109.3(10)	110.7(11)	C(7)-C(6)-N(5)	127.3(12)	127.1(13)
N(5)-N(4)-C(3)	112.1(10)	115.8(11)	C(6)-N(5)-N(4)	107.7(10)	108.5(12)

phosphorus atoms coordinated to the chromium in mutually *cis* positions. The conformation of the 9-membered ring is particularly interesting with essentially an extended conformation for the *E*,*Z*-CH$_2$-C=N-N=C-CH$_2$ moiety. The geometry of the chromium atom is that of a distorted octahedron, the P-Cr-P bond angles being 98.3 and 98.2°.

We previously reported the ^{1}H and ^{13}C-{^{1}H} NMR data at ambient temperature with each CH$_2$ group showing chemically equivalent hydrogens. We have now studied the ^{1}H and ^{1}H-{^{31}P} NMR spectra of **2b** at various temperatures and show the results for the two sets of CH$_2$ protons. As can be seen from Fig. 2, at 308 K each CH$_2$ shows equivalent protons but as the temperature is lowered the resonance for the CH$_2$ protons broaden and decoalesce, so that at 188 K all four of these methylene protons are non-equivalent; *e.g.* in the ^{1}H-{^{31}P} NMR spectrum two AB patterns are observed. At this temperature it is possible that the conformation of the 9-membered ring complex **2b** is that found in the crystal structure. As can be seen from Fig. 2, the range of temperatures studied 308 K to 188 K correspond to the fast exchange limit at the highest temperature (308 K) and to the slow exchange limit at 188 K. Presumably, the process which causes the geminal methylene protons to become equivalent at high temperature involves a 9-membered ring inversion that effectively generates a plane of symmetry through the molecule.

In the ^{13}C-{^{1}H} NMR spectrum we observed a corresponding temperature dependence for those reso-

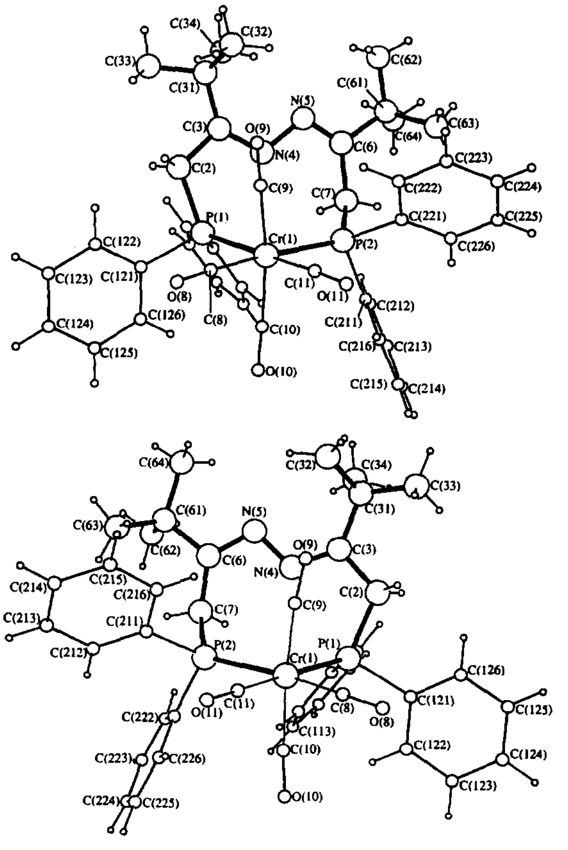

Fig. 1. ORTEP representation of the crystal and molecular structure of molecule 1 (upper) and molecule 2 (lower) of compound **2b**. In the interests of clarity the phenyl carbon atoms, the carbonyl groups and all hydrogen atoms are represented by spheres with an arbitary small value.

TABLE 2. Fractional non-hydrogen atomic co-ordinates ($\times 10^4$) for compound **2b** with e.s.d's in parentheses

Molecule 1			
Cr(1)	173(1)	3149(2)	3565 [a]
P(1)	1452(2)	3019(3)	3594(1)
P(2)	60(2)	5574(3)	3518(1)
C(2)	1923(6)	2719(12)	3189(3)
C(3)	1865(6)	3843(12)	2938(3)
C(31)	2191(7)	3668(14)	2588(3)
C(32)	1608(7)	3532(14)	2335(3)
C(33)	2659(7)	2427(13)	2578(4)
C(34)	2625(8)	4847(16)	2492(4)
N(4)	1480(5)	4822(10)	3072(2)
N(5)	1328(5)	5840(9)	2832(2)
C(6)	939(6)	6749(11)	2986(3)
C(61)	796(7)	7973(15)	2758(4)
C(62)	975(9)	7736(18)	2393(4)
C(63)	10(7)	8418(16)	2781(4)
C(64)	1219(7)	9167(13)	2886(3)
C(7)	729(6)	6790(12)	3360(3)
C(8)	137(5)	1333(13)	3599(3)
O(8)	44(5)	169(10)	3622(2)
C(9)	240(6)	2779(14)	3093(3)
O(9)	242(5)	2507(8)	2812(3)
C(10)	91(5)	3168(11)	4040(3)
O(10)	−7(4)	3047(9)	4322(2)
C(11)	−796(6)	3133(11)	3524(3)
O(11)	−1410(4)	3082(9)	3507(2)
C(111)	1979(3)	4301(7)	3819(2)
C(112)	1647(3)	4977(7)	4084(2)
C(113)	2047(3)	5773(7)	4302(2)
C(114)	2780(3)	5892(7)	4256(2)
C(115)	3112(3)	5215(7)	3990(2)
C(116)	2712(3)	4420(7)	3772(2)
C(121)	1738(4)	1515(6)	3832(2)
C(122)	2011(4)	378(6)	3675(2)
C(123)	2195(4)	−733(6)	3869(2)
C(124)	2106(4)	−706(6)	4220(2)
C(125)	1832(4)	431(6)	4377(2)
C(126)	1648(4)	1542(6)	4183(2)
C(211)	−137(4)	6366(7)	3933(2)
C(212)	272(4)	7392(7)	4072(2)
C(213)	79(4)	7962(7)	4380(2)
C(214)	−524(4)	7506(7)	4551(2)
C(215)	−932(4)	6480(7)	4413(2)
C(216)	−739(4)	5910(7)	4104(2)
C(221)	−724(4)	6092(9)	3275(2)
C(222)	−893(4)	5418(9)	2977(2)
C(223)	−1470(4)	5833(9)	2781(2)
C(224)	−1878(4)	6922(9)	2884(2)
C(225)	−1709(4)	7596(9)	3183(2)
C(226)	−1132(4)	7181(9)	3378(2)

TABLE 2 (continued)

Molecule 2				
Cr(1)	2740(1)	3156(2)	768(1)	
P(1)	4008(2)	2991(3)	720(1)	
P(2)	2648(2)	5573(3)	803(1)	
C(2)	4506(7)	2696(13)	1109(3)	
C(3)	4450(6)	3781(12)	1372(3)	
C(31)	4810(7)	3537(13)	1716(3)	
C(33)	4994(9)	2092(18)	1784(5)	
C(32)	4277(13)	3817(25)	2005(5)	
C(34)	5401(9)	4490(21)	1736(5)	
N(4)	4090(6)	4793(10)	1254(3)	
N(5)	3970(6)	5846(11)	1485(3)	
C(6)	3563(7)	6724(13)	1340(3)	
C(61)	3402(7)	7954(16)	1560(4)	
C(62)	3818(8)	9158(16)	1388(4)	
C(63)	2641(8)	8292(18)	1576(4)	
C(64)	3732(8)	7773(17)	1926(4)	
C(7)	3333(6)	6757(13)	969(3)	
C(8)	2677(6)	1388(15)	732(4)	
O(8)	2595(5)	180(10)	713(2)	
C(9)	2824(6)	2931(14)	1232(3)	
O(9)	2857(6)	2608(10)	1512(4)	
C(10)	2625(6)	3152(13)	287(3)	
O(10)	2530(4)	3032(9)	−1(2)	
C(11)	1769(6)	3159(12)	808(3)	
O(11)	1154(5)	3122(9)	839(2)	
C(111)	4539(3)	4250(7)	489(2)	16(2)
C(112)	4213(3)	4935(7)	223(2)	23(3)
C(113)	4618(3)	5736(7)	8(2)	24(3)
C(114)	5350(3)	5852(7)	59(2)	31(3)
C(115)	5676(3)	5167(7)	325(2)	35(3)
C(116)	5270(3)	4367(7)	539(2)	31(3)
C(121)	4295(4)	1477(6)	482(2)	24(3)
C(122)	4178(4)	1482(6)	133(2)	27(3)
C(123)	4367(4)	374(6)	−61(2)	28(3)
C(124)	4672(4)	−738(6)	94(2)	24(3)
C(125)	4789(4)	−742(6)	443(2)	37(3)
C(126)	4600(4)	366(6)	637(2)	38(3)
C(211)	1866(3)	6121(8)	1055(2)	24(3)
C(212)	1445(3)	7196(8)	955(2)	30(3)
C(213)	880(3)	7610(8)	1159(2)	41(4)
C(214)	737(3)	6949(8)	1462(2)	43(3)
C(215)	1159(3)	5874(8)	1562(2)	42(3)
C(216)	1724(3)	5460(8)	1358(2)	31(3)
C(221)	2441(4)	6370(8)	390(2)	27(3)
C(222)	2848(4)	7404(8)	255(2)	27(3)
C(223)	2655(4)	7989(8)	−52(2)	43(4)
C(224)	2053(4)	7540(8)	−224(2)	34(4)
C(225)	1645(4)	6506(8)	−89(2)	34(3)
C(226)	1839(4)	5921(8)	218(2)	31(3)

[a] Co-ordinate fixed in order to define origin.

nances arising from carbon atoms related by this plane of symmetry, *viz.* the two mutually *trans*-carbonyl carbons and the phosphine phenyl groups. We reported previously [1] that at ambient temperature the two mutually *trans*-carbonyls gave a triplet at $\delta = 221.4$ ppm, $^1J(PC) = 16$ Hz. This corresponds to the fast exchange limit, and we now find that on cooling of the solution this resonance splits, and at the slow exchange limit (188 K) two triplets, each corresponding to one carbonyl, are observed, at $\delta = 222.4$ ppm and $\delta = 219.6$ ppm, $^1J(PC)$ *ca.* 15 Hz in each case. We did not report the carbon-13 data for the phenyl carbons previously, but we now find that, at 308 K, there are two broad doublets, at *ca.* 140.0 and 138.0 ppm $^1J(PC)$ *ca.* 30 Hz, each due to two *ipso*-carbon atoms made equivalent by rapid inversion of the 9-membered ring, but at 188 K

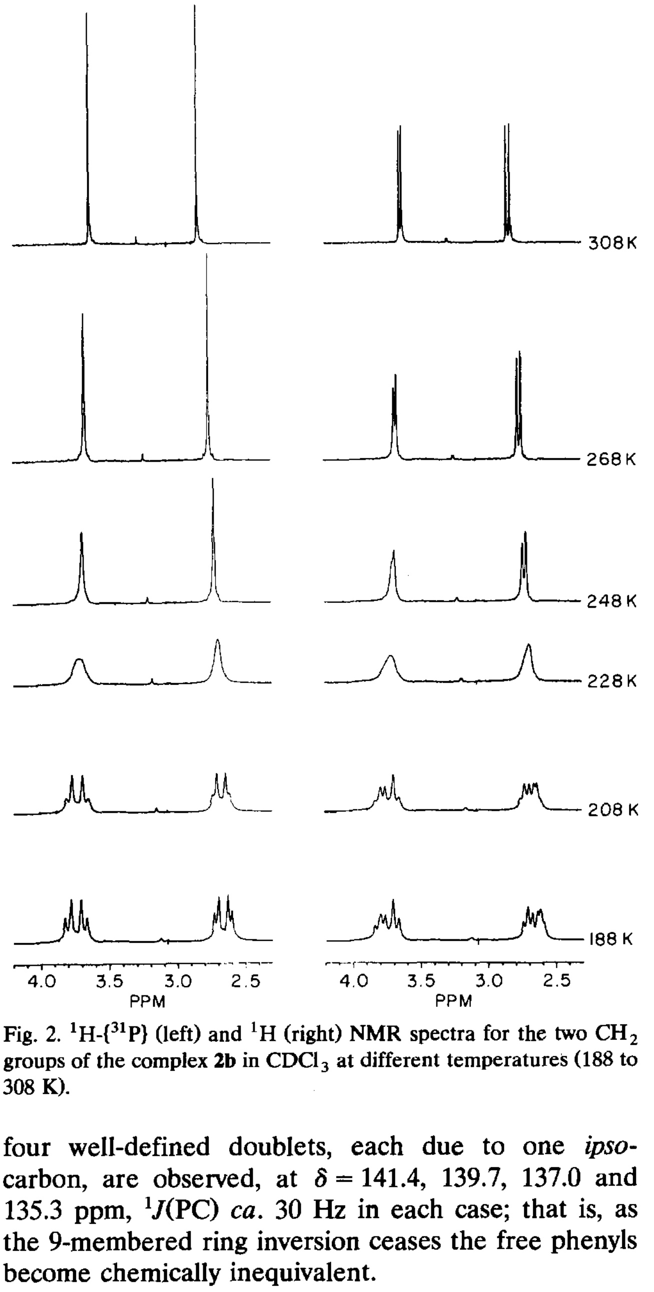

Fig. 2. ^1H-{^{31}P} (left) and ^1H (right) NMR spectra for the two CH_2 groups of the complex **2b** in $CDCl_3$ at different temperatures (188 to 308 K).

four well-defined doublets, each due to one *ipso*-carbon, are observed, at $\delta = 141.4$, 139.7, 137.0 and 135.3 ppm, $^1J(PC)$ *ca.* 30 Hz in each case; that is, as the 9-membered ring inversion ceases the free phenyls become chemically inequivalent.

To our knowledge this is the first report of a 9-membered ring inversion process for an organometallic species, although fluxionality has been studied by NMR in 9- and 10-membered organic rings for example in 1,4,7-cyclononatriene [3] and in some paracyclophanes [4].

1. Experimental details

The complex **2b** was prepared as described previously [1]. A Bruker AM400 spectrometer (operating frequencies for ^1H and ^{13}C of 400.13 and 100.6 MHz) was used to record the NMR spectra; ^1H and ^{13}C shifts are relative to tetramethylsilane.

1.1. Single crystal X-ray diffraction analysis of 2b

All crystallographic measurements were carried out on a Stoe STADI4 diffractometer operating in the ω/θ scan mode and graphite monochromated Mo-K_αX-radiation ($\lambda = 71.069$ pm). The data set was corrected for absorption semi-empirically using azimuthal ψ-scans.

The structure was determined by direct methods using SHELXS-86 [5] and was refined by full-matrix least-squares using SHELX76 [6]. Systematic absences allowed for two possibilities, $Pna2_1$ or $Pnam$, however whilst no reasonable solution could be found for $Pnam$, a solution was readily obtained for $Pna2_1$. This solution gave two molecules in the asymmetric unit which are mirror images of each other and differ principally by the relative rotations of their t-butyl groups. The two molecules are not related to one another by a pseudo-symmetry axis. Due to the large number of parameters involved only the heavier atoms (Cr and P) were refined with anisotropic thermal parameters. All other non-hydrogen atoms were refined with isotropic 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; final residuals $R = 0.0678$, $R_w = 0.0702$. The inverted solution led to slightly larger residuals. The weighting scheme $w = [\sigma^2(F_o) + 0.0002(F_o)^2]^{-1}$ was used. Final non-hydrogen atomic co-ordinates are given in Table 2. An ORTEP [7] diagram of **2b** is given in Fig. 1.

Crystal data. $C_{40}H_{42}CrN_2O_4P_2$, $M = 728.73$, monoclinic, space group $Pna2_1$, $a = 1880.8(3)$, $b = 1002.4(1)$, $c = 3948.3(6)$ pm, $U = 7.444(2)$ nm^3, $Z = 8$, $D_x = 1.30$ Mg m^{-3}, $\mu = 3.76$ cm^{-1}, $F(000) = 2936$.

Data collection. $4.0 < 2\theta < 50.0°$, 7309 Data collected, 4572 with $I > 2.0\sigma(I)$ considered observed, $T = 200$ K.

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References

1 S.D. Perera, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1992) 1469.
2 C.E. Housecroft, B.A.M. Shykh, A.L. Rheingold and B.S. Haggery, *Inorg. Chem., 30* (1991) 125 and references therein.
3 F.A.L. Anet and M. Ghiaci, *J. Am. Chem. Soc., 102* (1980) 2528.
4 S. Sternhell, C.W. Tansey, Y. Tobe, K. Kakiuchi and K. Kobiro, *Magn. Res. Chem., 28* (1990) 902.
5 G.M. Sheldrick, *Acta Crystallogr., Sect. A, A46* (1990) 467.
6 G.M. Sheldrick, *SHELX76, program system for X-ray structure determinations*, University of Cambridge, UK, 1976.
7 C.K. Johnson, *ORTEP II, Report ORNL-5138*, Oak Ridge National Laboratory, TN, USA, 1976.