

# Crystal Structures of Diphosphinated Chromium Fischer Amino Carbenes

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**Abstract** The crystal structures of four new diphosphinated chromium Fischer amino carbenes with the compositions  $fac\text{-}[(\text{P-P})(\text{CO})_3\text{Cr}=\text{C}(\text{NR}_2')(\text{R})]$  ( $\text{R} = \text{Me}$ ,  $\text{NR}_2' = \text{pyrrolidino}$ ,  $\text{P-P} = \text{dppe}$ , **1**;  $\text{R} = \text{Me}$ ,  $\text{NR}_2' = \text{pyrrolidino}$ ,  $\text{P-P} = \text{dppp}$ , **2**;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ,  $\text{P-P} = \text{dppe}$ , **3**;  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Me}$ ,  $\text{P-P} = \text{dppp}$ , **4**) have been determined at 243 K. Compound **1** crystallizes in the monoclinic system, space group  $P2_1/n$  with  $a = 12.1597(11) \text{ \AA}$ ,  $b = 20.1556(17) \text{ \AA}$ ,  $c = 14.0557(12) \text{ \AA}$ ,  $\beta = 114.163(3)^\circ$ ,  $V = 3143.0(5) \text{ \AA}^3$ , and  $Z = 4$ . Compound **2** crystallizes in the triclinic system, space group  $P-1$  with  $a = 7.4424(3) \text{ \AA}$ ,  $b = 10.8830(5) \text{ \AA}$ ,  $c = 20.6040(9) \text{ \AA}$ ,  $\alpha = 100.9880(10)^\circ$ ,  $\beta = 91.7650(10)^\circ$ ,  $\gamma = 97.6610(10)^\circ$ ,  $V = 1620.90(12) \text{ \AA}^3$ , and  $Z = 2$ . Compound **3** crystallizes in the monoclinic system as a mono-solvate of  $d^5$ -pyridine, space group  $P2_1/c$  with  $a = 11.485(2) \text{ \AA}$ ,  $b = 22.825(5) \text{ \AA}$ ,  $c = 14.092(3) \text{ \AA}$ ,  $\beta = 108.53(3)^\circ$ ,  $V = 3502.7(12) \text{ \AA}^3$ , and

$Z = 4$ . Compound **4** crystallizes in the orthorhombic system, space group  $P2_12_12_1$  with  $a = 8.359(3) \text{ \AA}$ ,  $b = 15.364(6) \text{ \AA}$ ,  $c = 23.784(9) \text{ \AA}$ ,  $V = 3055(2) \text{ \AA}^3$ , and  $Z = 4$ . Steric repulsions with the diphosphine ligand favor a conformation with the amino moiety directed away from the diphosphine backbone in **1–4**.

**Keywords** Fischer carbenes · Diphosphine · X-ray structure · dppe · dppp · Conformation

## Introduction

Fischer carbenes are an important class of organometallic compounds that have been used in a wide variety of synthetic applications, including asymmetric synthesis and the total synthesis of natural products. Manipulation of the coordination sphere of Fischer carbenes has been used to good effect to control the reactivity of these complexes. It is known, for example, that monophosphinated chromium Fischer alkoxy carbenes [1] and pentacarbonyl chromium Fischer amino carbenes [1, 2] show altered reactivity in comparison to pentacarbonyl chromium Fischer alkoxy carbenes, including increased reactivity of the deprotonated Fischer carbenes toward a variety of electrophiles. However, relatively few reports have explored the potential of *phosphinated* chromium Fischer *amino* carbenes [3]. Towards this end, we have synthesized a series of diphosphinated chromium Fischer amino carbenes and have begun to examine their reactivity.<sup>1</sup> Herein, we describe the single crystal X-ray structures of four previously

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<sup>1</sup> The syntheses, characterizations and some reactivity studies of compounds **1–3** have been published: Ref. [4].

unreported chromium Fischer dimethylamino and pyrrolidino carbene complexes containing a chelating 1,2-bis(diphenylphosphino)ethane (dppe) or 1,3-bis(diphenylphosphino)propane (dppp) ligand, the composition of which are indicated in Scheme 1.

## Experimental

### Preparations

Compounds **1–4** were prepared according to the following general procedure using standard Schlenk techniques [4]. An equimolar amount of the requisite pentacarbonyl amino carbene and dppe or dppp were dissolved in a 3:1 mixture of hexanes:benzene followed by heating the stirred mixture under nitrogen to reflux for 14–18 h [5]. The yellow-orange precipitates that formed were filtered off after cooling, and recrystallized from a minimum of methylene chloride by addition of excess methanol. The purified products were obtained in yields of 82–88% as a mixture of *fac* and *mer* isomers.

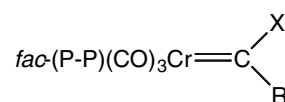
X-ray quality single crystals of *fac* isomers **1–4** were obtained by slow diffusion of methanol into 80–120 mg of the *fac/mer* mixture of the compound dissolved in a minimum of  $d^5$ -pyridine in an NMR tube.<sup>2,3</sup> The NMR tube was placed in a freezer at  $-10\text{ }^\circ\text{C}$  and allowed to crystallize over a period of several weeks.

### NMR Spectra

The  $^1\text{H}$  NMR spectra of compounds **1–4** were obtained at 300.075 MHz on a Varian Gemini 300 spectrometer, in  $\text{CDCl}_3$ , at room temperature, and referenced to residual  $\text{CHCl}_3$  at 7.24 ppm. **1**:  $\delta$  7.23–7.60 (overlapping mults, 20H), 4.64 (t, 2H), 2.91 (t, 2H) 2.66–2.75 (overlapping mults, 4H), 1.91–2.03 (overlapping mults, 4H), 0.98 (s, 3H). **2**:  $\delta$  7.20–7.55 (overlapping mults, 20H), 4.53 (t, 2H), 3.01 (t, 2H), 2.8–3.0 (overlapping mults, 2H), 2.2–2.6 (overlapping mults, 4H), 1.97 (overlapping mults, 4H), 1.69 (s, 3H). **3**:  $\delta$  7.24–7.61 (overlapping mults, 20H), 4.06 (s, 3H), 2.80 (s, 3H), 2.66–2.73 (overlapping mults, 4H), 1.16 (s, 3H). **4**:  $\delta$  7.20–7.55 (overlapping mults, 20H), 3.91 (s, 3H), 2.91 (s, 3H), 2.9–3.0 (overlapping mults, 2H), 2.1–2.6 (overlapping mults, 4H), 2.00 (s, 3H).

<sup>2</sup> Deuterated solvent was used as the dissolved samples were first subjected to NMR analysis. Presumably, non-deuterated pyridine could be used in its place.

<sup>3</sup> Although the solutions contained an equilibrium mixture of *fac* and *mer* isomers, only the *fac* isomer was observed in the X-ray analyses. The *mer* isomer was the minor isomer in each case, and may not have crystallized out. Alternatively, crystals of the *fac* isomer may have been selected by happenstance.



- 1** P-P = dppe, X = pyrrolidino, R = Me
- 2** P-P = dppp, X = pyrrolidino, R = Me
- 3** P-P = dppe, X = dimethylamino, R = Me
- 4** P-P = dppp, X = dimethylamino, R = Me
- 5** P-P = dppe, X = ethoxy, R = Me<sup>16</sup>
- 6** P-P = dppe, X = methoxy, R = Ph<sup>16</sup>
- 7** P-P = dppe, C(X)(R) = 3-methyl-2-oxacyclopentylidene<sup>16</sup>

### Scheme 1

#### Crystallography

Single crystals were selected from each NMR tube by viewing them under a stereomicroscope equipped with crossed polarizers. Single crystals of appropriate size were mounted to the tip of a 0.1 mm glass capillary with petroleum jelly. Data were collected from single crystals of each sample at  $-30\text{ }^\circ\text{C}$  on a SMART© 1000 CCD detector system using graphite monochromated Mo  $K_\alpha$  radiation. An entire hemisphere of data was collected in multi-run mode with  $\omega$  as the rotation axis. Detector-to-sample distance was 5.25 cm and the detector  $2\theta$  angle was  $-28^\circ$ . Rotation width was  $0.3^\circ$ , frame size was  $512 \times 512$  pixels, number of frames was 1868, data collection time per frame was 60 s, and the total time for data collection was  $\sim 36$  h per data set.

SMART v5.050© was used for data collection, indexing of reflections, and determination of lattice parameters [6]. SAINT+ v5.01© was used for integration of reflection intensities [7]. Absorption corrections were applied using SADABS [8]. SHELXTL v5.1© was used for data reduction, space group determination, structure determination, structure refinement, graphics, and structure reporting [9]. All X-ray crystallographic hardware, including analysis programs and diffraction unit, are copyrights of Bruker Analytical X-ray Systems, Inc.

Details of crystal parameters, data collections, and refinement results are summarized for **1–4** in Table 1. Refined atomic coordinates and equivalent isotropic displacement factors for **1–4** are given in Tables 2–5, respectively. Selected bond distances and bond angles for **1–4** are listed in Table 6.

## Results and Discussion

Complexes **1–4** crystallize in the four different space groups,  $P2_1/n$ ,  $P-1$ ,  $P2_1/c$ , and  $P2_12_12_1$ , respectively. Disorder was present in the conformation of the pyrrolidino ring in **2**; the ratio of disordered atoms C7 and C7B refined

**Table 1** Summary of crystallographic data and intensity data collection for **1**, **2**, **3**·C<sub>5</sub>H<sub>5</sub>N and **4**

Compound	<b>1</b>	<b>2</b>	<b>3</b> ·C <sub>5</sub> H <sub>5</sub> N	<b>4</b>
CCDC code	195049	195050	195051	609930
Chemical formula	C35 H35 Cr N O3 P2	C36 H37 Cr N O3 P2	C38 H38 Cr N2 O3 P2	C34 H35 Cr N O3 P2
Formula weight	631.58	645.61	684.64	619.57
Temperature, K	243	243	243	243
Crystal system	Monoclinic	Triclinic	Monoclinic	Orthorhombic
Space group	P21/n	P-1	P21/c	P212121
<i>Unit cell dimensions</i>				
<i>a</i> , Å	12.1597 (11)	7.4424 (3)	11.485 (2)	8.359 (3)
<i>b</i> , Å	20.1556 (17)	10.8830 (5)	22.825 (5)	15.364 (6)
<i>c</i> , Å	14.0557 (12)	20.6040 (9)	14.092 (3)	23.784 (9)
$\alpha$	90	100.988 (1)	90	90
$\beta$	114.163 (3)	91.7661 (1)	108.53 (3)	90
$\gamma$	90	97.661 (1)	90	90
Volume	3143.0 (5)	1620.90 (12)	3502.7(12)	3055(2)
<i>Z</i>	4	2	4	4
Density (calculated), mg/m <sup>3</sup>	1.335	1.323	1.298	1.347
Absorption coefficient, mm <sup>-1</sup>	0.502	0.488	0.456	0.515
Diffractometer/scan	Bruker SMART/CCD	Bruker SMART/CCD	Bruker SMART/CCD	Bruker SMART/CCD
Scan	$\omega$ scan	$\omega$ scan	$\omega$ scan	$\omega$ scan
$\theta$ range for data collection, degree	1.88–28.31	1.01–28.51	1.77–28.28	1.58–28.28
Reflections measured	27,894	14,880	29,384	27,124
Independent observed reflections	7,503	7,385	8,152	7,225
Independent reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	5,087	6,443	6,632	6,786
<i>R</i> <sub>int</sub>	0.0721	0.0583	0.0251	0.0330
Data/restraints/parameters	7503/0/380	7385/2/399	8152/195/473	7225/5/406
Goodness of fit on <i>F</i> <sup>2</sup>	1.116	1.040	1.048	1.148
Final <sup>a</sup> <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0548, <i>wR</i> 2 = 0.1554	<i>R</i> 1 = 0.0414, <i>wR</i> 2 = 0.1091	<i>R</i> 1 = 0.0350, <i>wR</i> 2 = 0.0861	<i>R</i> 1 = 0.0296, <i>wR</i> 2 = 0.0737

to 59/41. Complex **3** crystallizes with one disordered molecule of pyridine solvent per unit cell, and the two disordered conformations have been refined to an occupancy ratio of 71/29. No  $\pi$  interaction was observed between the pyridine ring and the phenyl ring of the P-P ligand. Complex **4** crystallizes with the carbene ligand disordered in two conformations rotated 180° to each other, whose occupancies have been refined to a ratio of 70/30. The thermal displacement diagrams with atomic numbering schemes and thermal ellipsoids are depicted in Figs. 1–4.

The coordination geometry of complexes **1–4** is pseudo-octahedral with the greatest distortion from 90° C–Cr(1)–C bond angles for the *cis* carbonyls exhibited by C(1)–Cr(1)–C(2) in **1** (82.77(12)°). All other C–Cr(1)–C angles between *cis* carbonyls in these complexes fall in the range

85.19(9)–94.37(12)°. The bite angle (P(1)–Cr(1)–P(2)) for the 5-member chelate of dppe complexes **1** and **3** averages 83.06(3)°, while the 6-member chelate of dppp complexes **2** and **4** averages 95.67(3)°. In the dppe complexes, the chelate ring adopts the most common twist (C<sub>2</sub> symmetry) conformation noted for dppe complexes, similar to that of a related tungsten nitrene complex, *fac*-(dppe)(CO)<sub>3</sub>W = NNMe<sub>2</sub> [10, 11]. In the dppp complexes, five of the six atoms in the ring defining the diphosphine metal chelate (Cr(1), P(1), C(22), C(24), P(2) in **2** and Cr(1), P(1), C(20), C(22), P(2) in **4**) are essentially coplanar with a maximum deviation from the least-squares plane of 0.030 Å for **2** and 0.0221 Å for **4**. The central methylene carbons in the dppp backbone, C(23) in **2** and C(21) in **4**, are an average of 0.769 Å out of the plane, directed away from the carbene ligand. The M–P bond distances in **1–4** fall in the range of

**Table 2** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **1**

	X	y	z	U(eq)
C(1)	2,005(2)	1,988(1)	4,402(2)	49(1)
C(2)	3,385(3)	1,058(1)	4,847(2)	49(1)
C(3)	1,191(3)	945(1)	4,888(2)	52(1)
C(4)	1,561(2)	114(1)	3,439(2)	48(1)
C(5)	6,96(3)	-110(2)	2,352(2)	59(1)
C(6)	1,888(3)	-1,113(1)	3,679(3)	68(1)
C(7)	2,810(4)	-1,497(2)	4,589(3)	78(1)
C(8)	3,009(4)	-1,074(2)	5,521(3)	82(1)
C(9)	2,979(3)	-375(2)	5,104(2)	61(1)
C(10)	2,721(2)	699(2)	1,908(2)	52(1)
C(11)	2,153(3)	579(2)	838(2)	64(1)
C(12)	2,339(3)	-19(2)	427(3)	74(1)
C(13)	3,085(3)	-497(2)	1,067(3)	73(1)
C(14)	3,672(3)	-376(2)	2,117(3)	64(1)
C(15)	3,498(3)	214(2)	2,532(2)	56(1)
C(16)	3,719(2)	1,952(2)	2,789(2)	53(1)
C(17)	3,959(3)	2,481(2)	3,463(3)	83(1)
C(18)	4,862(4)	2,934(2)	3,566(3)	97(1)
C(19)	5,546(3)	2,847(2)	3,005(4)	90(1)
C(20)	5,318(4)	2,330(2)	2,339(5)	102(2)
C(21)	4,415(3)	1,882(2)	2,236(3)	77(1)
C(22)	1,224(2)	1,901(1)	1,573(2)	47(1)
C(23)	-25(2)	1,638(1)	1,393(2)	45(1)
C(24)	-593(2)	2,282(1)	2,996(2)	43(1)
C(25)	-751(3)	2,852(1)	2,417(2)	55(1)
C(26)	-1,097(3)	3,437(2)	2,739(3)	65(1)
C(27)	-1,321(3)	3,456(2)	3,615(3)	63(1)
C(28)	-1,159(3)	2,890(2)	4,206(3)	60(1)
C(29)	-800(3)	2,310(1)	3,897(2)	54(1)
C(30)	-1,528(2)	1,029(1)	2,272(2)	41(1)
C(31)	-2,567(2)	1,256(1)	1,469(2)	49(1)
C(32)	-3,646(3)	910(2)	1,183(2)	58(1)
C(33)	-3,666(3)	330(2)	1,693(3)	62(1)
C(34)	-2,650(3)	109(2)	2,487(2)	62(1)
C(35)	-1,581(3)	451(1)	2,788(2)	54(1)
Cr(1)	1,807(1)	1136(1)	3,915(1)	41(1)
N(1)	2,090(2)	-403(1)	4,016(2)	52(1)
O(1)	2,169(2)	2,511(1)	4,790(2)	69(1)
O(2)	4,379(2)	1,082(1)	5,466(2)	72(1)
O(3)	803(2)	859(1)	5,505(2)	77(1)
P(1)	2,423(1)	1,409(1)	2,581(1)	44(1)
P(2)	-102(1)	1,486(1)	2,667(1)	40(1)

U(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

2.3502(7)–2.4033(6) Å, which can be compared to the 2.42 Å distance found in *cis*-(PPh<sub>3</sub>)(CO)<sub>4</sub>Cr=C(OMe)(Me) [12].

Relative to pentacarbonyl alkoxy carbenes, pentacarbonyl amino carbenes are known to display greater  $\pi$ -donation from the heteroatom substituent [13]. This can be pictured as being due to a greater contribution from the respective zwitterionic resonance form in Fig. 5. Among other things, this results in longer M–C<sub>carbene</sub> bond distances for the amino complexes. This trend is also found in comparison of **1–4** to recently structurally characterized diphosphinated chromium *alkoxy* carbenes *fac*-(dppe)(CO)<sub>3</sub>Cr=C(OR')(R) (R' = Et, R = Me, **5**; R' = Me, R = Ph, **6**; C(OR')(R)=3-methyl-2-oxacyclopentylidene, **7**) [14]. The range of 2.126(2)–2.151(2) Å for the Cr–C<sub>carbene</sub> bonds in **1–4** compares to the range of 1.9784(15)–1.991(2) Å found for the diphosphinated alkoxy carbenes **5–7**. The Cr–C<sub>carbene</sub> bond distances for **1–4** are in the normal range associated with pentacarbonyl chromium amino carbenes, including the 2.09 Å, 2.132(2) Å and 2.16(1) Å distances reported for (CO)<sub>5</sub>Cr=C(NH(Me))(Me), (CO)<sub>5</sub>Cr=C(NC<sub>4</sub>H<sub>6</sub>)(Me), and (CO)<sub>5</sub>Cr=C(NEt<sub>2</sub>)(Me), respectively [15]. This suggests that the presence of the *cis* phosphino moieties in **1–4** does not significantly affect the  $\pi$ -contribution of the amino moiety (i.e., the importance of the zwitterionic resonance form shown in Fig. 5). As expected, molecules **1–4** are essentially planar in this region of  $\pi$ -overlap (Cr(1), C(4), C(5), N(1), C(6), and C(9) in **1** and **2**, Cr(1), C(4), C(5), N(1), C(6), and C(7) in **3** and **4**). The carbene plane approximately bisects the P(1)–Cr(1)–P(2) bite angle, with angles to the plane containing P(1), Cr(1) and C(4) or P(2), Cr(1), and C(4) of 24°–48°, which are typical values for Fischer carbenes [15].

Not surprisingly, given the relatively small differences, the substitution pattern (i.e., –NC<sub>4</sub>H<sub>8</sub> versus –NMe<sub>2</sub> or dppe versus dppp) did not have any significant impact on the carbene functionality in **1–4**. This is apparent in the very close Cr(1)–C(4) and C(4)–N(1) distances, respectively, for **1–4**, and in an Cr(1)–C(4)–N(1) angle that varies only a small amount (range = 126.7(2)–128.8(3)°). These latter values are larger than the comparable Cr–C<sub>carbene</sub>–O angles in **5–7**, but near the value of 129.4(1)° found in the pentacarbonyl chromium amino carbene (CO)<sub>5</sub>Cr=C(NEt<sub>2</sub>)(Me) [16]. The N(1)–C(4)–C(5) angle averages 110.6(2)° in pyrrolidino analogs **1** and **2**, which is nearly identical to the analogous average angle of 110.7(2)° in dimethylamino analogs **3** and **4**. The pyrrolidino rings in **1** and **2** have an envelope conformation, with C(8) out of the plane, as defined by average C(6)–N(1)–C(9)–C(8) and N(1)–C(6)–C(7)–C(8) torsion angles of 17.2(4)° and 7.6(6)° for **1** and **2**, respectively.

The M–C bond lengths for carbonyl ligands *trans* to the carbene moiety have been correlated with the degree of  $\pi$ -donation associated with the carbene ligand in pentacarbonyl Fischer alkoxy and amino carbenes [15]. The

**Table 3** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **2**

	X	Y	z	U(eq)
C(1)	6,021(2)	4,447(2)	1,933(1)	30(1)
Cr(1)	4,670(1)	3,561(1)	2,484(1)	24(1)
N(1)	3,305(2)	1,895(2)	3,497(1)	36(1)
O(1)	6,922(2)	4,994(2)	1,596(1)	45(1)
P(1)	2,657(1)	2,735(1)	1,520(1)	26(1)
C(2)	6,030(2)	2,267(2)	2,232(1)	29(1)
O(2)	7,017(2)	1,532(2)	2,084(1)	44(1)
P(2)	3,289(1)	5,407(1)	2,837(1)	26(1)
C(3)	6,468(2)	4,203(2)	3,143(1)	29(1)
O(3)	7,705(2)	4,598(2)	3,515(1)	46(1)
C(4)	2,896(2)	2,594(2)	3,070(1)	29(1)
C(5)	883(3)	2,652(2)	3,027(1)	37(1)
C(6)	1,997(4)	1,211(3)	3,890(2)	65(1)
C(7)	3,164(9)	267(8)	4,134(5)	77(3)
C(7B)	3,211(12)	1,065(16)	4,498(6)	75(4)
C(8)	4,947(4)	945(4)	4,218(2)	79(1)
C(9)	5,155(3)	1,670(2)	3,663(1)	46(1)
C(10)	1,468(2)	1,109(2)	1,393(1)	29(1)
C(11)	24(3)	678(2)	922(1)	40(1)
C(12)	-860(3)	-550(2)	832(1)	48(1)
C(13)	-302(3)	-1,371(2)	1,209(1)	46(1)
C(14)	1,124(3)	-958(2)	1,673(1)	45(1)
C(15)	2,023(3)	267(2)	1,766(1)	36(1)
C(16)	3,818(2)	2,637(2)	7,24(1)	29(1)
C(17)	3,575(3)	3,406(2)	2,67(1)	37(1)
C(18)	4,538(3)	3,320(2)	-314(1)	45(1)
C(19)	5,756(3)	2,465(2)	-445(1)	48(1)
C(20)	5,999(3)	1,681(2)	-4(1)	45(1)
C(21)	5,040(3)	1,766(2)	578(1)	37(1)
C(22)	791(2)	3,632(2)	1,388(1)	32(1)
C(23)	1,314(3)	5,073(2)	1,578(1)	32(1)
C(24)	1,303(2)	5,629(2)	2,335(1)	30(1)
C(25)	4,872(2)	6,858(2)	2,842(1)	31(1)
C(26)	4,893(3)	7,489(2)	2,311(1)	40(1)
C(27)	6,152(3)	8,544(2)	2,307(1)	48(1)
C(28)	7,415(3)	8,974(2)	2,828(1)	52(1)
C(29)	7,427(3)	8,356(2)	3,361(1)	52(1)
C(30)	6,161(3)	7,308(2)	3,370(1)	43(1)
C(31)	2,523(2)	5,799(2)	3,697(1)	31(1)
C(32)	1,374(3)	6,705(2)	3,880(1)	45(1)
C(33)	851(4)	7,003(3)	4,538(1)	55(1)
C(34)	1,473(3)	6,416(3)	5,018(1)	51(1)
C(35)	2,619(3)	5,524(2)	4,849(1)	46(1)
C(36)	3,146(3)	5,219(2)	4,190(1)	38(1)

U(eq) is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

**Table 4** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **3·C<sub>5</sub>H<sub>5</sub>N**

	X	y,	z	U(eq)
Cr(1)	3,346(1)	6,675(1)	1,528(1)	31(1)
N(1)	3,679(2)	5,314(1)	1,739(1)	48(1)
O(1)	3,161(1)	7,941(1)	2,043(1)	52(1)
O(2)	5,345(2)	6,588(1)	3,504(1)	68(1)
O(3)	1,381(2)	6,377(1)	2437(1)	73(1)
P(1)	4,841(1)	6,962(1)	805(1)	32(1)
P(2)	1,968(1)	6,934(1)	-57(1)	32(1)
C(1)	3,229(2)	7,453(1)	1,826(1)	37(1)
C(2)	4,565(2)	6,605(1)	2,734(1)	43(1)
C(3)	2,125(2)	6,486(1)	2,067(1)	44(1)
C(4)	3,544(2)	5,778(1)	1,158(1)	38(1)
C(5)	3,622(2)	5,615(1)	131(1)	44(1)
C(6)	3,961(3)	4,714(1)	1,464(2)	71(1)
C(7)	3,610(2)	5,330(1)	2,761(2)	60(1)
C(8)	6,178(2)	6,510(1)	844(1)	38(1)
C(9)	6,912(2)	6,657(1)	260(2)	51(1)
C(10)	7,981(2)	6,348(1)	357(2)	63(1)
C(11)	8,332(2)	5,894(1)	1,029(2)	59(1)
C(12)	7,608(2)	5,739(1)	1,603(2)	52(1)
C(13)	6,533(2)	6,049(1)	1,514(1)	43(1)
C(14)	5,679(2)	7,640(1)	1,297(1)	40(1)
C(15)	5,455(2)	8,168(1)	791(2)	56(1)
C(16)	6,170(3)	8,658(1)	1,180(2)	76(1)
C(17)	7,107(2)	8,620(1)	2,069(2)	77(1)
C(18)	7,324(2)	8,104(1)	2,592(2)	76(1)
C(19)	6,609(2)	7,617(1)	2,212(2)	60(1)
C(20)	4,125(2)	7,119(1)	-544(1)	37(1)
C(21)	2,827(2)	7,364(1)	-728(1)	39(1)
C(22)	679(2)	7,437(1)	-142(1)	40(1)
C(23)	148(2)	7,764(1)	-1,002(2)	57(1)
C(24)	-834(2)	8,136(1)	-1,065(2)	73(1)
C(25)	-1302(2)	8,180(1)	-284(2)	72(1)
C(26)	-782(2)	7,867(1)	565(2)	73(1)
C(27)	215(2)	7,500(1)	646(2)	57(1)
C(28)	1,142(1)	6,366(1)	-942(1)	36(1)
C(29)	1,151(2)	6,302(1)	-1,920(1)	51(1)
C(30)	537(2)	5,838(1)	-2,505(2)	61(1)
C(31)	-102(2)	5,439(1)	-2,136(2)	54(1)
C(32)	-134(2)	5,498(1)	-1,173(2)	48(1)
C(33)	495(2)	5,953(1)	-576(1)	40(1)
N(2)	3,351(4)	5,145(3)	6,498(4)	87(2)
C(34)	3,009(5)	5,690(3)	6,322(5)	78(2)
C(35)	2,198(7)	5,902(3)	5,474(5)	81(2)
C(36)	1,665(9)	5,509(4)	4,705(6)	114(3)
C(37)	2,025(10)	4,927(3)	4,887(6)	119(3)

**Table 4** continued

	<i>X</i>	<i>y</i> ,	<i>z</i>	<i>U</i> (eq)
C(38)	2,836(8)	4,781(4)	5,761(7)	102(3)
N(2B)	1,460(16)	4,852(7)	5,094(14)	116(5)
C(34B)	2,490(20)	4,774(10)	5,800(20)	123(7)
C(35B)	3,290(20)	5,206(9)	6,120(20)	145(8)
C(36B)	2,990(15)	5,772(7)	5,840(20)	98(5)
C(37B)	1,864(19)	5,836(9)	5,098(19)	112(7)
C(38B)	1,111(18)	5,381(8)	4,843(15)	105(5)

Cr–C<sub>carbonyl</sub> bond distances for carbonyls *trans* to the carbene ligand (Cr(1)–C(1)) in **1–4** are shorter than diphosphinated chromium alkoxy carbenes **5–7**, again indicating greater  $\pi$ -donation from the amino carbene ligands [14]. This is in accord with reports comparing amino and alkoxy  $\pi$ -donation in pentacarbonyl chromium carbenes [15]. Further, in **1–4**, the respective Cr(1)–C(1) distances are very close to the average of the Cr(1)–C(2) and Cr(1)–C(3) bond distances for the two carbonyls *trans* to phosphorus atoms. The greatest deviations are for complexes **1** and **4**. Complex **1** has a Cr(1)–C(1) distance that is 0.014(6) Å shorter than the averages of Cr(1)–C(2) and Cr(1)–C(3), while in **2** the respective bond is 0.014(4) Å longer. This suggests that the extent of donation from the phosphine moieties is near that of the dimethylamino and pyrrolidino carbene ligands in these complexes [17].<sup>4</sup>

Interestingly, in the solid-state structures of **1–3**, it is the carbene *alkyl* moiety that is oriented towards the diphosphine backbone, “sandwiched” between two diphosphine phenyl rings, one on each phosphorus atom. The carbene amino moiety, by contrast, is oriented away from the diphosphine backbone and lies outside of these phenyl rings.<sup>5</sup> In complex **4**, the carbene ligand is disordered in a 70/30 ratio, favoring a conformation analogous to **1–3**, while the minor conformation is simply related by a *ca.* 180° rotation of the carbene moiety. The preferred conformation of **1–4** is just the opposite of that observed for analogous diphosphinated alkoxy Fischer carbenes, **5–7** [14]. This result is easily reconciled in that the planar amino moiety has two alkyl substituents compared to the single alkyl substituent (which is in E geometry) on the alkoxy oxygen atom. For the amino carbenes, the opposite conformation (i.e., 180° rotation about the Cr(1)–C(4) bond) would result in less favorable steric interactions for the amino substituent (methyl or –CH<sub>2</sub>CH<sub>2</sub>– of the pyrrolidino ring) directed toward the diphosphine backbone. Complex **4** represents an

<sup>4</sup> In all of these complexes, the steric impact of the diphosphine ligand may also affect the observed bond lengths.

<sup>5</sup> <sup>1</sup>H NMR results indicate that **1–3** adopt the same conformation in solution [4].

**Table 5** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **4**

	<i>x</i>	<i>y</i> ,	<i>z</i>	<i>U</i> (eq)
Cr(1)	–668(1)	3,783(1)	8,616(1)	32(1)
O(1)	–3,572(2)	4,724(1)	8,178(1)	57(1)
O(3)	–1,905(2)	2,202(1)	8,017(1)	61(1)
O(2)	–2,894(2)	3,122(1)	9,507(1)	64(1)
P(1)	–134(1)	5,083(1)	9,130(1)	35(1)
P(2)	839(1)	4,189(1)	7,804(1)	34(1)
C(1)	–2,419(2)	4,376(1)	8,335(1)	39(1)
C(3)	–1,371(2)	2,816(1)	8,233(1)	41(1)
C(2)	–1,969(3)	3,401(1)	9,183(1)	42(1)
N(1)	1,807(3)	2,425(2)	9,089(1)	43(1)
C(4)	1,534(5)	3,223(2)	8,912(1)	38(1)
C(7)	3,417(6)	2,074(4)	9,218(4)	56(1)
C(5)	3,190(3)	3,784(2)	8,914(1)	53(1)
C(6)	528(3)	1,857(2)	9,151(1)	62(1)
N(1B)	2,599(7)	3,028(4)	9,010(2)	38(2)
C(4B)	1,047(10)	2,904(5)	8,948(4)	39(2)
C(7B)	3,761(18)	2,344(10)	9,178(11)	69(4)
C(5B)	528(3)	1,857(2)	9,151(1)	62(1)
C(6B)	3,190(3)	3,784(2)	8,914(1)	53(1)
C(8)	760(2)	5,057(1)	9,841(1)	38(1)
C(9)	1,050(2)	4,266(1)	10,103(1)	44(1)
C(10)	1,716(3)	4,236(2)	10,640(1)	51(1)
C(11)	2,107(3)	4,992(2)	10,916(1)	55(1)
C(12)	1,809(3)	5,787(2)	10,663(1)	56(1)
C(13)	1,120(3)	5,820(1)	10,131(1)	46(1)
C(14)	–1,989(2)	5,678(1)	9,295(1)	39(1)
C(15)	–3,015(3)	5,317(2)	9,692(1)	48(1)
C(16)	–4,467(3)	5,702(2)	9,821(1)	58(1)
C(17)	–4,921(3)	6,463(2)	9,554(1)	60(1)
C(18)	–3,941(3)	6,821(2)	9,155(1)	63(1)
C(19)	–2,473(3)	6,436(1)	9,023(1)	53(1)
C(20)	1,112(3)	5,925(1)	8,783(1)	44(1)
C(21)	879(3)	5,981(1)	8,144(1)	44(1)
C(22)	1,787(3)	5,284(1)	7,805(1)	42(1)
C(23)	–342(2)	4,225(1)	7,146(1)	38(1)
C(24)	–1,409(3)	4,904(2)	7,057(1)	57(1)
C(25)	–2,371(3)	4,929(2)	6,582(1)	63(1)
C(26)	–2,279(3)	4,284(2)	6,187(1)	61(1)
C(27)	–1,228(3)	3,612(2)	6,266(1)	64(1)
C(28)	–269(3)	3,574(2)	6,744(1)	51(1)
C(29)	2,487(2)	3,471(1)	7,581(1)	37(1)
C(34)	3,908(2)	3,777(2)	7,348(1)	48(1)
C(33)	5,122(3)	3,208(2)	7,204(1)	59(1)
C(32)	4,929(3)	2,323(2)	7,271(1)	57(1)
C(31)	3,527(3)	2,005(2)	7,491(1)	51(1)
C(30)	2,318(3)	2,569(1)	7,652(1)	45(1)

*U*(eq) is defined as one-third of the trace of the orthogonalized *U*<sub>ij</sub> tensor

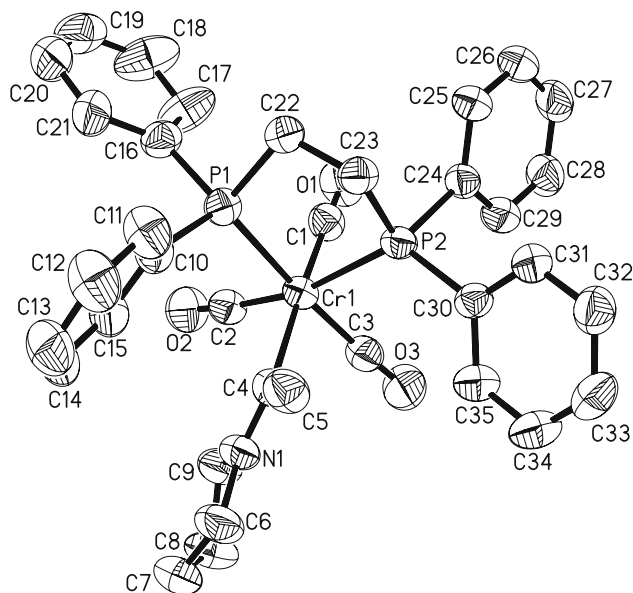
**Table 6** Selected bond distances (Å) and bond angles (°) for **1**, **2**, **3**·C<sub>5</sub>H<sub>5</sub>N and **4**

	1	2	3·C <sub>5</sub> H <sub>5</sub> N	4
<i>Bond distances</i>				
Cr(1)–C(1)	1.827(3)	1.859(2)	1.839(2)	1.849(2)
Cr(1)–C(2)	1.834(3)	1.847(2)	1.835(2)	1.830(2)
Cr(1)–C(3)	1.848(3)	1.844(2)	1.846(2)	1.839(2)
Cr(1)–C(4)	2.149(3)	2.126(2)	2.143(2)	2.151(2)
Cr(1)–P(1)	2.3525(8)	2.4033(5)	2.3502(7)	2.3842(9)
Cr(1)–P(2)	2.3728(8)	2.3795(5)	2.3645(9)	2.3880(8)
C(1)–O(1)	1.167(3)	1.170(2)	1.165(2)	1.163(3)
C(2)–O(2)	1.166(3)	1.162(2)	1.167(2)	1.172(3)
C(3)–O(3)	1.157(3)	1.159(2)	1.162(2)	1.162(3)
C(4)–N(1)	1.314(3)	1.321(2)	1.317(2)	1.315(4)
C(4)–C(5)	1.526(4)	1.508(3)	1.524(2)	1.631(4)
<i>Bond angles</i>				
C(1)–Cr(1)–C(2)	82.77(12)	87.53(8)	87.85(8)	87.37(9)
C(2)–Cr(1)–C(3)	94.37(12)	86.03(8)	93.06(8)	85.19(9)
C(1)–Cr(1)–C(3)	87.13(13)	88.01(8)	90.61(8)	88.07(9)
C(1)–Cr(1)–C(4)	176.05(11)	174.42(7)	177.65(7)	173.26(12)
P(1)–Cr(1)–P(2)	82.85(3)	95.78(2)	83.30(2)	95.57(3)
C(2)–Cr(1)–P(2)	166.95(9)	172.46(6)	169.09(6)	173.46(7)
C(3)–Cr(1)–P(1)	175.08(9)	172.06(6)	176.88(6)	172.15(7)
N(1)–C(4)–C(5)	110.2(2)	111.1(2)	111.3(2)	110.1(3)
Cr(1)–C(4)–N(1)	126.7(2)	128.5(1)	128.2(1)	128.8(3)
Cr(1)–C(4)–C(5)	123.09(19)	120.5(1)	120.4(1)	121.0(2)

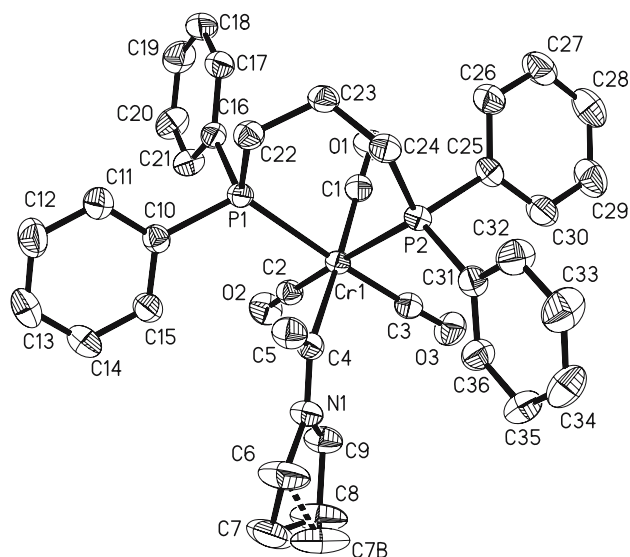
Only the bond distances and angles for the major component of compound **4** are shown in the table

interesting intermediate case in which the additional flexibility in the three-carbon backbone of dppp allows room for the dimethylamino moiety to be oriented towards

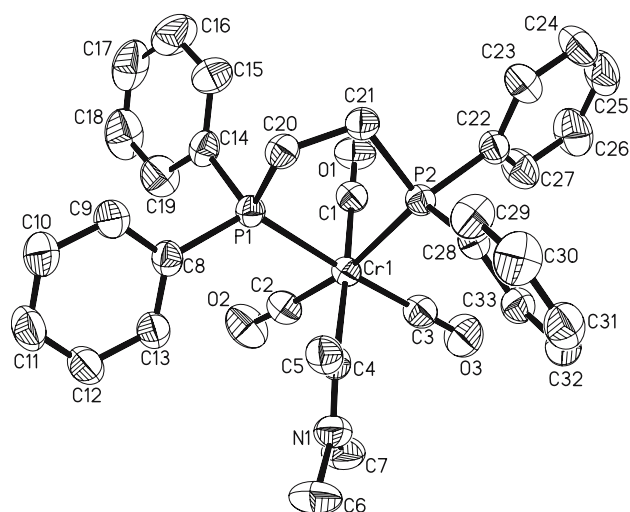
the dppp ligand in the minor conformation. Stated as a preference for orienting a given carbene moiety towards the diphosphine backbone, the following



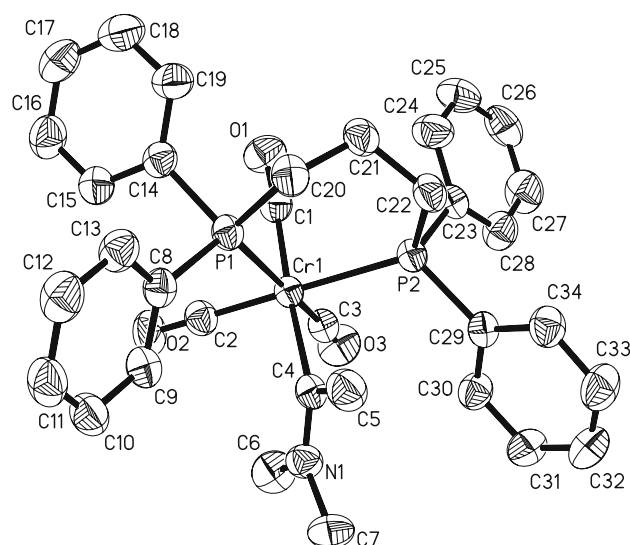
**Fig. 1** Molecular structure of **1** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity



**Fig. 2** Molecular structure of **2** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. Hydrogen atoms have been omitted for clarity



**Fig. 3** Molecular structure of **3**-C<sub>5</sub>H<sub>5</sub>N with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. The pyridine solvent molecule was disordered in two conformations with a ratio of 71/29. No  $\pi$  interaction was observed between the pyridine ring and the phenyl ring of the P-P ligand. Hydrogen atoms and the molecule of disordered pyridine solvent have been omitted for clarity



**Fig. 4** Molecular structure of **4** with atom numbering. Thermal ellipsoids are plotted at the 50% probability level. The C(NMe<sub>2</sub>)Me ligand was disordered in two conformations with a ratio of 70/30. Hydrogen atoms and the disordered portion of the ligand have been omitted for clarity

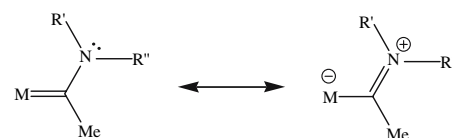
hierarchy is apparent in these related complexes: OMe, OEt > Me > NMe<sub>2</sub> > pyrrolidino. Similar steric interactions are likely at work in dictating the conformations of related dppe complexes involving carbene, nitrene, and acylsilane functionalities [11, 18, 19].

Dppe complexes **1** and **3** demonstrate that there is sufficient flexibility in the coordination environment of the diphosphinated octahedral complexes to accommodate a carbene alkyl substituent oriented toward the dppe backbone, despite the preference against this in **5** and **7**.<sup>6</sup> Indeed, although the twist conformation of the dppe ligand is qualitatively the same in all of these complexes (*vide supra*), subtle geometry differences are observed that can accommodate the greater steric impact of the methyl group relative to the alkoxy moiety [14]. The non-bonded distance from C(5) to the closer methylene carbon in the dppe backbone is significantly greater in **1** (3.746(4) Å) and **3** (3.657(3) Å) than the distance from the alkoxy oxygen atom to the respective closer methylene carbon in **5** (3.244(4) Å), **6** (3.152(2) Å), and **7** (3.256(3) Å).<sup>7,8</sup> The average non-bonded distances between the ipso carbons in

<sup>6</sup> For discussion, the –CH<sub>2</sub>CH<sub>2</sub>– and –OCH(Me)– fragments of the 3-methyl-2-oxacyclopentylidene ligand in **7** are considered to be the alkyl and alkoxy carbene substituents, respectively.

<sup>7</sup> The distance from C(5) to the more distant dppe methylene carbon is 4.315(4) Å and 4.186(3) Å in **1** and **3**, respectively. The distance from the alkoxy oxygen to the more distant dppe methylene carbon is 3.855(3) Å, 3.738(2) Å, and 3.848(2) Å in **5**, **6**, and **7**, respectively.

<sup>8</sup> In **2**, the distance from C(5) to either of the two methylene carbons attached to a phosphorus is essentially identical and averages 3.747(3) Å.



**Fig. 5** Resonance structures describing the bonding in carbene fragment of Fischer amino carbenes

the two phenyls making up the “sandwich” to C(5) are greater in **1** (3.367(5) Å) and **3** (3.354(3) Å) than the respective distances from these carbons to the alkoxy oxygen in **5** (3.002(3) Å), **6** (3.1160(19) Å), and **7** (3.064(2) Å).<sup>9</sup> Interestingly, the P–C–P torsion angle in the dppe backbone also shows a significant and consistent change, with values of 45.9(2)° and 45.38(15)° for **1** and **3**, respectively, compared to 49.1(3)°, 49.36(13)°, and 48.97(19)° in **5**, **6**, and **7**, respectively. However, the exact relationship, if any, between the trends in the abovementioned non-bonded distances and the torsion angles is not immediately obvious.

In summary, a series of four new diphosphinated amino Fischer carbenes have been synthesized. The solid-state structures of three of these complexes display a conformation of the Fischer carbene functionality that is just the opposite of a related series of diphosphinated alkoxy Fischer carbenes, while the fourth amino complex appears to be an intermediate case with the carbene functionality disordered over both conformations. Since the steric environment of the Fischer carbene alpha carbon is

<sup>9</sup> The analogous average distance in **2** is 3.506(3) Å.

severely impacted by the conformation of the carbene ligand, the conformation is likely to be an important factor in the degree of nucleophilicity of the complexes upon deprotonation. Ongoing reactivity studies in our labs are examining the relationship between the observed conformational differences in the diphosphinated amino and alkoxy Fischer carbene complexes in the solid state and the relative reactivities of the deprotonated complexes with a variety of electrophiles in solution.

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