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Structural investigation into the surprising stability of free and complexed bis(amino)phosphine azides

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Abstract

The reaction of $(^{i}Pr_2N)_2PN_3$ (**1**) with $Fe_2(CO)_9$ in toluene solution at 25°C produces the complex $(^{i}Pr_2N)_2P(N_3)$–$Fe(CO)_4$ (**3**) with a high yield. The cophotolysis of **1** and $Cr(CO)_6$ in tetrahydrofuran solution results in the formation of $(^{i}Pr_2N)_2P(N_3)$–$Cr(CO)_5$ (**4**). Complexes **3** and **4** were found to be stable to UV irradiation (254 nm). The chromium complex **4** and the free phosphine azide $(c\text{-}Hex_2N)_2PN_3$ (**2**) have been characterized by single-crystal X-ray diffraction.

Keywords: Bis(amino)phosphine azide complexes; Reactivity; X-ray structure

1. Introduction

Recently, we have shown that bis(diisopropylamino) phosphine azide (**1**) [1] and bis(dicyclohexylamino) phosphine azide (**2**) [2] require photolytic conditions to react with most of the boranes [2]. The formation of adducts featuring a phosphorus–boron dative linkage was never observed, thus substantiating the poor accessibility of the phosphorus lone pair in this class of compound [3]. Nevertheless, the nature of the products suggested the transient formation of phosphinonitrene–borane adducts. As part of our continuing interest in the chemistry of phosphorus azides and phosphinonitrenes [2,4], we have investigated the reactivity of bis(dialkylamino)phosphine azides toward transition metal fragments in the hope of trapping and isolating phosphinonitrene complexes.

Herein, we report that $Fe_2(CO)_9$ and $Cr(CO)_6$ react with **1** to afford the corresponding bis(diisopropylamino)phosphine azide metal carbonyl complexes $(^{i}Pr_2N)_2$-$P(N_3)$–$Fe(CO)_4$ (**3**) and $(^{i}Pr_2N)_2P(N_3)$–$Cr(CO)_5$ (**4**) respectively. To rationalize the surprising stability of these complexes toward N_2 loss, X-ray crystal structure analyses of the free phosphine azide **2** and of **4** have been carried out.

2. Results and discussion

Since it is known that the usual course of the reaction of organic azides with transition metal derivatives is nitrogen elimination and nitrene complex formation [5], we have investigated the reaction of $(^{i}Pr_2N)_2PN_3$ with $Fe_2(CO)_9$ in toluene solution at 25°C. Interestingly, however, there was no evidence for decomposition of the azide moiety, and the phosphinoazide complex $(^{i}Pr_2N)_2P(N_3)$–$Fe(CO)_4$ (**3**) was produced with a high yield (Scheme 1). The coordination of the phosphine to the transition metal moiety was evident from the downfield ^{31}P chemical shift of 163 ppm. The detection of

3 1 4

R = *i*-Pr

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the molecular ion in a chemical ionization (CI) mass spectrometry (MS) experiment at $m/z = 441$, together with the presence of the azide stretching band at 2140 cm^{-1} in the IR spectrum, indicated that the azide moiety remained intact. It is note worthy that **3** was found to be stable when exposed to UV irradiation (254 nm).

In view of the observed lack of reactivity of **1** towards chromium hexacarbonyl, we decided to investigate the cophotolysis of **1** and $Cr(CO)_6$ with 254 nm light in tetrahydrofuran (THF) solution. Although the phosphine azide **1** is known to generate the corresponding phosphinonitrene under these experimental conditions [6], it is curious that the phosphinoazide complex **4** was the sole product of this reaction (Scheme 1). Preliminary identification of **4** was based on the observation of the molecular ion at $m/z = 466$ in the CI mass spectrum. Like **3**, **4** exhibits a downfield ^{31}P chemical shift (175 ppm) and an IR spectral band which is characteristic of the azide moiety (2122 cm^{-1}). Confirmation of the structure of **4** was provided by a single-crystal X-ray diffraction study (see later).

Compound **4** is also unaffected by irradiation with 254 nm light. In contrast with the photochemical stability of the phosphinoazide complexes **3** and **4**, it is note worthy that $Ph_2P(N_3)–Cr(CO)_5$ undergoes facile photolysis to produce the phosphino–isocyanate complex $Ph_2P(NCO)–Cr(CO)_5$, the formation of which has been postulated to proceed via a phosphinonitrene intermediate [7]. This striking difference in stability between aryl- and amino-substituted phosphinoazide transition metal complexes parallels that of the free phosphine azides. Examination of the literature [4c,8] reveals that free alkyl and aryl phosphine azides exhibit low thermal stabilities when compared with those of the corresponding amino-substituted derivatives. For example, neat diphenylphosphine azide decomposes sharply at 13°C [8a] and bis(trifluoromethyl)phosphine azide undergoes detonation upon contact even at −196°C [8b]. In contrast, the bis(dialkylamino)phosphine azides **1** and **2** have been found to exhibit an unexpected thermal stability; azide **1** can be distilled at 80°C (10^{-2} Torr) [1], while crystals of **2** melt at 119°C [2]. In order to understand the superior stability of aminophosphine azides, both in the coordination sphere of a metal and as free ligands, we have investigated the solid state molecular structure of **2** and **4** by X-ray crystallography.

Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Fig. 1 shows the molecular geometry together with the atom numbering scheme. Positional parameters are given in Table 1 and selected bond lengths and angles are assembled in Table 2. The sum of the angles at phosphorus (305.5(3)°) indicates a pyramidal geometry at this center. The orientation of the azide moiety is such that the lone pair at N(3) is directed in the opposite direction to that of the phosphorus lone pair. Examination of the phosphorus–nitrogen distances in **2** reveals that the P–N(3) bond (1.779(5) Å) is longer than the P–N(1)

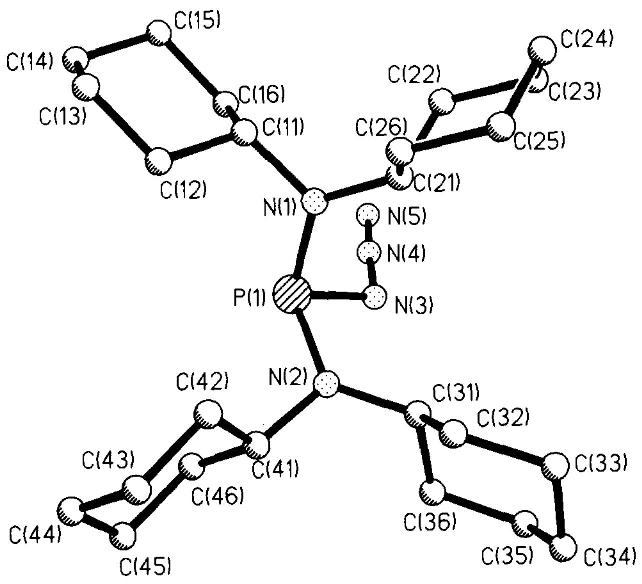


Fig. 1. Structure of 2 in the crystal.

Table 1
Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **2**

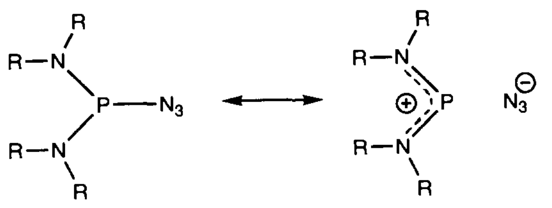
	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
P(1)	703(1)	423(2)	1865(1)	47(1)
N(1)	−400(4)	1460(4)	1653(2)	47(2)
N(2)	2109(4)	960(4)	1844(2)	49(2)
N(3)	492(5)	−345(5)	1109(2)	61(2)
N(4)	−384(6)	−1008(6)	956(3)	69(3)
N(5)	−1179(7)	−1648(7)	787(3)	112(4)
C(11)	−1335(5)	1524(5)	2051(2)	45(2)
C(12)	−740(5)	1835(6)	2764(3)	56(3)
C(13)	−1700(6)	1954(6)	3169(3)	67(3)
C(14)	−2501(6)	882(6)	3115(3)	71(3)
C(15)	−3110(5)	589(7)	2407(3)	70(3)
C(16)	−2132(5)	440(6)	2006(3)	60(3)
C(21)	−590(5)	2225(6)	1080(3)	50(2)
C(22)	−1806(6)	1963(6)	563(3)	66(3)
C(23)	−1928(7)	2743(7)	−37(3)	85(4)
C(24)	−1826(7)	4017(7)	138(3)	85(4)
C(25)	−647(7)	4292(7)	647(3)	85(4)
C(26)	−504(6)	3517(6)	1248(3)	61(3)
C(31)	2547(5)	1218(5)	1254(3)	45(2)
C(32)	3022(6)	2464(6)	1231(3)	58(3)
C(33)	3461(6)	2705(7)	613(3)	69(3)
C(34)	4423(7)	1811(8)	548(3)	87(4)
C(35)	3966(7)	554(8)	553(3)	82(4)
C(36)	3503(6)	305(6)	1159(3)	61(3)
C(41)	3018(5)	1081(6)	2485(3)	49(2)
C(42)	2793(6)	2125(6)	2872(3)	69(3)
C(43)	3822(7)	2268(8)	3494(3)	98(4)
C(44)	3981(7)	1189(9)	3910(3)	105(4)
C(45)	4184(6)	129(7)	3533(3)	86(4)
C(46)	3173(6)	−18(6)	2895(3)	71(3)

Table 2
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
P(1)–N(1)	1.678(5)	P(1)–N(2)	1.691(5)
P(1)–N(3)	1.779(5)	N(1)–C(11)	1.494(8)
N(1)–C(21)	1.459(7)	N(2)–C(31)	1.474(8)
N(2)–C(41)	1.478(6)	N(3)–N(4)	1.210(8)
N(4)–N(5)	1.132(10)		
Bond angles			
N(1)–P(1)–N(2)	111.2(2)	N(1)–P(1)–N(3)	100.4(2)
N(2)–P(1)–N(3)	93.9(3)	P(1)–N(1)–C(11)	116.8(4)
P(1)–N(1)–C(21)	125.6(4)	C(11)–N(1)–C(21)	117.4(4)
P(1)–N(2)–C(31)	126.7(3)	P(1)–N(2)–C(41)	115.9(4)
C(31)–N(2)–C(41)	117.2(4)	P(1)–N(3)–N(4)	117.4(5)
N(3)–N(4)–N(5)	176.3(8)	N(1)–C(11)–C(12)	112.0(4)

and P–N(2) bonds (average, 1.685(5) Å). A further important feature concerns the observation that the geometry at N(1) and N(2) are trigonal planar (average sum of the angles, 359.8(4)°). In turn, this implies that the N(1) and N(2) lone pairs are involved in N → Pπ interactions [8]. Taken collectively, the long P–N(3) bond distance, together with the planar geometries at N(1) and N(2), suggest a partial ionic character of the phosphorus azide bond, accompanied by a positive charge delocalization on the NPN framework (Scheme 2).

Molecules of **4** crystallize in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. Fig. 2 shows the molecular geometry together with the atom numbering scheme. Positional parameters are given in Table 3 and selected bond lengths and angles are assembled in Table 4. The geometric parameters and the conformation of the ligated $(^iPr_2N)_2PN_3$ molecule are extremely similar to those found for the uncoordinated phosphine **2**. Thus the sum of the angles at both amine nitrogen atoms (average, 359.6(7)°), as well as the P–N(3) bond distance of 1.760(4) Å, suggest that a similar development of partial ionic character of the phosphorus azide bond can be proposed for the coordinated phosphine in **4**. This partial ionic character, which seems to be a characteristic feature of free and coordinated bis(dialkylamino)phosphine azides, is not altogether surprising. For example, it is well known that amino substituents, in contrast with alkyl or aryl substituents, stabilize phosphenium cations [9]. So far, it has been believed that the stability of bis(dialkylamino)phosphine azides such as **1** and **2** was a result of the reluctance of this type of phosphine to engage in Staudinger-type reactions [3], because of the unaccessibility of the phosphorus lone pair. However, the formation of both **3** and **4**, as well as the difference in reactivity between $Ph_2P(N_3)–Cr(CO)_5$ and **4**, imply that an additional factor is involved, namely, the partial ionic character of the phosphorus azide bond.



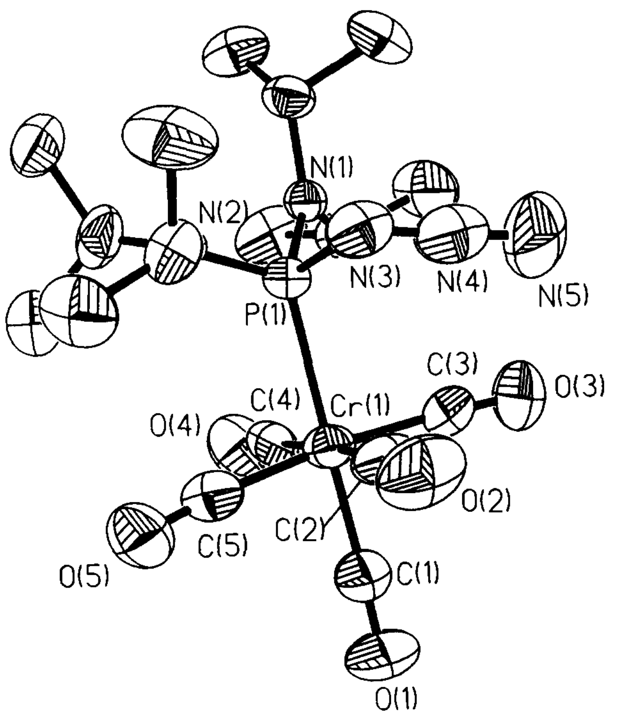


Fig. 2. Structure of **4** in the crystal.

3. Experimental section

All reactions were performed under a dry oxygen-free argon atmosphere or under vacuum using standard Schlenk line or dry-box techniques. All solvents used were distilled from sodium benzophenone under argon before use. The following reagents were purchased from Aldrich Chemicals and used without any further purification: sodium azide, diisopropylamine, dicyclohexylamine, diiron nonacarbonyl and chromium hexacarbonyl. The PCl_3 was purchased from Aldrich Chemicals and distilled prior to use. The compounds $(^iPr_2N)_2PN_3$ (**1**) [1] and $(c\text{-}Hex_2N)_2PN_3$ (**2**) [2] were prepared according to literature methods. The instruments used were as follows: CI mass spectra were run on a Finnigan MAT TSQ-70; NMR spectra were run on a GE QE-300 (^1H, 300.17 MHz; ^{13}C, 75.48 MHz; ^{31}P, 121.5 MHz). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 295 K. The chemical shifts are reported relative to $Si(CH_3)_4$ (0.00 ppm). ^{31}P NMR spectra were recorded at 295 K. The chemical shifts are reported relative to 85% (0.00 ppm) H_3PO_4 as an external standard. IR spectra were obtained with a Bio Rad FTS-40 spectrometer using KBr pellets. Melting points were obtained in sealed capillaries under argon (1 atm) and are uncorrected. In the photolysis experiments, a medium pressure mercury lamp was used as a radiation source and the sample was placed in front of a fan so that its temperature did not exceed 30°C.

3.1. Synthesis of $((^iC_3H_7)_2N)_2P(N_3)$–$Fe(CO)_4$ (3)

Diiron nonacarbonyl (1.09 g, 3 mmol) and $((^iPr)_2N)_2PN_3$ (**1**) (0.55 g, 2 mmol) were mixed in 20 ml of toluene and the mixture was stirred at 25°C for 24 h. The reaction mixture was filtered and the solvent was removed from the filtrate under reduced pressure. The resulting red oil crystallized upon cooling to −40°C for 24 h. Compound **3** was isolated with a 90% yield (0.79 g) (melting point (m.p.), 85°C (decomposition)).

^1H NMR ($CDCl_3$): δ 1.31, 1.33 (d, $^3J_{PH} = 7.2$ Hz, 24 H, CH_3), 4.10 (m, 4 H, CH) ppm. ^{13}C NMR ($CDCl_3$): δ 23.3, 24.6 (s, CH_3), 47.8 (d, $^3J_{PC} = 6.5$ Hz, CH), 212.8 (d, $^2J_{PC} = 19.3$ Hz, CO) ppm. IR: ν(CO) 1955 (E), 1969 (A_1), 2047 (A_1); $\nu(N_3)$ 2140 cm^{-1}. CI MS (CH_4): *m/z* 441 (M^+), 399 ($M^+ - N_3$), 274 ($M^+ - Fe(CO)_4 + H$), 231 ($M^+ - N_3 - Fe(CO)_4$).

Table 3
Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms of **4**

	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)	U_{eq} ($\times 10^{-3}$ Å^2)
Cr(1)	22(1)	3611(1)	3369(1)	50(1)
P(1)	2166(1)	2498(1)	2305(1)	40(1)
N(1)	3816(3)	2514(3)	2440(2)	39(2)
N(2)	2598(4)	760(4)	2107(3)	51(2)
N(3)	1719(5)	3520(5)	1052(3)	67(2)
N(4)	1390(5)	4918(7)	869(3)	84(3)
N(5)	1088(8)	6191(7)	635(4)	135(4)
O(1)	−2689(5)	5022(5)	4628(3)	107(2)
O(2)	−2040(4)	5048(5)	1574(3)	106(2)
O(3)	456(5)	6565(4)	3030(3)	102(2)
O(4)	1800(5)	2010(5)	5302(3)	88(2)
O(5)	−906(4)	960(5)	3834(3)	90(2)
C(1)	−1664(6)	4502(6)	4137(4)	69(3)
C(2)	−1227(6)	4514(6)	2239(4)	72(3)
C(3)	336(5)	5435(6)	3149(4)	63(2)
C(4)	1168(5)	2627(5)	4558(4)	57(2)
C(5)	−484(5)	1930(6)	3628(4)	60(2)
C(11)	4971(6)	1882(7)	4114(4)	86(3)
C(12)	4006(5)	3125(5)	3248(3)	52(2)
C(13)	4511(7)	4450(7)	2877(5)	100(4)
C(14)	6585(5)	876(6)	2170(4)	73(3)
C(15)	5067(4)	1966(5)	1702(3)	51(2)
C(16)	5202(7)	3276(6)	855(4)	88(3)
C(21)	2628(8)	608(8)	334(4)	101(4)
C(22A) [a]	2129(37)	113(42)	1470(15)	51(10)
C(22B) [a]	1598(25)	877(37)	1247(16)	55(8)
C(23A) [a]	409(32)	808(51)	1421(12)	73(13)
C(23B) [a]	950(26)	−273(41)	1567(13)	82(10)
C(24)	4879(7)	−1787(6)	2332(6)	132(4)
C(25)	3606(5)	−609(5)	2819(4)	73(3)
C(26)	2816(6)	−1419(6)	3622(4)	74(3)

[a] The methyl groups of one of the isopropyl at N(2) are disordered. The site occupation factors are 0.45(4) for C(22A) and C(23A), and 0.55(4) for C(22B) and C(23B).

Table 4
Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths			
Cr(1)–P(1)	2.427(1)	Cr(1)–C(1)	1.855(5)
Cr(1)–C(2)	1.888(6)	Cr(1)–C(3)	1.899(7)
Cr(1)–C(4)	1.900(5)	Cr(1)–C(5)	1.869(7)
P(1)–N(1)	1.666(4)	P(1)–N(2)	1.677(4)
P(1)–N(3)	1.760(4)	N(1)–C(12)	1.480(7)
N(1)–C(15)	1.500(5)	N(2)–C(22A)	1.445(42)
N(2)–C(22B)	1.596(29)	N(2)–C(25)	1.468(5)
N(3)–N(4)	1.235(9)	N(4)–N(5)	1.121(9)
Bond angles			
P(1)–Cr(1)–C(1)	177.7(2)	P(1)–Cr(1)–C(2)	89.2(2)
C(1)–Cr(1)–C(2)	88.6(2)	P(1)–Cr(1)–C(3)	92.2(1)
C(1)–Cr(1)–C(3)	87.7(2)	C(2)–Cr(1)–C(3)	90.1(3)
P(1)–Cr(1)–C(4)	93.6(1)	C(1)–Cr(1)–C(4)	88.7(2)
C(2)–Cr(1)–C(4)	175.2(3)	C(3)–Cr(1)–C(4)	93.7(2)
P(1)–Cr(1)–C(5)	93.3(1)	C(1)–Cr(1)–C(5)	86.7(2)
C(2)–Cr(1)–C(5)	88.2(3)	C(3)–Cr(1)–C(5)	174.2(2)
C(4)–Cr(1)–C(5)	87.7(2)	Cr(1)–P(1)–N(1)	120.1(1)
Cr(1)–P(1)–N(2)	120.1(1)	N(1)–P(1)–N(2)	105.4(2)
Cr(1)–P(1)–N(3)	108.9(1)	N(1)–P(1)–N(3)	103.0(2)
N(2)–P(1)–N(3)	95.1(2)	P(1)–N(1)–C(12)	120.2(3)
P(1)–N(1)–C(15)	118.5(3)	C(12)–N(1)–C(15)	121.2(4)
P(1)–N(2)–C(22A)	138.5(11)	P(1)–N(2)–C(22B)	111.9(12)
P(1)–N(2)–C(25)	117.6(4)	C(22A)–N(2)–C(25)	103.4(12)
C(22B)–N(2)–C(25)	129.7(13)	P(1)–N(3)–N(4)	115.4(4)
N(3)–N(4)–N(5)	175.1(6)		

3.2. Synthesis of $((^iC_3H_7)_2N)_2P(N_3)$–$Cr(CO)_5$ (4)

Chromium hexacarbonyl (0.48 g, 2.2 mmol) and $((^iPr)_2N)_2PN_3$ (**1**) (0.55 g, 2 mmol) were mixed in 15 ml of THF. The resulting mixture was photolyzed with 254 nm light for 1 h. The solvent was then removed under vacuum and the excess $Cr(CO)_6$ eliminated by sublimation at 40°C (10^{-2} Torr). The resulting residue was dissolved in 5 ml of Et_2O. Cooling of this solution to −20°C for 24 h afforded a 70% yield (0.65 g) of green crystalline **4** (m.p., 90°C (decomposition)). ^1H NMR ($CDCl_3$): δ 1.37 (d, $^3J_{PH} = 6.9$ Hz, 24 H, CH_3), 3.96 (m, 4 H, CH) ppm ^{13}C NMR ($CDCl_3$): δ 23.3, 25.1 (s, CH_3), 47.3 (d, $^3J_{PC} = 10.2$ Hz, CH), 215.7 (d, $^2J_{PC} = 16.0$ Hz, CO equatorial), 220.6 (d, $^2J_{PC} = 5.7$ Hz, CO axial) ppm. IR: ν(CO) 1919 (A_1), 1935 (E), 1993 (B_2), 2061.(A_1); $\nu(N_3)$ 2122 cm^{-1}. CI MS (CH_4): *m/z* 466 ($M^+ + H$), 423 ($M^+ - N_3$), 274 ($M^+ - Cr(CO)_5 + H$), 231 ($M^+ - N_3 - Cr(CO)_5$).

4. X-ray experimental data

Crystals of **2** and **4** were mounted in thin-walled glass capillaries and sealed under argon. Details of

Table 5
Crystal data, details of intensity measurement and structure refinement for **2** and **4**

Compound	**2**	**4**
Formula	$C_{24}H_{44}N_5P$	$C_{17}H_{18}CrN_5O_5P$
Molecular weight	433.6	465.4
Crystal dimensions (mm)	0.4 × 0.2 × 0.4	0.35 × 0.5 × 0.64
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P1$
a (Å)	11.138(2)	9.835(1)
b (Å)	11.338(2)	9.905(1)
c (Å)	21.087(4)	13.905(2)
α (°)	90	73.960(0)
β (°)	104.49(3)	82.260(0)
γ (°)	90	64.210(0)
V (Å^3)	2578.2(8)	1171.9(3)
D_c (g cm^{-3})	1.12	1.32
Z	2	2
Radiation	Mo Kα	Mo Kα
Number of independent reflections	3761	2618
Number of observed reflections	1770 ($F > 4\sigma(F)$)	2049 ($F > 4\sigma(F)$)
Number of parameters	257	283
Final R	0.0653	0.0429
Final R_w	0.0703	0.0604

crystal data and a summary of intensity data collection parameters for **2** and **4** are given in Table 5. Data were collected at 298 K on a Siemens R3m/V diffractometer with a 2θ range between 3.4 and 45° (for **2**) and between 3.5 and 42.8° (for **4**) using graphite-monochromated Mo Kα radiation. The intensity standards for each data collection indicated a decrease of less than 2% over the course of the data collection, and no decay correction was applied. All calculations were performed on IBM PC using Siemens SHELXTL PLUS programs. For each structure, the data were corrected for Lorentz and polarization effects. The observed structure factors of equivalent reflections were averaged. The structures were solved by direct methods with successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated using a standard riding model with fixed isotorpic displacement parameters. A weighting scheme of $(\sigma F)^2 + 0.0008F^2$ was used in the final stages of the refinement of **2** and **4**.

Acknowledgments

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