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The crystal structures of $(R_3P)_2$Ni–anthracene ($R = Et$, Bu)

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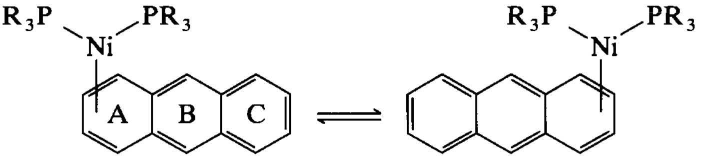
Abstract

The title complexes have solid state structures in which the Ni atom is bound η^2 to the anthracene. Crystal packing forces and interactions between an alkyl group of one molecule and the anthracene ring system of a second molecule may favour the η^2 structure over the η^4 structure observed in solution.

Introduction

Bis(trialkylphosphine)nickel anthracene undergoes a haptotropic rearrangement in which the bis(trialkylphosphine)nickel moiety migrates between the two side rings of the anthracene (Scheme 1) [1]. The kinetics and the establishement of the unimolecular nature of the process have been reported [1,2], but the nature of the



Scheme 1. Haptotropic rearrangement in $(R_3P)_2$Ni-anthracene.

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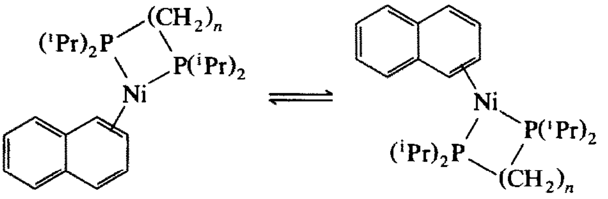
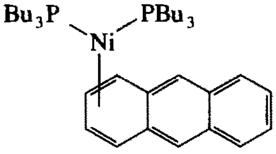
ground state bonding between the $(R_3P)_2Ni$ moiety and the anthracene remained unknown. Knowledge of the bonding in these complexes (*i.e.* whether η^2 or η^4, or in electronic terminology 16e or 18e respectively) is important for the understanding of catalytic processes because the crucial step in reactions catalyzed by organometallic compounds is the transformation of the catalyst to a coordinatively unsaturated state.

Nickel complexes are good probes for the study of coordination number changes because they are stable in either 16e or 18e configurations, depending on the ligands; thus, the 18e $Ni(CO)_4$ is much more stable than the 16e $Ni(CO)_3$, whereas the 16e tris(ethene)nickel is more stable than the 18e tetrakis(ethene)nickel. Arene-nickel complexes probably exhibit both coordination numbers. Thus, the coordination between the nickel and the anthracene in the solid state structure of $(Cy_3P)_2Ni$-anthracene (Cy = cyclohexyl) is η^2 [3]. The same coordination is found for the naphthalene complexes **1** [4], which undergo haptotropic rearrangement between the two η^2 structures (eq. 1). This equilibrium is also observed in solution at low temperatures [4a]. However, **2** and **3** show η^4 coordination in solution even at −100°C. Thus, if there is an equilibrium between two η^2 structures (similar to that observed for **1**, eq. 1), the barrier for this process must be < 4 kcal mol^{-1} [1].

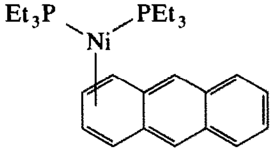


(1)

(1)



(2)



(3)

In the previous cases studied [3,4] the phosphines (and in the naphthalene case also the aromatic ligand) are very different from these in **2** and **3**. Tricyclohexylphosphine is much bulkier than the phosphines in **2** and **3** (the phosphorus cone angles are 170° for PCy_3 and 132° for PBu_3 and PEt_3 [5]), and in **1** the phosphines are bridged. These differences, considered together with the solution behaviour of **2** and **3** (which show unambiguous η^4 structure), led us to the study of their solid state structures in order to gain more understanding of the bonding.

Results and discussion

Figure 1 and Tables 1–4 show the structures of **2** and **3**, and list the relevant structural data according to which the molecules adopt η^2 coordination in the solid state, and in general the structures are similar to $(Cy_3P)_2Ni$-anthracene [3].

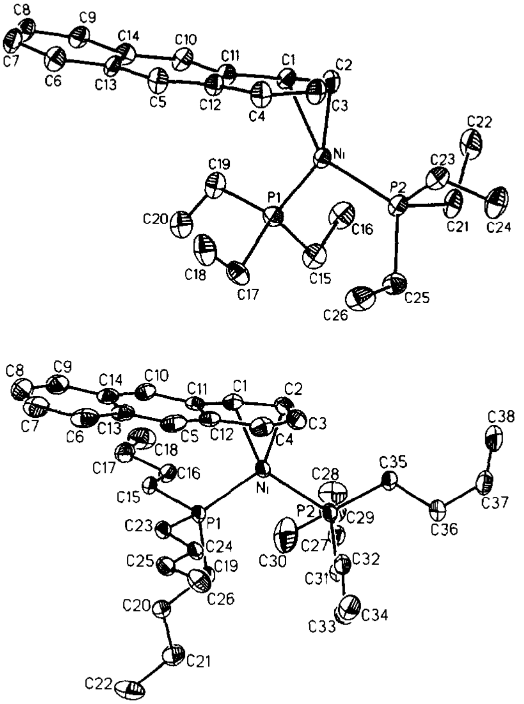


Fig. 1. Molecular structures of $(Et_3P)_2Ni$–anthracene (above) and $(Bu_3P)_2Ni$–anthracene (below).

However, examination of the unit cells (Fig. 2) shows that in both compounds intermolecular interactions cause the molecules to form pairs. Thus in **2**, the molecules are arranged so that C18 is 3.8 Å away from the centre of ring C of the anthracene ring system of another molecule (Fig. 2, bottom). Similarly, in **3** C17 is just 3.46 Å from the centre of ring B of another molecule (Fig. 2, top). The distances between the aromatic moieties and the alkyl carbons are almost optimal for bonding interaction between the two [6]. From gas-phase experiments it is estimated that the stabilization energy in such an interaction is *ca.* 1.7 kcal mol^{-1} [7].

Are there any further factors that can stabilize the η^2 relative to the η^4 structure in the crystal? The answer is yes, although no definite value of the stabilization energy can be assigned. Thus, the only known X-ray structure of an η^4 anthracene complex is that of the $(dmpe)_2(Cl)Ta$–anthracene [8] in which the angle between the coordinated ring and the naphthalenic residue is *ca.* 42°. Thus, it is clear that the packing for the η^2 nickel–anthracene (in which the anthracene system deviates only slightly from planarity) is better. This type of crystal packing forces is usually estimated to have energies of a few kcal mol^{-1}.

Although the η^2 complexes are almost planar the difference in the phosphines causes changes in the angle between the coordinated ring and the naphthalenic residue. Thus, in $(Cy_3P)_2Ni$–anthracene [3] this angle is 5.3°, whereas in **2** and **3** these angles are 8.3 and 14.1°, respectively. Figure 3 presents a pictorial comparison between **2** and **3**. Thus, although these three complexes are structurally very

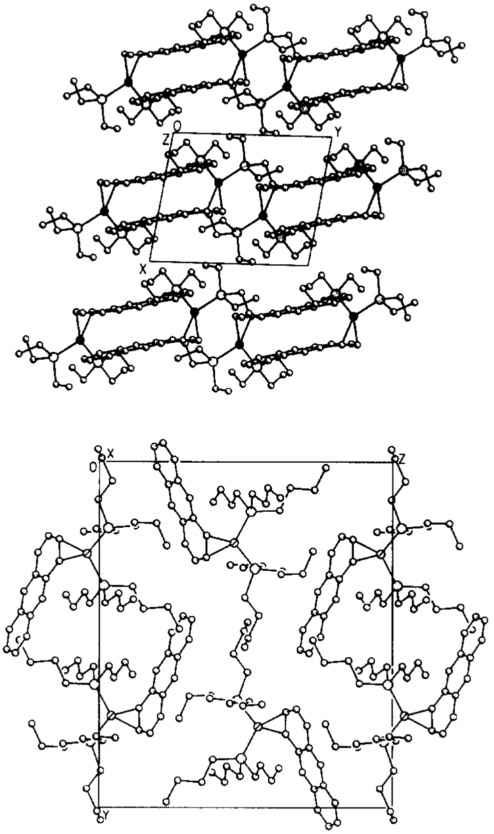


Fig. 2. Unit cells of $(Et_3P)_2Ni$–anthracene (above) and $(Bu_3P)_2Ni$–anthracene (below).

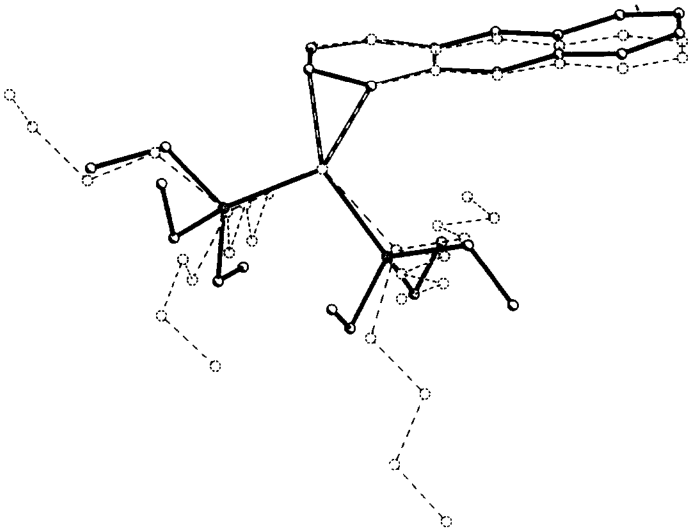


Fig. 3. A comparison between **2** (dashed lines) and **3** (solid lines).

similar, the angle between the coordinated ring and the naphthalenic residue seems to depend on the phosphine in such a way that it is larger for more compact phosphine. It is noteworthy that the corresponding angle in the η^4 Ta complex is > 40°. Thus, although the bonding in **2** and **3** is η^2 there are indications that the use of more compact (and possibly bridged) phosphines as the ligands on nickel would lead to formation of η^4 complexes with the anthracene. We are currently studying a variety of these complexes containing various phosphines (electronically and structurally different) in order to learn more about this effect.

In summary, **2** and **3** have solid state structures in which the Ni atom is bound η^2 to the anthracene. Crystal packing forces and interactions between an alkyl group of one molecule and the anthracene ring system of a second molecule favour the η^2 structure over the η^4 structure that is observed in solution. The maximum energetic difference between the two possible structures (4 kcal mol^{-1}) is within the range of the factors stabilizing the η^2 relative to the η^4, and so it is (as yet) not possible to decide whether the stable coordination number between the $(R_3P)_2Ni$ (R = Et, Bu) moieties and the anthracene in the isolated molecule or in solution is 2 or 4.

Table 1

Atomic coordinates ($\times 10^4$) for **2**. Standard deviations are given in parentheses

Atom	*x*	*y*	*z*
Ni	3786.4(10)	3409.9(8)	7780.7(6)
P(1)	2101(2)	2037(2)	8191(1)
P(2)	2431(2)	4871(2)	7449(1)
C(1)	6012(8)	2999(6)	8056(5)
C(2)	5981(9)	3982(7)	7566(5)
C(3)	5925(9)	3595(7)	6544(5)
C(4)	5995(9)	2352(7)	6038(5)
C(5)	6492(9)	119(7)	6021(5)
C(6)	7193(9)	−2062(7)	5994(5)
C(7)	7649(9)	−2916(7)	6483(5)
C(8)	7725(9)	−2582(8)	7474(6)
C(9)	7377(8)	−1412(7)	7989(5)
C(10)	6639(8)	770(7)	8014(5)
C(11)	6285(8)	1681(6)	7543(5)
C(12)	6227(8)	1353(6)	6517(5)
C(13)	6841(8)	−820(6)	6487(5)
C(14)	6940(8)	−486(7)	7503(5)
C(15)	742(9)	2751(7)	9017(5)
C(16)	1675(10)	3579(8)	9994(5)
C(17)	714(9)	947(7)	7171(5)
C(18)	1585(10)	323(7)	6341(5)
C(19)	2911(9)	884(7)	8786(5)
C(20)	1744(10)	−58(7)	9087(6)
C(21)	2203(9)	6114(7)	8553(5)
C(22)	3763(10)	6814(7)	9136(5)
C(23)	3328(9)	5872(7)	6730(5)
C(24)	2602(10)	7088(8)	6653(6)
C(25)	340(8)	4402(7)	6858(5)
C(26)	181(10)	3566(8)	5817(5)

Experimental

2 and **3** were prepared as previously described [1]. Crystals suitable for the X-ray study were obtained by slow cooling (*i.e.* 24–48 h) of concentrated hexane solution of **2** or **3** from room temperature to −85°C. Data were collected on a Nicolet R3m/V X-ray diffractometer with Mo-K_α radiation.

Table 2

Atomic coordinates ($\times 10^4$) for **3**. Standard deviations are given in parentheses

Atom	*x*	*y*	*z*
Ni	1865(1)	7344(1)	411(1)
P(1)	1767(1)	6431(1)	−157(1)
P(2)	2403(1)	8085(1)	−301(1)
C(1)	1296(3)	7130(2)	1358(2)
C(2)	1841(4)	7761(2)	1364(2)
C(3)	3257(4)	7848(2)	1733(2)
C(4)	4041(4)	7371(2)	2090(2)
C(5)	4271(3)	6252(2)	2556(2)
C(6)	4506(4)	5138(2)	3055(2)
C(7)	3923(5)	4564(2)	3145(2)
C(8)	2529(5)	4463(2)	2849(2)
C(9)	1738(4)	4938(2)	2459(2)
C(10)	1516(3)	6038(2)	1934(2)
C(11)	2077(3)	6625(1)	1818(2)
C(12)	3498(3)	6738(2)	2162(2)
C(13)	3716(3)	5649(2)	2655(2)
C(14)	2299(3)	5539(2)	2344(2)
C(15)	260(3)	5921(1)	−196(2)
C(16)	−1074(3)	6202(2)	−658(2)
C(17)	−2278(3)	5750(2)	−725(2)
C(18)	−3619(4)	6029(2)	−1155(2)
C(19)	1932(3)	6401(1)	−1133(2)
C(20)	2007(3)	5747(1)	−1499(2)
C(21)	1932(4)	5802(2)	−2329(2)
C(22)	2020(4)	5164(2)	−2715(2)
C(23)	3162(3)	5908(1)	332(2)
C(24)	4545(3)	6235(1)	497(2)
C(25)	5714(3)	5797(1)	881(2)
C(26)	7064(3)	6152(2)	1129(2)
C(27)	1232(3)	8150(2)	−1231(2)
C(28)	−249(4)	8242(2)	−1191(2)
C(29)	−1288(4)	8225(2)	−1940(2)
C(30)	−1472(5)	7579(2)	−2281(2)
C(31)	4061(3)	8008(1)	−550(2)
C(32)	5304(3)	8054(1)	111(2)
C(33)	6638(3)	7939(2)	−106(2)
C(34)	7885(3)	7980(2)	543(2)
C(35)	2450(3)	8915(1)	46(2)
C(36)	2861(4)	9448(2)	−429(2)
C(37)	2987(4)	10104(2)	−68(2)
C(38)	1710(5)	10358(2)	51(3)

Table 3

Selected bond lengths (Å) and angles (deg) for **2**

Ni-P(1)	2.161(1)	Ni-P(2)	2.174(1)
Ni-C(1)	2.007(3)	Ni-C(2)	1.963(3)
P(1)-C(15)	1.837(3)	P(1)-C(19)	1.843(3)
P(1)-C(23)	1.835(3)	P(2)-C(27)	1.838(3)
P(2)-C(31)	1.836(3)	P(2)-C(35)	1.842(3)
C(1)-C(2)	1.423(5)	C(1)-C(11)	1.459(4)
C(2)-C(3)	1.436(5)	C(3)-C(4)	1.340(5)
C(4)-C(12)	1.445(5)	C(5)-C(12)	1.374(5)
C(5)-C(13)	1.405(5)	C(6)-C(7)	1.358(6)
C(6)-C(13)	1.426(5)	C(7)-C(8)	1.393(6)
C(8)-C(9)	1.362(5)	C(9)-C(14)	1.411(5)
C(10)-C(11)	1.384(4)	C(10)-C(14)	1.410(4)
C(11)-C(12)	1.438(4)	C(13)-C(14)	1.422(4)
C(15)-C(16)	1.525(4)	C(16)-C(17)	1.515(5)
C(17)-C(18)	1.508(5)	C(19)-C(20)	1.531(4)
C(20)-C(21)	1.515(5)	C(21)-C(22)	1.520(5)
C(23)-C(24)	1.512(4)	C(24)-C(25)	1.524(4)
C(25)-C(26)	1.517(5)	C(27)-C(28)	1.519(5)
C(28)-C(29)	1.520(5)	C(29)-C(30)	1.477(6)
C(31)-C(32)	1.526(4)	C(32)-C(33)	1.505(5)
C(33)-C(34)	1.515(4)	C(35)-C(36)	1.529(5)
C(36)-C(37)	1.515(5)	C(37)-C(38)	1.450(7)
P(1)-Ni-P(2)	108.9(1)	P(1)-Ni-C(1)	103.6(1)
P(2)-Ni-C(1)	147.4(1)	P(1)-Ni-C(2)	144.4(1)
P(2)-Ni-C(2)	106.3(1)	C(1)-Ni-C(2)	42.0(1)
Ni-P(1)-C(15)	118.1(1)	Ni-P(1)-C(19)	119.8(1)
C(15)-P(1)-C(19)	101.9(1)	Ni-P(1)-C(23)	110.1(1)
C(15)-P(1)-C(23)	101.7(1)	C(19)-P(1)-C(23)	102.9(1)
Ni-P(2)-C(27)	114.7(1)	Ni-P(2)-C(31)	117.2(1)
C(27)-P(2)-C(31)	101.1(1)	Ni-P(2)-C(35)	116.7(1)
C(27)-P(2)-C(35)	102.3(1)	C(31)-P(2)-C(35)	102.6(1)
Ni-C(1)-C(2)	67.3(2)	Ni-C(1)-C(11)	116.0(2)
C(2)-C(1)-C(11)	120.7(3)	Ni-C(2)-C(1)	70.7(2)
Ni-C(2)-C(3)	104.9(3)	C(1)-C(2)-C(3)	117.1(3)
C(2)-C(3)-C(4)	122.7(3)	C(3)-C(4)-C(12)	122.1(3)
C(12)-C(5)-C(13)	122.5(3)	C(7)-C(6)-C(13)	121.1(4)
C(6)-C(7)-C(8)	120.5(4)	C(7)-C(8)-C(9)	120.2(4)
C(8)-C(9)-C(14)	121.4(4)	C(11)-C(10)-C(14)	122.6(3)
C(1)-C(11)-C(10)	123.0(3)	C(1)-C(11)-C(12)	118.5(3)
C(10)-C(11)-C(12)	118.4(3)	C(4)-C(12)-C(5)	122.9(3)
C(4)-C(12)-C(11)	117.8(3)	C(5)-C(12)-C(11)	119.3(3)
C(5)-C(13)-C(6)	123.2(3)	C(5)-C(13)-C(14)	118.8(3)
C(6)-C(13)-C(14)	118.0(3)	C(9)-C(14)-C(10)	123.0(3)
C(9)-C(14)-C(13)	118.7(3)	C(10)-C(14)-C(13)	118.4(3)
P(1)-C(15)-C(16)	114.0(2)	C(15)-C(16)-C(17)	112.7(3)
C(16)-C(17)-C(18)	113.5(3)	P(1)-C(19)-C(20)	118.9(2)
C(19)-C(20)-C(21)	112.2(3)	C(20-C(21)-C(22)	114.2(3)
P(1)-C(23)-C(24)	112.9(2)	C(23)-C(24)-C(25)	113.2(2)
C(24)-C(25)-C(26)	112.6(3)	P(2)-C(27)-C(28)	112.5(2)
C(27)-C(28)-C(29)	115.0(3)	C(28)-C(29)-C(30)	113.4(3)
P(2)-C(31)-C(32)	114.6(2)	C(31)-C(32)-C(33)	113.0(3)
C(32)-C(33)-C(34)	113.9(3)	P(2)-C(35)-C(36)	118.2(2)
C(35)-C(36)-C(37)	114.3(3)	C(36)-C(37)-C(38)	114.3(3)

Table 4

Selected bond lengths (Å) and angles (deg) for **3**

Ni–P(1)	2.159(2)	Ni–P(2)	2.177(2)
Ni–C(1)	2.013(7)	Ni–C(2)	1.961(7)
P(1)–C(15)	1.831(8)	P(1)–C(17)	1.830(6)
P(1)–C(19)	1.847(8)	P(2)–C(21)	1.839(7)
P(2)–C(23)	1.835(8)	P(2)–C(25)	1.837(7)
C(1)–C(2)	1.422(12)	C(1)–C(11)	1.471(9)
C(2)–C(3)	1.429(10)	C(3)–C(4)	1.353(10)
C(4)–C(12)	1.448(11)	C(5)–C(12)	1.386(9)
C(5)–C(13)	1.398(11)	C(6)–C(7)	1.368(12)
C(6)–C(13)	1.418(10)	C(7)–C(8)	1.385(11)
C(8)–C(9)	1.364(11)	C(9)–C(14)	1.427(11)
C(10)–C(11)	1.379(11)	C(10)–C(14)	1.422(10)
C(11)–C(12)	1.434(9)	C(13)–C(14)	1.417(9)
C(15)–C(16)	1.541(9)	C(17)–C(18)	1.522(11)
C(19)–C(20)	1.501(11)	C(21)–C(22)	1.491(10)
C(23)–C(24)	1.534(12)	C(25)–C(26)	1.526(10)
P(1)–Ni–P(2)	106.4(1)	P(1)–Ni–C(1)	108.2(2)
P(2)–Ni–C(1)	144.3(2)	P(1)–Ni–C(2)	149.6(3)
P(2)–Ni–C(2)	103.9(3)	C(1)–Ni–C(2)	41.9(3)
Ni–P(1)–C(15)	116.0(3)	Ni–P(1)–C(17)	113.2(3)
C(15)–P(1)–C(17)	102.8(3)	Ni–P(1)–C(19)	118.1(2)
C(15)–P(1)–C(19)	102.0(4)	C(17)–P(1)–C(19)	102.7(3)
Ni–P(2)–C(21)	111.0(3)	Ni–P(2)–C(23)	117.0(3)
C(21)–P(2)–C(23)	102.3(3)	Ni–P(2)–C(25)	120.7(3)
C(21)–P(2)–C(25)	101.1(3)	C(23)–P(2)–C(25)	102.1(4)
Ni–C(1)–C(2)	67.1(4)	Ni–C(1)–C(11)	115.9(4)
C(2)–C(1)–C(11)	119.9(6)	Ni–C(2)–C(1)	71.0(4)
Ni–C(2)–C(3)	104.4(5)	C(1)–C(2)–C(3)	118.2(6)
C(2)–C(3)–C(4)	122.6(8)	C(3)–C(4)–C(12)	121.2(7)
C(12)–C(5)–C(13)	122.3(6)	C(7)–C(6)–C(13)	121.2(7)
C(6)–C(7)–C(8)	119.7(7)	C(7)–C(8)–C(9)	122.0(8)
C(8)–C(9)–C(14)	119.7(7)	C(11)–C(10)–C(14)	121.3(6)
C(1)–C(11)–C(10)	122.4(6)	C(1)–C(11)–C(12)	118.5(6)
C(10)–C(11)–C(12)	119.1(6)	C(4)–C(12)–C(5)	121.8(6)
C(4)–C(12)–C(11)	118.7(6)	C(5)–C(12)–C(11)	119.3(7)
C(5)–C(13)–C(6)	122.9(6)	C(5)–C(13)–C(14)	118.4(6)
C(6)–C(13)–C(14)	118.5(7)	C(9)–C(14)–C(10)	121.6(6)
C(9)–C(14)–C(13)	118.9(6)	C(10)–C(14)–C(13)	119.5(7)
P(1)–C(15)–C(16)	111.4(5)	P(1)–C(17)–C(18)	112.2(5)
P(1)–C(19)–C(20)	118.3(6)	P(2)–C(21)–C(22)	113.7(6)
P(2)–C(23)–C(24)	118.7(6)	P(2)–C(25)–C(26)	113.3(5)

Crystal data

2: Crystal *ca.* 0.38 × 0.28 × 0.19 mm^3, data obtained at 110 K. Cell dimensions: $a = 10.045(1)$, $b = 20.846(2)$, $c = 18.392(2)$ Å, $\beta = 103.66(1)°$, $V = 3742.2(7)$ Å^3; $Z = 4$, $d_{\text{calc}} = 1.106$ g cm^{-3}, $\mu = 0.63$ mm^{-1}, monoclinic, space group $P2_1/c$, 6563 unique intensities ($2\theta_{\text{max}} = 50°$) collected and 5007 treated as observed ($F_o \geq 4\sigma(F)$), 414 parameters, $R = 0.042$, $R_w = 0.038$, $w^{-1} = (\sigma^2(F_o) + 10^{-4}F_o^{\,2})$.

3: Crystal *ca.* 0.18 × 0.12 × 0.09 mm^3. Data obtained at 115 K. Cell dimensions: $a = 8.456(5)$, $b = 10.722(4)$, $c = 14.552(6)$ Å, $\alpha = 105.34(3)$, $\beta = 95.57(4)$, $\gamma = 97.16(4)°$, $V = 1251(1)$ Å^3, $Z = 2$, $d_{\text{calc}} = 1.257$ g cm^{-3}, $\mu = 0.91$ mm^{-1}, triclinic, space group $P\bar{1}$, 3280 unique intensities ($2\theta_{max} = 40°$) collected and 2608 treated as observed, 304 parameters, $R = 0.067$, $R_w = 0.066$, $w^{-1} = (\sigma^2(F_o) + 2 \times 10^{-2}F_o^2)$. Structure solutions by direct methods and refinement by full matrix least squares, hydrogen atoms placed in calculated positions with common isotopic U values for each group and ADP's for all other atoms.

Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein–Leopoldshafen 2 (Germany) on quoting the depository numbers CSD-320411 for **2** and CSD-320412 for **3**, and the names of the authors and the journal citation.

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