# *N′,N′,N′′,N′′*-Tetramethylguanidine-Substituted Phosphoryl Compounds as Ligands in Transition Metal Chemistry − Unusual Modes of Coordination[☆]

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Methyl- and *tert*-butylphosphonic bis(*N′,N′,N″,N″*-tetramethylguanidinide) **1** and **2** were allowed to react with various transition metal compounds. The resulting complexes were studied by IR spectroscopy, mass spectrometry and, in the case of **10**, by NMR spectroscopy. In the case of the compounds **7**−**10** the metal was coordinated only via the imino nitrogen atoms of **2** (IR evidence). X-ray structure analyses were performed for $[L^1CoBr_2]_2$ **5**, $L^2Mn(acac)_2$ **6**, $L^2CuCl_2$ **9**, and $L^2PdCl_2$ **10** ($L^1$ = **1**, $L^2$ = **2**). In **5** $L^1$ acts as an N,O bridging ligand, leading to tetrahedral coordination at Co and eight-membered $(-Co-O-P-N-)_2$ rings. In **6** coordination by $L^2$ is solely through the P=O group, occupying the apical site of the square pyramidal ($O_5$) geometry at Mn. In **9** and **10** $L^2$ chelates the metal atom through two N atoms, leading to $PN_2M$ rings; the coordination geometry is distorted planar.

## Introduction

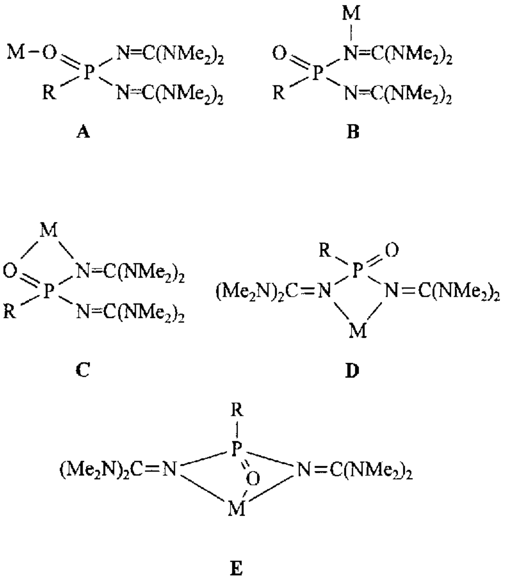
Phosphane oxides form coordination compounds with a variety of metals from groups 1−15 of the periodic table of the elements. By changing the substituents at phosphorus, especially by introducing functional groups able to coordinate to the metal centre, it is possible to vary the ligand properties over a wide range.

*N′,N′,N′′,N′′*-tetramethylguanidine-(TMG-)substituted phosphoryl compounds are especially suitable in this respect. They contain three different groups capable of coordinating to a transition metal: the imino or the amino nitrogen atoms and the phosphoryl oxygen atom. In our studies concerning the synthesis and reactivity of TMG-substituted phosphorus compounds we found that TMG-substituted phosphanes form chelate complexes via phosphorus and the amino nitrogen atoms[1]. In compounds of tetracoordinate phosphorus(V) the amino nitrogen atoms displayed no reactivity[2]. Neglecting the amino nitrogen atoms, five different modes of coordination can be envisaged for TMG-substituted phosphoryl compounds (Scheme 1).

Type **A** (Scheme 1) is the mode of coordination most frequently found in coordination compounds with phosphoryl ligands[3][4][5]. To the best of our knowledge there are no reports of coordination of types **B**− **E** with amino-substituted phosphoryl compounds as ligands.

The structures of cyclic metallaphosphazenes show a certain similarity to the situation encountered in type **C** and **D** (Scheme 1), even though in these cases the metal−nitrogen bonds are covalent, in some cases with a bonding order greater than one[6][7][8][9]. Likewise, the structures observed for chalkogenophosphinic *N*-organylamidato transition metal complexes are similar to type **C**[10][11]. Phosphonic hydrazides form complexes where the metal is coordinated as in structures **A** or **C**−**E** (Scheme 1), even though in this case the coordinating centre is the nitrogen in β position and not in α position to phosphorus[12]. Closely related to type **D** are the compounds that are formally obtained from TMG-substituted phosphanes and aluminium trichloride. These contain pentacoordinate aluminium bonded to the imino nitrogen atoms of the phosphane TMG-substituents[13].

Scheme 1



## Results and Discussion

Methylphosphonic bis(*N′,N′,N′′,N′′*-tetramethylguanidinide) **1** was allowed to react with $NiBr_2 \cdot 2$ DME [→**A** in

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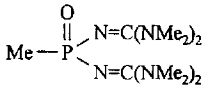
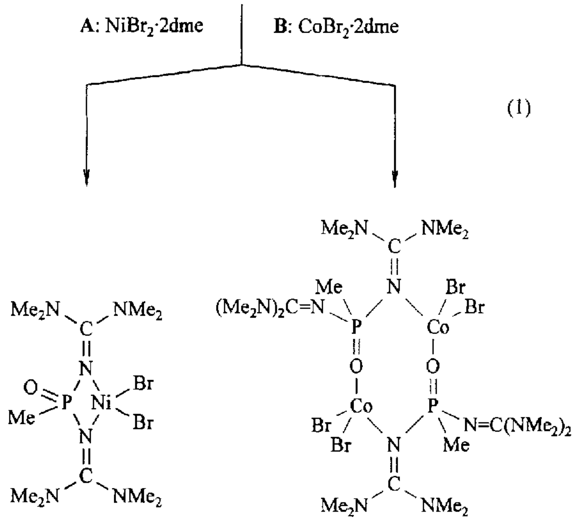
Eq. (1)] and with $CoBr_2 \cdot 2$ DME [→**B** in Eq. (1)], respectively. The resulting compounds were paramagnetic and thus not suitable for NMR studies (as were all the other complexes studied here, with the exception of **10**). In the IR spectrum of the nickel complex **4** the P(=O) vibration was split and shifted hypsochromically (Table 1). The CN vibration at the highest wavenumber was considerably less intense than the corresponding vibration in the IR spectrum of the starting compound. The remaining CN vibrations were shifted bathochromically from those of the starting materials. This shows that the nickel atom is coordinated to the imino nitrogen atoms. Thus, the π interaction between phosphorus and nitrogen is reduced, and the double-bond character of the P(=O) bond increases.



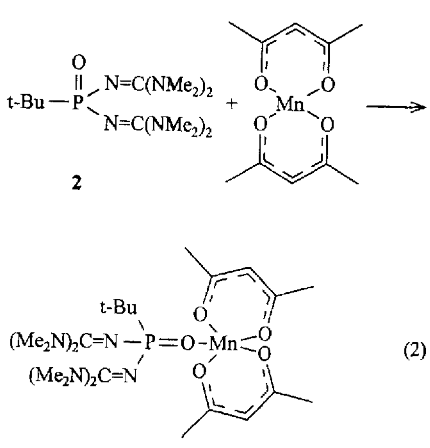
**1**



(1)

**4** **5**

The CN vibrations in the IR spectrum of the cobalt complex **5** were broadened, but only slightly shifted from those of the starting material (Table 1). The P(=O) vibration was split, as in **4**. However, in this case the vibration was shifted bathochromically, indicating coordination of the metal via the phosphoryl oxygen atom. The broadening of the CN band implies that at least one of the imino nitrogen atoms also takes part in the bonding of the metal. The X-ray investigation of **5** showed that, instead of the expected four-membered ring, a dimeric species was present (see below).



(2)

**6**

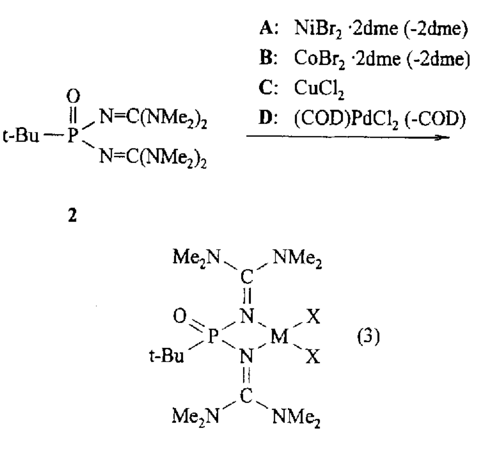
In the complex **6** formed in the reaction of *tert*-butylphosphonic bis(*N′*,*N′*,*N′′*,*N′′*-tetramethylguanidinide) **2** with manganese(II) acetylacetonate, the metal was coordinated to the phosphoryl oxygen atom [Eq. (2)]. The P(=O) vibration in the IR spectrum of **6** was shifted to a lower wavenumber, compared to that of the starting material (Table 1). The CN vibrations seemed unchanged, even though no exact assignment could be made because of overlapping with the CO vibrations of the acetylacetonate ligand. The X-ray structure analysis performed on **6** confirmed the structure proposed. Coordination compounds containing pentacoordinated manganese(II) are quite common, but the subset of compounds containing pentacoordinated manganese(II) as part of two chelate rings are rare. Most structures described in the literature involve addition of two ligand molecules to manganese(II) acetylacetonate with formation of a complex containing hexacoordinate manganese(II)[14].

Table 1. Selected IR data of compounds **1**−**11**

| | $\tilde{\nu}$(CN) | $\tilde{\nu}$[P(=O)] | |
|---|---|---|---|
| **1**[a] | 1620, 1570, 1560, 1515 | 1160 | $CH_2Cl_2$ |
| **2**[a] | 1635, 1575, 1539, 1506 | 1130 | $CH_2Cl_2$ |
| **4** | 1624, 1545, 1475 | 1190, 1159 | KBr |
| | 1617, 1561, 1534, 1471 | 1153 | $CH_2Cl_2$ |
| **5** | 1628, 1561, 1522, 1463 | 1153, 1130 | KBr |
| | 1625, 1569, 1523, 1468 | 1162, 1139 | $CH_2Cl_2$ |
| **6** | 1606[b],1552, 1523, 1474 | 1125 | KBr |
| | 1592[b], 1560, 1543, 1517, 1471 | 1138, 1118 | $CH_2Cl_2$ |
| **7** | 1624, 1571, 1531, 1468 | 1155 | KBr |
| | 1610, 1521, 1422 | 1104 | $CH_2Cl_2$ |
| **8** | 1623, 1564, 1529, 1467 | 1170, 1157 | KBr |
| **9** | 1618, 1565, 1519, 1468 | 1144 | KBr |
| | 1569, 1517, 1446 | 1141 | $CH_2Cl_2$ |
| **10** | 1619, 1567, 1519, 1475 | 1160, 1145 | KBr |
| | 1563, 1519, 1469 | 1113 | $CH_2Cl_2$ |
| **11** | 1625, 1575, 1550, 1525, 1470 | 1110 | KBr |
| | 1625, 1593, 1579, 1538, 1470 | 1125, 1108 | $CH_2Cl_2$ |

[a] See ref.[2].– [b] Broadened by overlapping (CO) vibrations.

In the same way as **1** in Eq. (1), **2** was allowed to react with $NiBr_2 \cdot 2$ DME and with $CoBr_2 \cdot 2$ DME [→**A** and **B** in Eq. (3)]. The IR spectrum of the resulting nickel complex **7** (as a solid in KBr) exhibited a bathochromic shift of the P(=O) vibration and a hypsochromic shift of the CN vibrations, relative to the starting compound. This signifies that the metal is coordinated via the imino nitrogen atoms. Similar changes were observed in the IR spectrum of the cobalt complex **8**, leading to the same conclusion: the cobalt atom was bonded to the imino nitrogen atoms, unlike in **4**.



**2**

(3)

**7** M = Ni; X = Br
**8** M = Co; X = Br
**9** M = Cu; X = Cl
**10** M = Pd; X = Cl

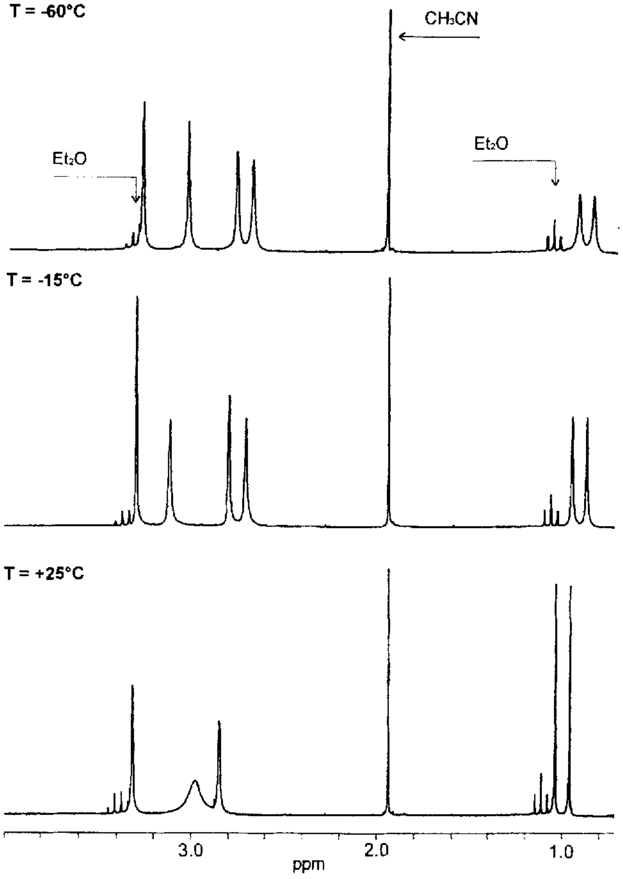
The nickel complex **7** was obtained as a blue solid. Solutions of **7** in polar and in nonpolar solvents are violet, suggesting different structures for **7** in solution and in the solid state. This was confirmed by the IR spectrum recorded in $CH_2Cl_2$: the CN vibration exhibited a slight, and the P(=O) vibration a strong bathochromic shift, compared to the solid state IR spectrum, suggesting that in solution the phosphoryl oxygen atom coordinates to nickel. Either the coordination number of nickel is increased or one bromine is substituted, with formation of a cationic complex and a bromide anion.

Compound **2** reacted with copper(II) chloride and with (cyclooctadiene) palladium(II) chloride to give the copper complex **9** and the palladium complex **10**, respectively [**C** and **D** in Eq. (3)]. The structure of these is similar to that of **7** and **8**, as is the pattern of the IR spectra. The CN vibrations were observed at lower wavenumber and the P(=O) vibration at higher wavenumber than those of **2** (Table 1).This implies that the structure involves coordination to the metal via the imino nitrogen atoms. The X-ray structure analyses performed on **9** and **10** (see below) confirmed this.

The IR spectrum of **9** as a solid in KBr did not differ significantly from that of the solution in $CDCl_3$. In contrast to this, the IR spectra of **10** in the solid state and in solution showed differences similar to those observed for **7**. It seems possible that in solution the palladium atom in **10** is coordinated via the phosphoryl oxygen.

The palladium compound **10** is the only compound studied here that was not paramagnetic. The $\delta(^{31}P)$ value of **10** ($\delta = 53.2$) was shifted to lower field, relative to that of the starting compound **2** ($\delta = 18.0$)[2]. This downfield shift was observed for all products of reactions occurring at the imino nitrogen atom of TMG-substituted phosphoryl compounds[2][15].

Figure 1. Temperature-dependent $^1$H-NMR spectrum of compound **10**



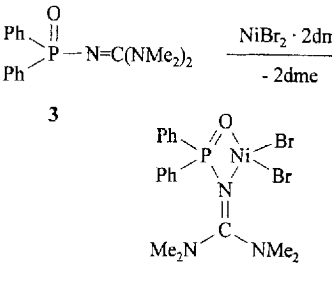
In the $^1$H-NMR spectrum of **10** three signals were observed for the protons of the TMG methyl groups [$\delta = 2.90$ (6 H), 3.03 (12), and 3.35 (6)]. At low temperature the signal at $\delta = 3.03$ was found to be split into two signals of equal intensity (Figure 1).

There are two possible explanations for this:

1. The TMG substituents are placed symmetrically on both sides of the Pd−N−P−N ring in solution, as in the solid state (see X-ray analysis below). The rotation about one imino−carbon amino nitrogen bond is hindered at room temperature, the rotation about the second imino carbon-amino nitrogen bond becomes hindered at low temperature. Thus the four methyl groups at each TMG substituent become nonequivalent.

2. In solution the palladium is coordinated via the phosphoryl oxygen and one imino nitrogen. The dimethylamino groups at the coordinating TMG-substituent are nonequivalent at room temperature, while the dimethylamino groups of the free TMG-substituent become nonequivalent at low temperature, due to the slow *cis*/*trans* isomerization at the CN double bond under these conditions. The second explanation is in good accordance with the IR data.

The reaction of **3** with $NiBr_2 \cdot 2$ DME led to a complex **11** where the metal is bonded to the phosphoryl oxygen and the imino nitrogen atom [Eq. (4)].



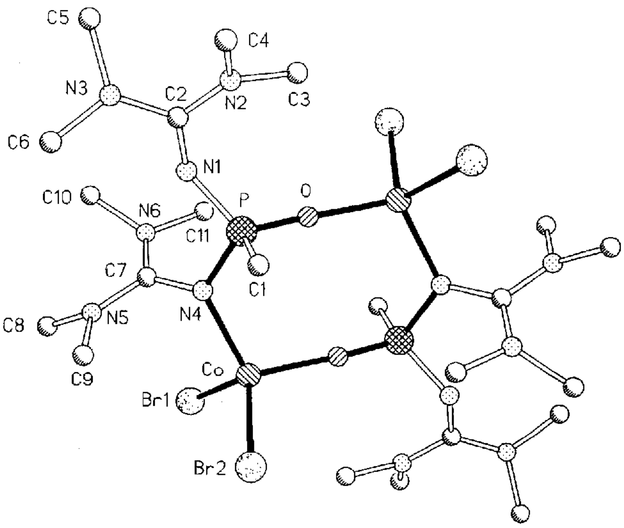
(4)

The CN vibration and the P(=O) vibration are shifted to lower wavenumbers, compared to the starting material. Whether **11** is monomeric or dimeric could not be established.

### Molecular Structure of $[(MeP(=O)(TMG)_2) \cdot CoBr_2]_2$ (5):

The central feature of the structure of compound **5** (Figure 2) is an eight-membered ring with alternating Co−N−P−O moieties. The molecule possesses crystallographic inversion symmetry. The geometry of the ring is best described as a chair[16] conformation. The phosphorus atom lies 34.5 pm above, the nitrogen N4 atom 30.4 pm below the plane formed by Co, O, Co′, and O′. The symmetry equivalent atoms P′ and N4′ necessarily lie on the opposite sides of this plane. The endocyclic torsion angles are −132.2° (N4−P−O−Co′), 91.7° (P−O−Co′−N4′), −36.7° (O′−Co−N4−P) and 51.9° (O−P−N4−Co).

Figure 2. Molecular structure of compound **5**. Hydrogen atoms and solvent have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Br(1)−Co 242.41(10), Br(2)−Co 239.31(11), Co−O#1 191.2(4), Co−N(4) 202.5(4), P−O 150.2(4), P−N(1) 160.3(5), P−N(4) 165.7(4), P−C(1) 177.7(7), N(4)−C(7) 136.3(7), O#1−Co−N(4) 108.4(2), O#1−Co−Br(2) 105.4(2), N(4)−Co−Br(2) 118.50(13), O#1−Co−Br(1) 112.1(2), N(4)−Co−Br(1) 101.10(12), Br(2)−Co−Br(1) 111.45(4), O−P−N(1) 117.5(3), O−P−N(4) 110.3(2), N(1)−P−N(4) 104.8(2), O−P−C(1) 108.2(3), N(1)−P−C(1) 110.3(3), N(4)−P−C(1) 105.2(3), P−O−Co#1 166.5(3), C(7)−N(4)−P 120.5(4), C(7)−N(4)−Co 116.6(3), P−N(4)−Co 121.4(2), Symmetry operator: #1 $-x+1,-y+2,-z+1$

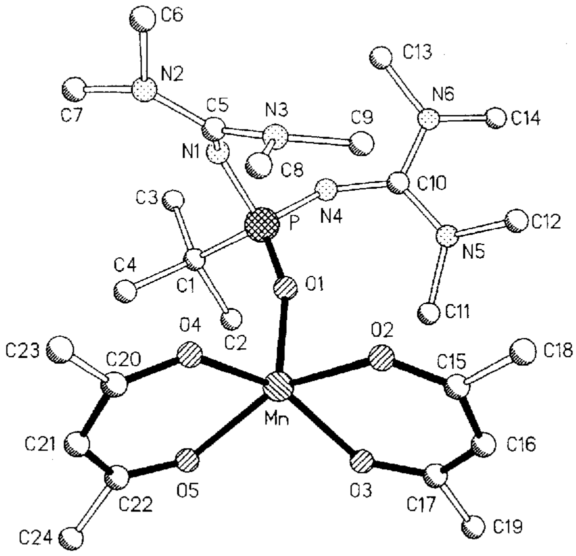
The cobalt atom displays slightly distorted tetrahedral coordination geometry, with the largest deviations from ideal angles for N4−Co−Br1 [101.1(1)°] and N4−Co−Br2 [118.5(1)°]. The Co−Br bond lengths differ by 3.1 pm.

The phosphorus atom occupies the centre of a distorted tetrahedron. The P(=O) bond length [150.2(4) pm] is not greatly lengthened from that in $PhP(=O)(TMG)_2$ [148.7(3) pm][2], despite the additional coordinative P(=O)−Co bond. The oxygen atom participates in the largest angles at phosphorus [O−P−N1 117.5(3)°, O−P−N4 110.3(2)°] because of the high steric demand of the P(=O) double bond. The remaining angles at phosphorus vary from 104.8(2)° (N1−P−N4) to 110.3(3)° (N1−P−C1).

Because of the coordinative N4−Co bond, the P−N4 bond [165.7(4) pm] is 5.4 pm longer than P−N1 [160.3(5) pm].

The N4−C7 bond [136.3(7) pm] is the longest imino N−C bond observed in TMG-substituted phosphorus compounds, whereas N5−C7 [133.8(7) pm] and N6−C7 [133.4(7) pm] are appreciably shorter, implying that N4−C7 displays less double bond character than N5−C7 or N6−C7. The bonding situation in **5** thus corresponds to structure **B** in Scheme 1, rather than to structure **A**. The nitrogen N1 shows a deviation from $sp^2$ towards sp hybridization, typical of TMG-substituted phosphorus compounds [P−N1−C2 131.4(4)°].

Figure 3. Molecular structure of compound **6**. Hydrogen atoms have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: P−O(1) 149.8(2), P−N(4) 162.0(2), P−N(1) 163.2(2), P−C(1) 182.5(3), Mn−O(1) 206.2(2), Mn−O(4) 208.7(2), Mn−O(5) 210.4(2), Mn−O(3) 211.6(2), Mn−O(2) 211.7(2), O(1)−P−N(4) 117.60(11), O(1)−P−N(1) 114.36(12), N(4)−P−N(1) 106.39(12), O(1)−P−C(1) 109.10(12), N(4)−P−C(1) 103.59(12), N(1)−P−C(1) 104.50(12), O(1)−Mn−O(4) 104.49(8), O(1)−Mn−O(5) 108.77(8), O(4)−Mn−O(5) 85.07(8), O(1)−Mn−O(3) 101.08(8), O(4)−Mn−O(3) 154.38(8), O(5)−Mn−O(3) 88.13(8), O(1)−Mn−O(2) 97.52(8), O(4)−Mn−O(2) 90.93(8), O(5)−Mn−O(2) 153.59(8), O(3)−Mn−O(2) 84.28(8), P−O(1)−Mn 160.83(12), C(15)−O(2)−Mn 129.5(2), C(17)−O(3)−Mn 129.6(2), C(20)−O(4)−Mn 129.4(2), C(22)−O(5)−Mn 129.1(2)

### Molecular Structure of [(*t*BuP(=O)(TMG)$_2$)·Mn(acac)$_2$](6):

The sum of the squared angle deviations from idealized values at manganese is a measure of the degree of distortion from trigonal bipyramidal (TBP) or square pyramidal (SP) geometry[17]. This sum amounts to 2392 (TBP) or 112 (SP), showing that the coordination geometry is nearly ideal square pyramidal (see Figure 3). The phosphoryl oxygen occupies the apical position, while the four oxygen atoms of the acetylacetonato ligands occupy the basal positions (average O···O intraligand 283.7 pm, O···O interligand 296.6 pm, mean deviation from the basal plane 0.7 pm); the Mn−O1 bond is within 3.1° of perpendicular to the base. The endocyclic angles at manganese [O2−Mn−O3 84.28(8)° and O4−Mn−O5 85.07(8)°] are smaller than the exocyclic angles [O2−Mn−O4 90.93(8)° and O3−Mn−O5 88.13(8)°].

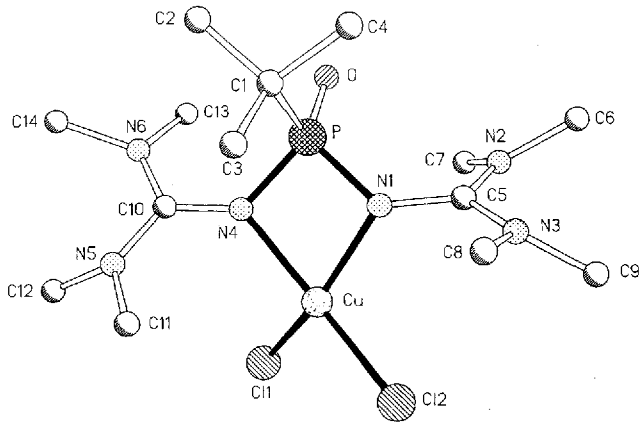
The phosphorus atom, as expected, displays somewhat distorted tetrahedral coordination geometry, the largest deviations from ideal angles being 117.60(11)° (O1−P−N4) and 103.6(1)° (C1−P−N4). As noted above for **5**, the P−O1 bond [149.8(2) pm] is not significantly longer than that in PhP(=O)(TMG)$_2$ [148.7(3) pm][2], despite the [P(=O)]-Mn coordination.

The P−N and the N−C bond lengths differ insignificantly from those in noncoordinating TMG-substituted $\sigma^4$-phosphorus compounds.

### Molecular Structure of [(*t*BuP(=O)(TMG)$_2$)·CuCl$_2$] (9) and [(*t*BuP(=O)(TMG)$_2$)·PdCl$_2$] (10):

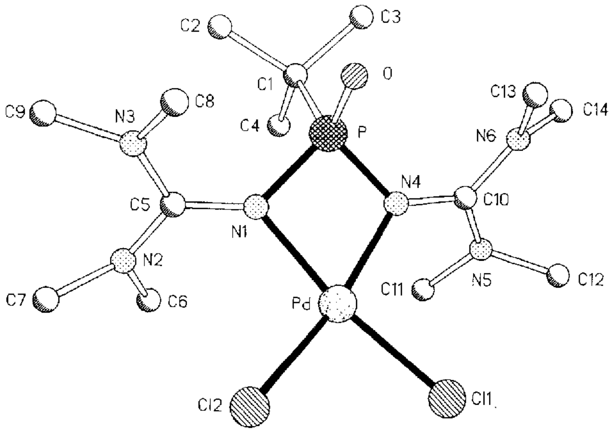
The single crystal X-ray structure determinations confirm the bidentate chelating mode of the *N,N'*-ligands in **9** and **10** (Figures 4 and 5). The characteristic structural element of both compounds is the four-membered ring, and both structures are thus discussed together. This ring is not planar; the fold angles between the planes M, N1, N4 and P, N1, N4 are 7.9° for **9** and 20.3° for **10**. The metal atom lies 22.2 pm (**9**) and 57.3 pm (**10**) outside the plane of P, N1, and N4.

Figure 4. Molecular structure of compound **9**. Hydrogen atoms have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Cu−N(4) 200.4(2), Cu−N(1) 200.6(3), Cu−Cl(2) 220.89(9), Cu−Cl(1) 223.24(10), P−O 147.5(2), P−N(1) 165.8(2), P−N(4) 167.5(3), P−C(1) 184.0(3), N(1)−C(5) 134.9(4), N(2)−C(5) 134.5(4), N(3)−C(5) 134.8(4), N(4)−C(10) 134.1(4), N(5)−C(10) 134.5(4), N(6)−C(10) 134.9(4), N(4)−Cu−N(1) 72.68(9), N(4)−Cu−Cl(2) 159.26(8), N(1)−Cu−Cl(2) 99.38(7), N(4)−Cu−Cl(1) 95.81(8), N(1)−Cu−Cl(1) 150.70(8), Cl(2)−Cu−Cl(1) 99.50(4), O−P−N(1) 119.38(14), O−P−N(4) 120.33(13), N(1)−P−N(4) 90.98(13), O−P−C(1) 108.4(2), N(1)−P−C(1) 107.84(14), N(4)−P−C(1) 108.4(2), C(5)−N(1)−P 128.9(2), C(5)−N(1)−Cu 125.6(2), P−N(1)−Cu 98.12(12), C(10)−N(4)−P 132.1(2), C(10)−N(4)−Cu 130.3(2), P−N(4)−Cu 97.60(12)

Figure 5. Molecular structure of compound **10**. Hydrogen atoms and solvent have been omitted for clarity[a]



[a] Selected bond lengths [pm] and angles [°]: Pd−N(1) 203.0(2), Pd−N(4) 204.5(2), Pd−Cl(1) 229.90(7), Pd−Cl(2) 230.77(9), P−O 147.5(2), P−N(4) 167.9(2), P−N(1) 168.0(2), P−C(1) 183.6(2), N(1)−C(5) 133.6(3), N(2)−C(5) 134.0(3), N(3)−C(5) 135.3(3), N(4)−C(10) 134.4(2), N(5)−C(10) 134.2(3), N(6)−C(10) 134.5(3), N(1)−Pd−N(4) 71.64(7), N(1)−Pd−Cl(1) 170.24(5), N(4)−Pd−Cl(1) 99.14(5), N(1)−Pd−Cl(2) 97.04(5), N(4)−Pd−Cl(2) 166.86(5), Cl(1)−Pd−Cl(2) 91.72(3), O−P−N(4) 117.37(8), O−P−N(1) 116.82(8), N(4)−P−N(1) 90.43(8), O−P−C(1) 110.29(9), N(4)−P−C(1) 110.40(9), N(1)−P−C(1) 110.10(9), C(5)−N(1)−P 132.53(14), C(5)−N(1)−Pd 129.70(13), P−N(1)−Pd 97.18(8), C(10)−N(4)−P 132.55(14), C(10)−N(4)−Pd 130.45(13), P−N(4)−Pd 96.65(8)

The coordination geometry is distorted square planar. In the d$^8$ Pd complex **10** the distortion from ideal planar geometry is much smaller than in the d$^9$ Cu complex **9**. The mean deviation from the plane formed by Pd, N1, N4, Cl1 and Cl2 in **10** is 4.1 pm, whereas this deviation is 30.2 pm in **9**. The coordination geometry around copper in compound **9** could thus also be described as distorted tetrahedral, but the angle between the planes Cl1−Cu−Cl2 and N1−Cu−N4 is only 31.9° (cf. 90° in an ideal tetrahedron). The endocyclic angles at the metal atom N1−M−N4 are, at 72.68(9)° for **9** and 71.64(7)° for **10**, necessarily smaller than 90° because of the restricted bite of the ligand. The exocyclic cis angles are larger than the ideal 90° [95.81(8)° (N4−Cu−Cl1) to 99.50(4)° (Cl2−Cu−Cl1) for **9** and 91.72(3)° (Cl1−Pd−Cl2) to 99.14(5)° (N4−Pd−Cl1) for **10**].

The coordination geometry at both phosphorus atoms is, because of the restrictions imposed by the four-membered ring, distorted tetrahedral. The smallest angle is, as expected, the endocyclic N1−P−N4 angle at 90.98(13)° for **9** and 90.43(8)° for **10**. The largest angle is, in both cases, O−P−N4 with 120.33(13)° (**9**), and 117.37(8)° (**10**). The P−O bond lengths are identical [147.5(2) pm], the P−C1

Table 2. Crystal data and refinement details for complexes **5**, **6**, **9**, and **10**

| Compound | **5** • 2 $CH_2Cl_2$ | **6** | **9** | **10** • $CH_3CN$ |
|---|---|---|---|---|
| Formula | $C_{24}H_{58}Br_4Cl_4Co_2N_{12}O_2P_2$ | $C_{24}H_{47}MnN_6O_5P$ | $C_{14}H_{33}Cl_2CuN_6OP$ | $C_{16}H_{36}Cl_2N_7OPPd$ |
| $M_r$ | 1188.06 | 585.59 | 466.87 | 550.79 |
| Crystal habit | blue prism | yellow tablet, cut | green prism | red prism, cut |
| Crystal size [mm] | 0.7 × 0.6 × 0.4 | 0.6 × 0.6 × 0.15 | 0.4 × 0.3 × 0.2 | 0.6 × 0.4 × 0.4 |
| Temperature [°C] | −100 | −130 | −100 | −130 |
| Crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| Space group | $P2_1/n$ | $P2_1/n$ | $P2_1/c$ | $P2_1/n$ |
| Cell constants | | | | |
| $a$ [pm] | 1080.8(2) | 996.5(3) | 911.35(10) | 937.6(2) |
| $b$ [pm] | 1054.7(2) | 1863.0(5) | 904.43(8) | 2028.0(4) |
| $c$ [pm] | 2036.6(3) | 1736.1(4) | 2733.9(2) | 1322.4(3) |
| $\beta$ [°] | 94.002(12) | 104.64(2) | 99.310(8) | 103.47(3) |
| $V$ [$nm^3$] | 2.3161(7) | 3.1183(14) | 2.2237(4) | 2.4452(8) |
| $Z$ | 2 | 4 | 4 | 4 |
| $D_x$ [$Mg\ m^{-3}$] | 1.704 | 1.247 | 1.395 | 1.496 |
| $\mu$ [$mm^{-1}$] | 4.504 | 0.515 | 1.309 | 1.064 |
| $F(000)$ | 1188 | 1252 | 980 | 1136 |
| $2\theta_{max}$[°] | 50 | 50 | 50 | 50 |
| No. of reflns.: | | | | |
| measured | 4233 | 5929 | 6690 | 7883 |
| independent | 4009 | 4485 | 3890 | 4315 |
| $R_{int}$ | 0.054 | 0.024 | 0.050 | 0.019 |
| Max. and min. trans. | 0.960 and 0.468 | | | 0.790 and 0.691 |
| $wR(F^2$, all refl.) | 0.121 | 0.096 | 0.054 | 0.052 |
| $R[F>4\sigma(F)]$ | 0.049 | 0.038 | 0.037 | 0.021 |
| No. of parameters | 235 | 349 | 237 | 266 |
| $S$ | 1.15 | 1.06 | 0.776 | 1.073 |
| max. $\Delta/\sigma$ | < 0.01 | < 0.01 | < 0.01 | < 0.01 |
| max. $\Delta\rho$ [$e\ nm^{-3}$] | 697 | 241 | 271 | 445 |

bond lengths differ insignificantly [184.0(3) pm for **9**, 183.6(2) pm for **10**]. One P−N bond of 9 [P−N1, 165.8(2) pm] is significantly shorter than the other P−N bonds [9: P−N4 167.5(3) pm; 10 P−N1 168.0(2) pm, P−N4 167.9(2) pm] for reasons that are not apparent.

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## Experimental Section

All operations were carried out in a nitrogen atmosphere, employing standard vacuum and inert gas techniques. The solvents were dried by standard procedures and were freshly distilled before use. − FT-IR spectra were recorded on a BIORAD 165 spectrometer. − The $^1H$ (200.1 MHz), $^{13}C$ (50.3 MHz), and $^{31}P$ (81.0 MHz) NMR spectra were recorded on a Bruker AC-200 spectrometer using, unless indicated otherwise, $CDCl_3$ as solvent. All shifts are reported relative to TMS ($^1H$, $^{13}C$) and $H_3PO_4$ ($^{31}P$). − The EI mass-spectra were recorded on a Finnigan MAT 8430 spectrometer at 70 eV. − The abbreviation "i.v." indicates a pressure of 0.1 mm Hg.

The following compounds were prepared according to published methods: Methylphosphonic bis($N',N',N'',N''$-tetramethylguanidinide) **1**[2], *tert*-butylphosphonic bis($N',N',N'',N''$-tetramethylguanidinide) **2**[2], cyclooctadiene palladium(II) chloride[18]. All the other reagents were commercially available.

*Reaction of Methylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**1**) *with* $NiBr_2 \cdot 2$ *DME. − Synthesis of the Nickel(II) Complex* **4**: To a solution of 1.00 g (3.44 mmol) of **1** in 20 ml of DME were added 1.37 g (3.43 mmol) of $NiBr_2 \cdot 2$ DME. A blue precipitate formed instantaneously. The mixture was stirred for 16 h at room temp., the precipitate was filtered off, washed three times with 5-ml portions of diethyl ether and dried i.v. Yield: 0.93 g (53%) blue solid, mp.: 171°C. − EI MS: *m/z* (%): 508 (<1) $[M]^+$, 429 (15) $[M - {}^{79}Br]^+$, 290 (100) $[MeP(=O)(TMG)_2]^+$, 106 (99) $[MeP(=O)NMe_2]^+$, 71 (46) $[HNCNMe_2]^+$. − IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) = 1624 (vs), 1545 (vs, br), 1475 (s) (CN); 1190 (m), 1159 (m, br) [P(=O)]. IR ($CH_2Cl_2$): $\tilde{\nu}$ ($cm^{-1}$) = 1617 (vs), 1561 (vs), 1534 (vs), 1471 (s) (CN); 1153 (vs) [P(=O)]. − $C_{11}H_{27}Br_2N_6NiOP$ (508.84): calcd.: C 25.97, H 5.35, N 16.52; found: C 25.29, H 5.52, N 16.14

*Reaction of Methylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**1**) *with* $CoBr_2 \cdot 2$ *DME. − Synthesis of the Cobalt(II) Complex* **5**: To a solution of 1.14 g (3.93 mmol) of **1** in 20 ml of DME were added 1.55 g (3.88 mmol) of $CoBr_2 \cdot 2$ DME. The mixture was stirred at room temp. for 16 h. The precipitate formed was filtered off, washed three times with 5 ml of diethyl ether and dried i.v. The solid was recrystallized from 5 ml of dichloromethane. Yield: 0.87 g (44%) blue crystals (bis-$CH_2Cl_2$ solvate), dec.: >120°C. − EI MS: *m/z* (%): 509 (2) $[(MeP(=O)(TMG)_2) \cdot CoBr_2]^+$, 428 (16) $[(MeP(=O)(TMG)_2) \cdot CoBr]^+$, 290 (46) $[MeP(=O)(TMG)_2]^+$, 106 (100) $[MeP(=O)NMe_2]^+$, 71 (28) $[HNCNMe_2]^+$. − IR (KBr): $\tilde{\nu}$ ($cm^{-1}$) = 1628 (s), 1561 (vs, br), 1522 (vs, br), 1463 (s) (CN); 1153 (vs), 1130 (vs). IR ($CH_2Cl_2$): $\tilde{\nu}$ ($cm^{-1}$) = 1625 (m), 1569 (vs), 1523 (vs), 1468 (s) (CN); 1162 (s), 1139 (s). − $C_{24}H_{58}Br_4Cl_4Co_2N_{12}O_2P_2$ ( = $C_{22}H_{54}Br_4Co_2N_{12}O_2P_2 \cdot 2\,CH_2Cl_2$) (1188.06): calcd.: C 24.26, H 4.92, N 14.15; found: C 24.10, H 5.02,N 14.78.

*Reaction of tert-Butylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**2**) *with Manganese(II) Acetylacetonate. − Synthesis of the Manganese(II) Complex* **6**: To a solution of 0.5 g (1.50 mmol) of **2** in 10 ml of toluene were added 0.38 g (1.50 mmol) of manganese(II) acetylacetonate. The mixture was stirred for 16 h at room temp., the solvent was removed i.v. and the residue recrystallized from a mixture of 3 ml of toluene and 7 ml of *n*-hexane.

Yield: 0.42 g (47.8%) yellow crystals, mp.: 163°C. – IR (KBr): ṽ (cm$^{-1}$) = 1606 (vs, br) (CO overlapping with CN); 1552 (s), 1523 (s), 1474 (s) (CN); 1138 (s) 1125 (s) [P(=O)]. IR ($CH_2Cl_2$): ṽ (cm$^{-1}$) = 1592 (vs, br) (CO overlapping with CN); 1560 (s), 1543 (s), 1517 (vs), 1471 (s) (CN); 1138 (s) 1118 (s) [P(=O)]. – $C_{24}H_{47}MnN_6O_5P$ (585.59): calcd.: C 49.23, H 8.09, N 14.35; found: C 49.17, H 8.24, N 14.17.

*Reaction of tert-Butylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**2**) *with $NiBr_2 \cdot 2$ DME. – Synthesis of the Nickel(II) Complex* **7**: To a solution of 0.5 g (1.50 mmol) of **2** in 20 ml of $CH_2Cl_2$ were added 0.6 g (1.50 mmol) of $NiBr_2 \cdot 2$ DME. The mixture changed color to violet instantaneously, and a solid precipitated. After 16 h of stirring at room temp. the solid was filtered off. The product was recrystallized from a mixture of 5 ml of $CH_2Cl_2$ and 5 ml of diethyl ether. Yield: 0.39 g (47.2%) blue solid, mp.: 189°C (dec.). – IR (KBr): ṽ (cm$^{-1}$) = 1624 (vs), 1571 (vs), 1531 (vs), 1468 (s) (CN); 1155 (s) [P(=O)]. IR ($CH_2Cl_2$): ṽ (cm$^{-1}$) = 1610 (m), 1521 (vs), 1422 (vs, br) (CN); 1104 (m), [P(=O)]. – $C_{14}H_{33}Br_2N_6NiOP$ (550.92): calcd.: C 30.52, H 6.04, N 15.25; found: C 30.68, H 6.43, N 14.68.

*Reaction of tert-Butylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**2**) *with $CoBr_2.2$ DME. – Synthesis of the Cobalt(II) Complex* **8**: To a solution of 0.24 g (0.72 mmol) of **2** in 5 ml of acetonitrile was added a solution of 0.22 g (0.71 mmol) of $CoBr_2 \cdot$ 2 DME in 10 ml of acetonitrile. The mixture was stirred for 16 h at room temp. After addition of 1 ml of *n*-hexane the mixture was held for 16 h at –20°C. The product thus formed was filtered off, and dried i.v. Yield: 0.30 g (76.7%), blue solid, mp.: 210°C. – IR (KBr): ṽ (cm$^{-1}$) = 1623 (vs), 1564 (vs), 1529 (vs), 1467 (s) (CN); 1170 (s), 1157 (s) [P(=O)]. – $C_{14}H_{33}Br_2CoN_6NiOP$ (551.16): calcd.: C 30.51, H 6.03, N 15.25; found: C 31.08, H 6.29, N 15.29.

*Reaction of tert-Butylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**2**) *with $CuCl_2$. – Synthesis of the Copper(II) Complex* **9**: To a suspension of 0.3 g (2.23 mmol) of copper(II) chloride in 20 ml of $CH_2Cl_2$ were added 0.64 g (1.93 mmol) of **2**. The mixture was stirred for 16 h at room temp. Solid impurities were filtered off, and half of the solvent was removed i. v. The solution was cooled to –20°C for 7 d, then the crystals formed were filtered off and dried i.v. Yield: 0.39 g (43.3%), green crystals, mp.: 145°C. – IR (KBr): ṽ (cm$^{-1}$) = 1618 (w), 1565 (s) 1519 (vs), 1468 (s), (CN), 1144 (w) [P(=O)]. IR ($CDCl_3$): ṽ (cm$^{-1}$) = 1569 (vs), 1517 (vs), 1446 (m), (CN); 1157 (w) 1141 (m) [P(=O)]. – $C_{14}H_{33}Cl_2CuN_6OP$ (466.87): calcd.: C 36.02, H 7.12, N 18.00; found: C 37.19, H 7.58, N 16.17.

*Reaction of tert-Butylphosphonic Bis(N',N',N'',N''-tetramethylguanidinide)* (**2**) *with Cyclooctadiene Palladium(II) Chloride. – Synthesis of the Palladium(II) Complex* **10**: A solution of 0.43 g (1.29 mmol) of **2** in 20 ml of toluene was added to a solution of 0.39 g (1.37 mmol) of cyclooctadiene palladium(II) chloride in 40 ml of a 1:1 mixture of toluene and acetonitrile. The mixture was stirred for 16 h at room temp. and was then held for 3 d at –20°C. The precipitate thus formed was filtered off and dried i.v. Yield: 0.42 g (63.9%), reddish-brown crystals, mp. 168°C. – $^1H$ NMR: $\delta = 1.05$ [d, $^3J(PH) = 16.07$, 9 H, $PC(CH_3)_3$]; 2.90 [s, 6 H, $N(CH_3)$]; 3.03 [s, br, 12 H, $N(CH_3)_2$]; 3.35 [s, 6 H, $N(CH_3)_2$]. – $^{13}C$ NMR: $\delta = 25.64$ [s, $PC(CH_3)_3$]; 37.72 [d, $^1J(PC) = 102.50$, $PC(CH_3)_3$]; 41.15 [s, $N(CH_3)_2$]; 41.36 [s, $N(CH_3)_2$]; 42.27 [s, $N(CH_3)_2$]; 166.22 [d, $^2J(PC) = 4.36$, N=*C*<]. – $^{31}P$ NMR: $\delta = 53.16$ (s). – EI MS: *m*/*z* (%): 510 (<1) $[M]^+$, 332 (15) $[tBuP(=O)(TMG)_2]^+$, 205 (89) $[Me_2NP(=O)(TMG)]^+$, 162 (100) $[HP(=O)(TMG)]^+$, 135 (76) $[(Me_2N)_2P(=O)]^+$, 92 (56) $[HP(=O)NMe_2]^+$, 71 (43) $[HNCNMe_2]^+$, 57 (10) $[tBu]^+$, 44 (21) $[NMe_2]^+$. – IR ($CH_2Cl_2$): ṽ (cm$^{-1}$) = 1563 (s), 1519 (vs), 1469 (s) (CN); 1113 (m) [P(=O)]. IR (KBr): ṽ (cm$^{-1}$) = 1619 (s), 1567 (vs), 1519 (vs), 1475 (s) (CN); 1160 (m), 1145 (m) [P(=O)]. – $C_{14}H_{33}Cl_2N_6OPPd$ (509.75): calcd.: C 32.99, H 6.53, N 16.49; found: C 31.85, H 6.11, N 15.76.

*Reaction of Diphenylphosphinic N',N',N'',N''-Tetramethylguanidinide* (**3**) *with $NiBr_2 \cdot 2$ DME. – Synthesis of the Nickel(II) Complex* **11**: To a solution of 0.78 g (2.47 mmol) of **3** in 20 ml of DME were added 1.04 g (2.60 mmol) of $NiBr_2 \cdot 2$ DME. The mixture was stirred for 3 d at room temp. Then the precipitate was filtered off, washed three times with 5 ml of diethyl ether and dried i.v. Yield: 0.70 g (53%), blue solid, mp. 198°C (dec.). – IR (KBr): ṽ (cm$^{-1}$) = 1625 (s), 1575 (vs), 1550 (vs), 1525 (s), 1470 (s), 1110 (s, br) [P(=O)]. IR ($CH_2Cl_2$): ṽ (cm$^{-1}$) = 1625 (vs), 1593 (s), 1579 (s), 1538 (vs), 1470 (s), 1125 (s), 1108 (m) [P(=O)]. – $C_{17}H_{22}Br_2N_3NiOP$ (533.85): calcd.: C 38.25, H 4.15, N 7.87; found: C 39.87, H 4.76, N 7.54.

*X-ray Crystal Structures. – Data Collection and Reduction:* Crystals were mounted on glass fibres in inert oil and transferred to the cold gas stream of the diffractometer (Siemens P4 for **5** and **9**, Stoe STADI-4 for **6** and **10**, both with LT–2 low temperature attachment). The orientation matrices for **5** and **9** were refined from setting angles of 64 (63) reflections in the 2θ range 5-25°. The cell constants for **6** and **10** were refined from ±ω angles of 58 (56) reflections in the 2θ range 20-23° (monochromated Mo-$K_\alpha$ radiation). – *Structure Solution and Refinement:* The structures were solved by direct methods and refined anisotropically on $F^2$ (program system: SHELXL-93, G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model or rigid methyl groups. The weighting scheme was of the form $w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP]$, with $P = (F_o^2 + 2F_c^2)/3$.

Full details of the crystal structure determinations (except structure factors) have been deposited under the number CCDC-100120 at the Cambridge Crystallographic Data Centre. Copies may be obtained free of charge from: The Director, CCDC, 12 Union Road, GB-Cambridge CB2 1EZ (Telefax: int. + 1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk.

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☆ Dedicated to Professor *Roald Hoffmann* on the occasion of his 60th birthday.

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