DOI: 10.1002/ejic.200600679

Synthesis and Crystal Structure of Three Carborane Complexes, [M{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$] (M = Cu, Zn) and [Ni(thf){7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$]·thf, and Two Carborane Compounds, 1-$(OPPh_2)$-2-(PPh_2)-1,2-$C_2B_{10}H_{10}$ and H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$]·0.25C_2H_5OH

Jianmin Dou,*[a] Daopeng Zhang,[a] Dacheng Li,[a] and Daqi Wang[a]

Keywords: Cu complexes / Zn complexes / Ni complexes / Carborane complexes / Oxidation / Degradation

Three new carborane complexes containing the bis(phosphoryl)-*nido*-carborane ligand, [Cu{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$] (**1**), [Zn{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$] (**2**), and [Ni(thf){7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$]·thf (**3**), were synthesized by the reactions of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with $CuCl_2$·$2H_2O$, $ZnCl_2$, and $NiCl_2$·$6H_2O$, respectively, in ethanol in air. Two other compounds, 1-$(OPPh_2)$-2-(PPh_2)-1,2-$C_2B_{10}H_{10}$ (**4**) and H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$]·0.25C_2H_5OH (**5**), were also obtained through the oxidation of the *closo* ligand in air. All new compounds were characterized by elemental analysis, FT-IR, ^1H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction. In complexes **1** and **2**, the metal atoms are coordinated to the four oxygen atoms of the two bidentate bis(phosphoryl) ligands [7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}]^-$ and adopt a square-planar geometry. For complex **3**, the molecular structure reveals that the geometry at the nickel atom is square-pyramidal, with four oxygen atoms from the four $OPPh_2$ groups and one additional one from a thf molecule.

Introduction

The synthesis and properties of dicarba-*closo*-dodecaborane, 1,2-$C_2B_{10}H_{12}$, and the -*nido*-species, $[7,8\text{-}C_2B_9H_{12}]^-$, were first reported in the early 1960s.[1–4] Since then, both *closo*- and *nido*-carboranes have proven to be excellent bulky and stable building blocks that allow for the synthesis of a wide range of carborane derivatives and have shown a lot of potential in various applications, including medicinal chemistry, especially Boron Neutron Capture Therapy (BNCT) of tumors, solvent extraction, materials science, catalysis, host–guest chemistry, and coordination chemistry,[5–18] which made carborane chemistry all along an interesting growth area.

In recent years, the 1,2-bis(phosphanyl) derivative of *o*-carborane, 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$, and its partially degraded anion, *nido*-[7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$, have attracted much attention because of the coordinating capabilities of the two phosphorus atoms. Up to now, complexes containing the 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ and *nido*-[7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}]^-$ ligands and Cu^I,[19] Ru^{II},[20] Ag^I,[21,22] Au^I,[23–29] Pd^{II},[30–33] and Rh[34] have been reported and characterized by single-crystal X-ray diffraction. We are also interested in these kinds of complexes and have reported on the synthesis and crystal structures of Cu^I,[35] Au^I,[36] Ni^{II}, Pd^{II}, and Pt^{II} complexes,[37] and we investigated the effect of different reaction conditions on the products. When the reaction of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with $NiCl_2$·$6H_2O$ was carried out in air, a new complex containing one bis(phosphanyl)-*nido*-carborane ligand and one unsymmetrical semi-oxidized (phosphoryl)(phosphanyl) ligand with the formula [Ni{7-$(OPPh_2)$-8-(PPh_2)-7,8-$C_2B_9H_{10}$}{7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$}] were obtained.[38]

This result indicates that the environment has an obvious influence on the reaction. To continue with the reactions of the bis(phosphanyl)-*closo*-carborane ligand with different metal ions without the protection of inert gases, we investigated three reactions of the bis(phosphanyl)-*closo*-carborane ligand with $CuCl_2$·$2H_2O$, $ZnCl_2$, and $NiCl_2$·$6H_2O$ in air and obtained three new carborane complexes containing the *nido*-[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}]^-$ anion, [Cu{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$] (**1**), [Zn{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$] (**2**), and [Ni(thf){7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}\}_2$]·thf (**3**). To the best of our knowledge, there has been no report on the metal ion complex of the bis(phosphoryl)carborane ligand [7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}]^-$, which has been reported by Teixidor's group.[39] In addition, the oxidation and degradation process of the free bis(phosphanyl)-*closo*-carborane ligand, 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$, in air was studied for the first time.

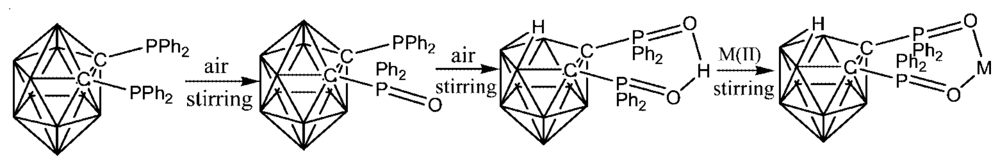
Results and Discussion

Synthesis and Spectral Characterization

In our recent work[38] we found that, with or without the protection of N_2, results of the reactions of the bis(phos-

---

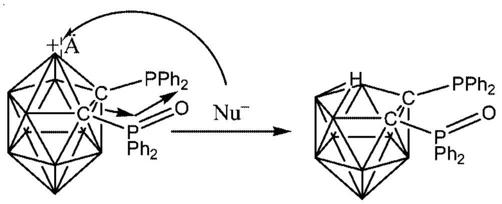
[a] Department of Chemistry, Liaocheng University,
Liaocheng 252059, P. R. China
E-mail: jmdou@lcu.edu.cn



Scheme 1. The rational reaction process for the preparation of the complexes **1** to **3** [M = Cu(**1**), Zn(**2**), Ni(**3**)].

phanyl)-*closo*-carborane ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with some Ni^{II} compounds were very different, indicating that the reaction environment could play an important role during the reaction process. By stirring the mixture of $NiCl_2$·$6H_2O$ and the *closo* ligand for 6 h in ethanol at room temperature, we obtained the complex [Ni{7-$(OPPh_2)$-8-(PPh_2)-7,8-$C_2B_9H_{10}$}{7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$}]. However, when the stirring time was increased to 12 h in air, both P atoms of the initial bis(phosphanyl)-*closo*-carborane ligand were oxidized, and a new complex containing the bis(phosphoryl)-*nido*-carborane ligand [7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$]$^-$ was obtained. This result showed that both of the P atoms could be oxidized, but the oxidation of the two P atoms did not take place at the same time. Subsequently, the reactions between $CuCl_2$·$2H_2O$, $ZnCl_2$, and the bis(phosphanyl)-*closo*-carborane ligand in a molar ratio of 1:1 in ethanol were carried out. After the stirring process was continued for 6 h in air at room temperature, two complexes with the formula [Cu{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$}$_2$] and [Zn{7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$}$_2$] were obtained. As indicated by their similar crystal data, listed in Table 2, these two complexes are isostructural. The difference in the reaction times of the above three reactions implied that the metal atom itself could also affect the reaction process. The rational reaction process for the preparation of these three complexes is shown in Scheme 1.

With an aim to find out whether the phosphorus atom of the *closo* ligand could be oxidized and the carborane skeleton could be converted from *closo* to *nido* by oxygen without the presence of the metal ion, we studied another experiment. The free *closo* ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ was suspended in ethanol, and the mixture was stirred for 8 h, while air was continually and slowly bubbled into the reaction mixture. Contrary to our expectation, a compound containing the *closo*-carborane skeleton, but not the *nido* form, with the formula 1-$(OPPh_2)$-2-(PPh_2)-1,2-$C_2B_{10}H_{10}$ (**4**), was obtained, in which also only one phosphorus atom was oxidized. A marked difference from the complex [Ni{7-$(OPPh_2)$-8-(PPh_2)-7,8-$C_2B_9H_{10}$}{7,8-$(PPh_2)_2$-7,8-$C_2B_9H_{10}$}] was that the *closo*-carborane skeleton in this compound was maintained. Following the procedure for the synthesis of compound **4**, the mixture was stirred for 18 h, and a compound with the formula H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$]·$0.25C_2H_5OH$ (**5**) was obtained. This compound is very similar to another neutral compound H[7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}$], which has been obtained with very high yield (94–97%) by oxidation of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with H_2O_2 in thf at 0 °C.[39] The aim of oxidizing another phosphorus atom of the semi-oxidized (phosphoryl)(phosphanyl)-*closo*-carborane ligand was fulfilled, but the *closo*-carborane skeleton degraded. The proposed mechanism for the partial degradation of the semi-oxidized (phosphoryl)(phosphanyl)-*closo*-carborane ligand, which is similar to the degradation of 1-SR-2-PPh_2-1,2-$C_2B_{10}H_{10}$,[40] is shown in Scheme 2.



Scheme 2. Proposed mechanism for the partial degradation of compound **4**.

The C_{cage}–P=O group pulls electron density off the cage, and its electron-withdrawing capacity favors the removal of the B(3) atom (the boron atom adjacent to the carbon atom), especially under the attack of the nucleophilic solvent. According to these results, we think that compound **4** is an intermediate formed during the oxidation and degradation process of the *closo* ligand. This process may be accomplished in three steps which occur in the following order: (1) the oxidation of one phosphorus atom, (2) the degradation of the *closo*-carborane skeleton, and (3) the oxidation of another phosphorus atom.

All the three carborane complexes and two bis(phosphoryl)carborane compounds were characterized by FT-IR, ^1H and ^{13}C NMR spectroscopy. The IR spectra of compounds **1**–**5** are very similar to each other and exhibit absorptions characteristic of terminal B–H vibrations at 2510–2550 cm^{-1}, which fall in the normal range of B–H vibration from 2450 to 2625 cm^{-1}.[41] The absorption at about 3100 cm^{-1} may be attributed to the ν_{C-H} stretching vibration of the benzene rings. Several peaks are found between 1689 and 1400 cm^{-1}, which may be assigned to the $\nu_{C=C}$ stretching vibration. The peak at ca. 1400 cm^{-1} is the in-plane deformation mode of the benzene ring, and the peak at ca. 1100 cm^{-1} is the absorption of $\nu_{C(aryl)-P}$, which is a little shifted, in keeping with phosphorus coordination to the carborane moiety. The strong absorption at about 1250–1260 cm^{-1} in all the compounds may be attributed to the P=O bond. The absorption at 700–750 cm^{-1} shows the existence of the deformation cage. The ^1H NMR spectra (400.15 MHz) of these carborane compounds display a common resonance pattern at about 7.1–7.6 ppm, which can be attributed to the aryl-H of the PPh_2 groups. The resonance at ca. –2.2 ppm is the bridging H atom of B–H–B in the three complexes.[19] In the ^{13}C NMR spectra (100.63 MHz), the resonance at about 132–139 ppm can be assigned to the benzene-ring C atoms, and that at ca. $\delta = 77$ can be attributed to the carbon atom of carborane cage.[42]

X-ray Crystallographic Study

The molecular structures of the new compounds **1**–**5** are shown in Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5 respectively, and the selected bond lengths and angles of the three carborane complexes are listed in Table 1. A common feature of the complexes **1**–**3** is that they all contain the same bis(phosphoryl)-*nido*-carborane ligand [7,8-$(OPPh_2)_2$-7,8-$C_2B_9H_{10}]^-$. The average P–C_{cage} distances in the three metal complexes are 1.804, 1.809, 1.816 Å, respectively, which are slightly shorter than the mean value 1.87 Å in $[NH_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$,[43] indicating that in these *nido* species the oxidation of the P atom has an influence on the P–C_{cage} bond length. This conclusion could also be proved by the corresponding bond lengths in $[Ni\{7\text{-}(OPPh_2)\text{-}8\text{-}(PPh_2)\text{-}7,8\text{-}C_2B_9H_{10}\}\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]$[38] [P–C(7): 1.769(7), P–C(8): 1.867(7) Å]. The C(7)–C(8) bond lengths, ranging from 1.593(7) to 1.606(8) Å in **1**–**3** are in good agreement with the corresponding distance 1.61(2) Å in $[NH_4][7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]$,[43] but obviously shorter than 1.697(4) Å in the *closo* ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$.[44] The angles P(1)–C(7)–C(8) and P(2)–C(8)–C(7) in complexes **1**–**3** [120.4(3)–

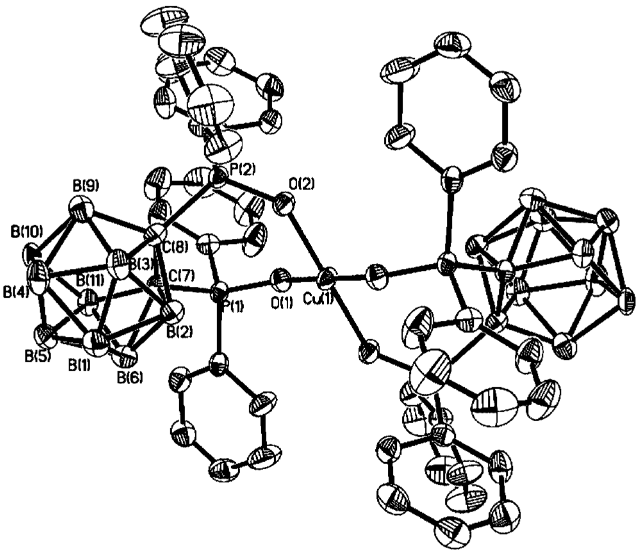


Figure 1. The crystal structure of complex **1**. The H atoms were omitted for clarity.

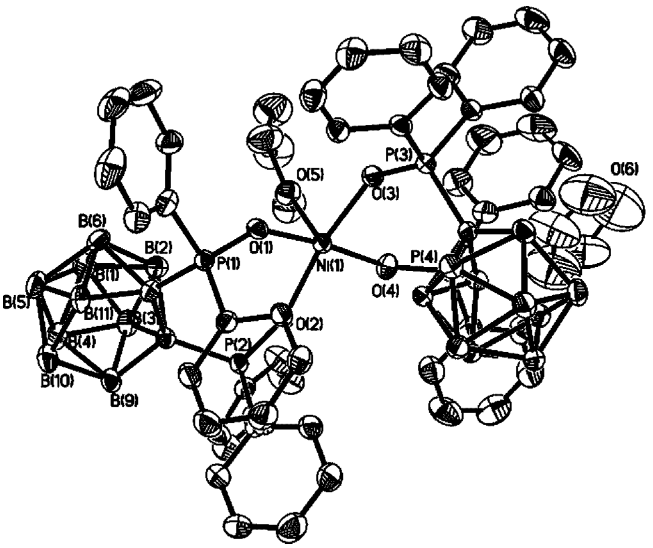


Figure 3. The crystal structure of complex **3**. The H atoms were omitted for clarity.

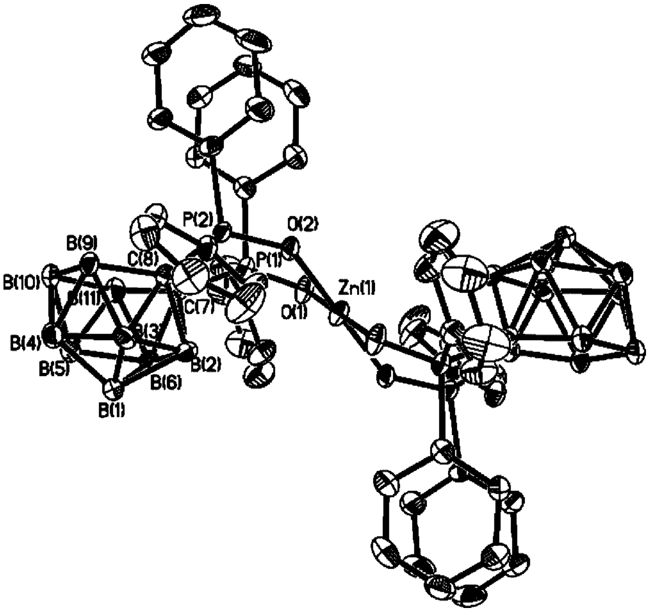


Figure 2. The crystal structure of complex **2**. The H atoms were omitted for clarity.

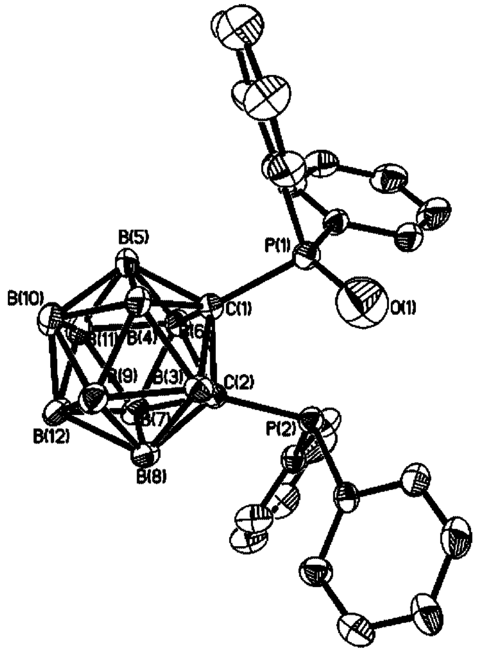


Figure 4. The crystal structure of compound **4**. The H atoms were omitted for clarity.

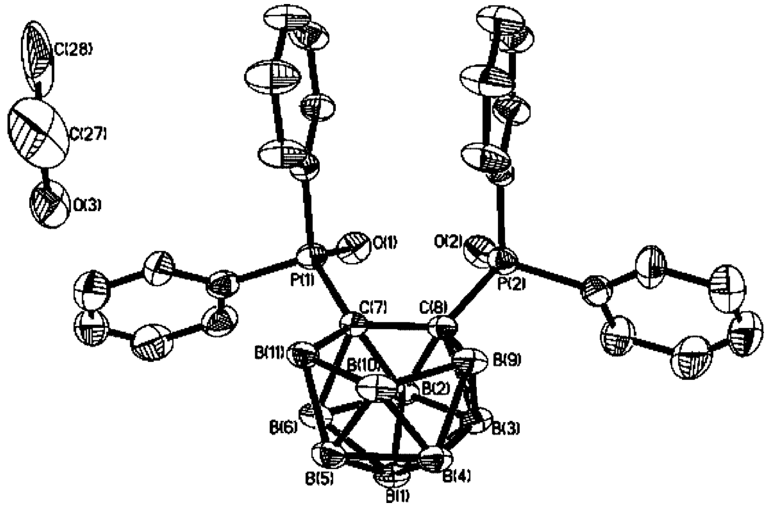


Figure 5. The crystal structure of compound **5**. The H atoms were omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**, **2**, and **3**.[a]

1		**2**		**3**	
Cu(1)–O(1)	1.913(4)	Zn(1)–O(1)	1.904(4)	Ni(1)–O(1)	2.011(4)
Cu(1)–O(2)	1.900(4)	Zn(1)–O(2)	1.931(3)	Ni(1)–O(2)	1.987(4)
P(1)–O(1)	1.525(4)	P(1)–O(1)	1.495(4)	P(1)–O(1)	1.501(4)
P(2)–O(2)	1.505(4)	P(2)–O(2)	1.506(4)	P(2)–O(2)	1.493(4)
P(1)–C(7)	1.804(6)	P(1)–C(7)	1.822(5)	P(1)–C(7)	1.801(6)
P(2)–C(8)	1.814(7)	P(2)–C(8)	1.810(6)	P(2)–C(8)	1.813(5)
C(7)–C(8)	1.606(8)	C(7)–C(8)	1.594(7)	C(7)–C(8)	1.608(8)
C(7)–B(11)	1.663(9)	C(7)–B(11)	1.654(8)	C(7)–B(11)	1.646(9)
C(8)–B(9)	1.652(10)	C(8)–B(9)	1.634(8)	C(8)–B(9)	1.631(9)
C(7)–B(2)	1.759(9)	C(7)–B(2)	1.720(8)	C(7)–B(2)	1.753(9)
C(8)–B(3)	1.742(2)	C(8)–B(3)	1.740(8)	C(8)–B(3)	1.738(8)
O(1)–Cu(1)–O(2)	90.03(19)	O(1)–Zn(1)–O(2)	90.63(16)	O(1)–Ni(1)–O(2)	86.28(16)
O(1)–Cu(1)–O(1)#1	180.0(1)	O(1)–Zn(1)–O(1)#1	180.0(1)	O(1)–Ni(1)–O(4)	170.68(15)
P(1)–O(1)–Cu(1)	143.0(3)	P(1)–O(1)–Zn(1)	137.1(2)	P(1)–O(1)–Ni(1)	141.1(2)
P(2)–O(2)–Cu(1)	136.9(3)	P(2)–O(2)–Zn(1)	141.6(2)	P(2)–O(2)–Ni(1)	161.6(2)
O(1)–P(1)–C(7)	112.8(3)	O(1)–P(1)–C(7)	115.6(2)	O(1)–P(1)–C(7)	117.1(2)
O(2)–P(2)–C(8)	115.7(3)	O(2)–P(2)–C(8)	113.5(2)	O(2)–P(2)–C(8)	113.3(2)
C(7)–C(8)–P(2)	122.8(4)	C(7)–C(8)–P(2)	122.3(4)	C(7)–C(8)–P(2)	120.4(4)
C(8)–C(7)–P(1)	122.4(4)	C(8)–C(7)–P(1)	122.8(4)	C(8)–C(7)–P(1)	124.6(4)

[a] Symmetry transformations used to generate equivalent atoms: complex **1**: $-x+1$, $-y+1$, $-z$; complex **2**: $-x+1$, $-y+1$, $-z+2$.

124.6(3)°] are slightly larger than the corresponding angles [113.4(9) and 116.5(9)°] in [NH_4][7,8-(PPh_2)$_2$-7,8-$C_2B_9H_{10}$]. The P=O bond lengths are within a narrow range from 1.488(4) to 1.525(4) Å, which is basically consistent with the average values 1.528 Å in H[7,8-($OPPh_2$)$_2$-7,8-$C_2B_9H_{10}$], 1.483(5) Å in [Ni{7-($OPPh_2$)-8-(PPh_2)-7,8-$C_2B_9H_{10}$}{7,8-(PPh_2)$_2$-7,8-$C_2B_9H_{10}$}], and 1.486(6) Å in 1-($OPPh_2$)-2-(PPh_2)-1,2-$C_2B_{10}H_{10}$.

The structures of complexes **1** and **2** are symmetrical, with the M^{II} (M = Cu, Zn) atom as the symmetry center. Symmetry transformations used to generate equivalent atoms are $-x+1$, $-y+1$, $-z$ for **1** and $-x+1$, $-y+1$, $-z+2$ for **2**. The bis(phosphoryl) ligand [7,8-($OPPh_2$)$_2$-7,8-$C_2B_9H_{10}$]$^-$ is coordinated in a bidentate fashion through the O atoms to the M^{II} ion. The M^{II} and four oxygen atoms can form a perfect plane in complexes **1** and **2**, and the O(1), M, O(1)# and O(2), M, O(2)# (# denotes the equivalent atom generated by symmetry) are in an ideal line. The two bis(phosphoryl)carborane moieties are located at two opposite sides of this plane with a *trans* conformation. The average M–O distances are 1.907 and 1.919 Å in complexes **1** and **2**, respectively, which are slightly shorter than the corresponding values of 2.113 Å in [Cu(dppf)(odppf)]$^{+}$[45] and 1.968 Å in $ZnBr_2(OPPh_3)_2$.[46] The O–M–O angles in these two complexes are almost equal to each other with a value of about 90°. As M, C(7), and C(8) are all out of the plane O(1)P(1)P(2)O(2) in the same orientation, a boat conformation between the seven atoms of the chelating ring between the ligand and the metal is formed, in which the O(1)P(1)P(2)O(2) plane can be used as the bottom of the boat.

As shown in Figure 3, the crystal structure of the complex **3** is a little different from the above two complexes. Although the two bis(phosphoryl) ligands are still coordinated in a bidentate fashion to the Ni atom, and a plane is also formed by the four oxygen atoms, the coordination sphere of the Ni atom has been changed by one tetrahydrofuran molecule whose oxygen atom is coordinated to the Ni^{II} atom. The Ni atom is therefore out of the plane by 0.1884 Å, positioned towards the fifth Ni–O bond. Therefore, the coordination sphere of the metal atom should be characterized as a square pyramid, different from the square-planar coordination mode in complexes **1** and **2**. Another difference is the P–O–M angles in the seven-membered ring formed by two P, two O, two C_{cage} atoms and the Ni atom. These two angles in complex **3** are 141.4(2) and 161.7(2)°, respectively, whereas there is no noticeable difference between these two angles in complexes **1** and **2**. In complex **3**, the five Ni–O bond lengths are almost equal to each other within a narrow range 1.992(4)–2.011(3) Å, which is obviously shorter than the average value of 2.112 Å in $[Ni\{CH_2(OPPh_2)_2\}_3(ClO_4)_2]\cdot CH_3OH$.[47]

Conclusions

In this work, we reported two free compounds with a *closo*- or *nido*-carborane skeleton and three new metal–carborane complexes containing the bis(phosphoryl)-*nido*-carborane ligand, which were obtained by the reactions of the *closo* ligand 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ with some inorganic metal compounds in air. The obtainment of the two free bis(phosphoryl)carborane compounds could give us some information for understanding the oxidation and degradation of the *closo* ligand in air. The results obtained from this paper and our recent work[38] indicated that the oxidation process occurs before the partial degradation, and that the oxidation of the two phosphorus atoms is not synchronous.

Experimental Section

Materials and Measurements: All reactions and subsequent manipulations were carried out in air. 1,2-bis(diphenylphosphanyl)-1,2-dicarba-*closo*-dodecaborane(10) was prepared according to the literature procedure.[48] All chemicals were purchased and used as received. Infrared spectra were recorded in the range 400–4000 cm^{-1} from KBr pellets with a Nicolet-460 FT-IR spectrophotometer. Elemental analysis (C, H) was carried out with a Perkin–Elmer 2400 II elemental analyzer. The ^1H and ^{13}C-NMR were recorded with a Varian Mercury 400 spectrometer in $CDCl_3$ solution, with tetramethylsilane (TMS) as the internal standard, at 400.15 and 100.63 MHz, respectively. The ^{13}C spectra are broadband proton decoupled. The chemical shifts are reported in parts per million with respect to the references and are stated relative to external TMS for ^1H and ^{13}C NMR spectroscopy.

Synthetic Procedures

Synthesis of $[Cu\{7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ (1): To a suspension of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) in ethanol (10 mL, 95%) was added $CuCl_2\cdot 2H_2O$ (17.1 mg, 0.10 mmol). The mixture was stirred for about 6 h in air at room temperature. The blue solid formed was filtered off and dried in vacuo (20.9 mg, 36.96%). M.p. 215–216 °C. A suitable crystal for X-ray diffraction was grown from a dichloromethane/*n*-hexane solution. FT-IR: $\tilde{\nu}_{KBr}$ = 3090 (m), 2550 (m), 1670 (s), 1400 (m), 1255 (s), 1100 (m), 756 (m), 660 (s), 530 (m) cm^{-1}. ^1H NMR (400.15 MHz, $CDCl_3$): δ = 7.128–7.400 (40 H, Aryl-H); –2.312 (2 H, B–H–B) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 25.212–135.856 (48 C, Aryl-C), 77.101 (4 C, C_{cage}) ppm. $C_{52}H_{60}B_{18}CuO_4P_4$ (1131.00): calcd. C 55.22, H 5.35; found C 55.30, H 5.38.

Synthesis of $[Zn\{7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ (2): $ZnCl_2$ (13.6 mg, 0.10 mmol) and 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) were mixed in ethanol (10 mL, 95%). The stirring process was continued for about 6 h in air at room temperature. The white solid was filtered off and dried in vacuo (19.7 mg, 34.78%). M.p. > 300 °C (dec.). A suitable crystal for X-ray diffraction was obtained from a dichloromethane solution after partial evaporation of the solvent. FT-IR: $\tilde{\nu}_{KBr}$ = 3100 (m), 2557 (m), 1625 (s), 1454 (m), 1263 (s), 1120 (m), 735 (m), 690 (s), 510 (m) cm^{-1}. ^1H NMR (400.15 MHz, $CDCl_3$): δ = 7.284–7.563 (40 H, Aryl-H), –2.301 (2 H, B–H–B) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 23.421–136.000 (48 C, Aryl-C), 76.863 (4 C, C_{cage}) ppm. $C_{52}H_{60}B_{18}O_4P_4Zn$ (1132.83): calcd. C 55.13, H 5.34; found C 55.10, H 5.30.

Synthesis of $[Ni\{7\text{-}(OPPh_2)\text{-}8\text{-}(PPh_2)\text{-}7,8\text{-}C_2B_9H_{10}\}\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}]$: $NiCl_2\cdot 6H_2O$ (23.8 mg, 0.10 mmol) and 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) were mixed in ethanol (10 mL, 95%). The stirring process was continued for about 6 h at room temperature in air, and then the yellow solid was filtered off, washed with ethanol, and dried in vacuo (27.5 mg, 51.01%). M.p. 207–208 °C. A single crystal for X-ray diffraction was grown from a dichloromethane/*n*-hexane solution. FT-IR: $\tilde{\nu}_{KBr}$ = 3000 (m), 2545 (m), 1475 (m), 1250 (s), 730 (m) cm^{-1}. ^1H NMR (400.15 MHz, $CDCl_3$): δ = 7.20–7.58 (40 H, Aryl-H); –2.24 (2 H, B–H–B) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 125.913–134.942 (48 C, Aryl-C); 76.198 (4 C, C_{cage}) ppm. $C_{52}H_{60}B_{18}NiOP_4$ (1078.17): calcd. C 57.92, H 5.61; found C 57.85, H 5.55.

Synthesis of $[Ni(thf)\{7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2]\cdot thf$ (3): $NiCl_2\cdot 6H_2O$ (23.8 mg, 0.10 mmol) was added to a suspension of 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) in ethanol (10 mL, 95%). After the mixture was stirred for 12 h in air at room temperature, the yellow solid was filtered off, washed with ethanol, and dried in vacuo (18.4 mg, 32.68%). M.p. 198–199 °C. A single crystal suitable for X-ray analysis was obtained from a tetrahydrofuran solution after partial evaporation of the solvent. FT-IR: $\tilde{\nu}_{KBr}$ = 3120 m, 2540 (m), 1689 (s), 1425 (m), 1260 (s), 1078 (m), 725 (m), 680 (s), 490 (m) cm^{-1}. ^1H NMR (400.15 MHz, $CDCl_3$): δ = 7.187–7.594 (40 H, Aryl-H), –2.222 (2 H, B–H–B) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 26.334–139.114 (48 C, Aryl-C), 77.007 (4 C, C_{cage}) ppm. $C_{60}H_{76}B_{18}NiO_6P_4$ (1270.38): calcd. C 56.72, H 6.03; found C 56.67, H 5.98.

Synthesis of $[1\text{-}(OPPh_2)\text{-}2\text{-}(PPh_2)\text{-}1,2\text{-}C_2B_{10}H_{10}]$ (4): 1,2-$(PPh_2)_2$-1,2-$C_2B_{10}H_{10}$ (51.2 mg, 0.10 mmol) was added to ethanol (10 mL, 95%). The suspension was stirred for 8 h; air was continuously and slowly bubbled into the mixture at room temperature. The white solid was filtered off and dried in vacuo (36.5 mg, 69.06%). M.p. 232–233 °C. A single crystal suitable for X-ray analysis was obtained from a dichloromethane/*n*-hexane solution. FT-IR: $\tilde{\nu}_{KBr}$ = 3045 (m), 2510 (m), 1669 (s), 1415 (m), 1250 (s), 1083 (m), 707 (m), 672 (s), 510 (m) cm^{-1}. ^1H NMR (400.15 MHz, $CDCl_3$): δ = 7.057–7.784 (20 H, Aryl-H) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 25.886–137.553 (24 C, Aryl-C), 76.825 (2 C, C_{cage}) ppm. $C_{26}H_{30}B_{10}OP_2$ (528.54): calcd. C 59.08, H 5.72; found C 59.11, H 5.80.

Synthesis of $H[7,8\text{-}(OPPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]\cdot 0.25C_2H_5OH$ (5): In a manner similar to the procedure for the preparation of compound **4**, the mixture was stirred for 18 h. The white solid was filtered off and dried in vacuo (46.4 mg, 84.94%). M.p. 208–209 °C. A suitable crystal for X-ray diffraction was grown from a dichloromethane solution layered with *n*-hexane. FT-IR: $\tilde{\nu}_{KBr}$ = 3050 (m), 2520 (m),

Table 2. Details of the crystal parameters, data collections and refinements for **1**–**5**.

Crystal data	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{52}H_{60}B_{18}CuO_4P_4$	$C_{52}H_{60}B_{18}O_4P_4Zn$	$C_{60}H_{76}B_{18}O_6P_4Ni$	$C_{26}H_{30}B_{10}OP_2$	$C_{26.5}H_{32.5}B_9O_{2.25}P_2$
Formula weight	1131.00	1132.83	1270.38	528.54	546.26
Temperature [K]	298(2)	298(2)	298(2)	298(2)	298(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	triclinic	monoclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P21/n$	$P\bar{1}$
a [Å]	11.576(4)	11.568(4)	13.990(3)	16.438(4)	11.424(3)
b [Å]	12.774(4)	12.748(4)	15.389(3)	10.423(2)	11.714(3)
c [Å]	13.332(4)	13.318(4)	20.441(4)	17.739(4)	13.559(4)
α [°]	101.423(5)	101.203(5)	93.069(3)	90	95.401(5)
β [°]	109.229(5)	109.358(5)	96.878(3)	111.868(3)	108.386(4)
V [Å^3]	1670.1(9)	1661.4(9)	3884.2(12)	2820.6(11)	1597.1(8)
Z	1	1	2	4	2
Absorption coefficient [mm^{-1}]	0.461	0.505	0.374	0.175	0.160
D [Mg·m^{-3}]	1.125	1.132	1.086	1.245	1.136
F(000)	583	584	1324	1096	1206
Crystal size [mm]	0.35 × 0.32 × 0.29	0.23 × 0.21 × 0.19	0.46 × 0.40 × 0.20	0.55 × 0.50 × 0.48	0.35 × 0.31 × 0.29
Theta range [°]	2.09 to 25.01	2.04 to 25.01	1.97 to 25.01	2.37 to 25.01	2.92 to 25.01
Limiting indices	$-13 \le h \le 13$	$-9 \le h \le 13$	$-16 \le h \le 14$	$-19 \le h \le 15$	$-13 \le h \le 13$
	$-15 \le k \le 15$	$-15 \le k \le 15$	$-18 \le k \le 18$	$-9 \le k \le 12$	$-13 \le k \le 13$
	$-8 \le l \le 15$	$-15 \le l \le 15$	$-19 \le l \le 24$	$-21 \le l \le 20$	$-10 \le l \le 16$
Independent reflection	5663	5573	13040	4921	5492
Max. and min. transmission	0.8778 and 0.8552	0.9102 and 0.8928	0.9290 and 0.8468	0.9206 and 0.9097	0.9551 and 0.9461
Goodness-of-fit on F^2	1.009	1.003	1.002	1.007	1.010
R [$I > 2\sigma(I)$]	R_1 = 0.0790	R_1 = 0.0715	R_1 = 0.0781	R_1 = 0.0616	R_1 = 0.0762
	wR_2 = 0.1825	wR_2 = 0.1755	wR_2 = 0.1894	wR_2 = 0.1678	wR_2 = 0.1777
R (all data)	R_1 = 0.1616	R_1 = 0.1375	R_1 = 0.1588	R_1 = 0.0917	R_1 = 0.1492
	wR_2 = 0.2264	wR_2 = 0.2237	wR_2 = 0.2482	wR_2 = 0.2093	wR_2 = 0.2193
Largest diff. peak and hole (× 10^2 electrons Å^{-3})	1.067 and –0.514	1.356 and –0.406	1.135 and –0.423	0.894 and –1.186	0.584 and –0.287

1669 (s), 1400 (m), 1260 (s), 1085 (m), 700 (m), 660 (s), 510 (m) cm^{-1}. ^{1}H NMR (400.15 MHz, $CDCl_3$): δ = 7.206–7.598 (20 H, Aryl-H); –2.105 (1 H, B–H–B) ppm. ^{13}C NMR (100.63 MHz, $CDCl_3$): δ = 22.300–135.198 (24 C, Aryl-C), 76.887 (2 C, C_{cage}) ppm. $C_{26.5}H_{32.5}B_9O_{2.25}P_2$ (546.26): calcd. C 58.26, H 5.99; found C 58.31, H 5.96.

X-ray Structure Determination

The collections of the crystallographic data for the three carborane complexes and two carborane compounds were carried out with a Bruker Smart-1000 CCD diffractometer, by using graphite-monochromatized Mo-K_α (λ = 0.71073 Å) at 298(2) K. The structures were solved by direct methods and expanded by using Fourier difference techniques with the SHELXTL-97 program package.[49] The solvent content in compound **5** is disordered. Partially occupied atoms of the solvent molecule were refined with isotropic displacement parameters, but the rest of the non-hydrogen atoms were refined anisotropically by full-matrix least-squares calculations on F^2. All the H atoms were located in a difference Fourier map and thereafter refined isotropically, except the H atoms of the solvent C_2H_5OH of compound **5**. The bridging H atoms of the *nido* carborane skeleton were refined isotropically with fixed U. Details of the crystal parameters, data collection, and refinement are summarized in Table 2.

CCDC-602225 (for **1**), -602226 (for **2**), -602227 (for **3**), -607283 (for **4**), and -609307 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

This work was supported by the National Natural Science Foundation of the P. R. China (project no. 20371025) and Open Research Fund Program of the Key Laboratory of Marine Drugs (Ocean University of China), Ministry of Education [project no. KLMD (OUC) 2004].

[1] T. L. Heying, J. W. Ager Jr, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, J. W. Szymanski, *Inorg. Chem.* **1963**, *2*, 1089–1092.

[2] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, M. S. Cohen, *Inorg. Chem.* **1963**, *2*, 1111–1115.

[3] R. A. Wiesboeck, M. F. Hawthorne, *J. Am. Chem. Soc.* **1964**, *86*, 1642–1643.

[4] M. F. Hawthorne, D. C. Young, P. M. Garrett, D. A. Owen, S. G. Schwerin, F. N. Tebbe, P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 862–868.

[5] J. F. Valliant, K. J. Guenther, A. S. King, P. Morel, P. Schaffer, O. O. Sogbein, K. A. Stephenson, *Coord. Chem. Rev.* **2002**, *232*, 173–230.

[6] M. F. Hawthorne, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 950–984.

[7] J. Plesek, *Chem. Rev.* **1992**, *92*, 269–278.

[8] R. N. Grimes, *J. Chem. Educ.* **2004**, *81*, 657–672.

[9] M. F. Hawthorne, X. G. Yang, Z. Zheng, *Pure Appl. Chem.* **1994**, *66*, 245–254.

[10] M. F. Hawthorne, Z. Zheng, *Acc. Chem. Res.* **1997**, *30*, 267–276.

[11] M. J. Hardie, C. L. Raston, *Angew. Chem. Int. Ed.* **2000**, *39*, 3835.

[12] M. J. Hardie, C. L. Raston, *Chem. Commun.* **2001**, 905–906.

[13] N. Malic, P. J. Nichols, C. L. Raston, *Chem. Commun.* **2002**, 16–17.

[14] A. K. Saxena, N. S. Hosmane, *Chem. Rev.* **1993**, *93*, 1081–1124.

[15] A. K. Saxena, J. A. Maguire, N. S. Hosmane, *Chem. Rev.* **1997**, *97*, 2421–2462.

[16] Z. Xie, *Coord. Chem. Rev.* **2002**, *231*, 23–46.

[17] G. X. Jin, *Coord. Chem. Rev.* **2004**, *248*, 587–602.

[18] Z. Xie, *Coord. Chem. Rev.* **2006**, *250*, 259–272.

[19] F. Teixidor, C. Viñas, M. M. Abad, M. Lopez, J. Casabó, *Organometallics* **1993**, *12*, 3766–3768.

[20] R. Nuñez, C. Viñas, F. Teixidor, M. M. Abad, *Appl. Organomet. Chem.* **2003**, *17*, 509–517.

[21] E. Bembenek, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *Chem. Ber.* **1994**, *127*, 835–840.

[22] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *J. Chem. Soc., Dalton Trans.* **1996**, 4583–4588.

[23] F. Teixidor, C. Viñas, M. M. Abad, R. Kivekäs, R. Sillanpää, *J. Organomet. Chem.* **1996**, *509*, 139–150.

[24] O. Crespo, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Chem. Soc., Dalton Trans.* **1992**, 1601–1605.

[25] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *J. Chem. Soc., Chem. Commun.* **1993**, 1696–1697.

[26] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *Inorg. Chem.* **1994**, *33*, 6128–6131.

[27] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, *Inorg. Chem.* **1996**, *35*, 1361–1366.

[28] M. J. Calhorda, O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, J. M. López-de-Luzuriaga, J. L. Perez, M. A. Ramón, L. F. Veiros, *Inorg. Chem.* **2000**, *39*, 4280–4285.

[29] O. Crespo, M. C. Gimeno, P. G. Jones, A. Laguna, M. D. Villacampa, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 993–995.

[30] C. Viňas, M. M. Abad, F. Teixidor, R. Sillanpaa, R. Kivekas, *J. Organomet. Chem.* **1998**, *555*, 17–23.

[31] S. Paavola, R. Kivekäs, F. Teixidor, C. Viňas, *J. Organomet. Chem.* **2000**, *606*, 183–187.

[32] S. Paavola, F. Teixidor, C. Viňas, R. Kivekäs, *J. Organomet. Chem.* **2002**, *645*, 39–45.

[33] S. Paavola, F. Teixidor, C. Viňas, R. Kivekäs, *J. Organomet. Chem.* **2002**, *657*, 187–193.

[34] F. Teixidor, C. Viňas, M. M. Abad, C. Whitaker, J. Rius, *Organometallics* **1996**, *15*, 3154–3160.

[35] D. P. Zhang, J. M. Dou, D. C. Li, D. Q. Wang, *Appl. Organomet. Chem.* **2006**, *20*, 632–637.

[36] D. P. Zhang, J. M. Dou, D. C. Li, D. Q. Wang, *J. Coord. Chem.*, in press.

[37] D. P. Zhang, J. M. Dou, D. C. Li, D. Q. Wang, *Inorg. Chim. Acta* **2006**, *359*, 4243–4249.

[38] J. M. Dou, D. P. Zhang, D. C. Li, D. Q. Wang, *J. Organomet. Chem.*, in press.

[39] C. Viňas, R. Nuňez, I. Rojo, F. Teixidor, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **2001**, *40*, 3259–3260.

[40] F. Teixidor, R. Benakki, C. Viňas, R. Kivekäs, R. Sillanpää, *Inorg. Chem.* **1999**, *38*, 5916–5919.

[41] J. E. Crook, N. N. Greenwood, J. D. Kennedy, *J. Chem. Soc., Dalton Trans.* **1972**, 171–175.

[42] V. P. Balema, M. Pink, J. Sieler, E. Hey-Hawkins, L. Hennig, *Polyhedron* **1998**, *17*, 2087–2093.

[43] F. Teixidor, C. Viňas, M. M. Abad, R. Nuňez, R. Kivekäs, R. Sillanpää, *J. Organomet. Chem.* **1995**, *503*, 193–203.

[44] D. P. Zhang, J. M. Dou, D. C. Li, D. Q. Wang, *Acta Crystallogr., Sect. E* **2006**, *62*, 418–419.

[45] G. Pilloni, B. Corain, M. Degano, B. Longato, G. Zanotti, *J. Chem. Soc., Dalton Trans.* **1993**, 1777–1778.

[46] C. A. Kosky, J. Gayda, J. F. Gibson, S. F. Jones, *Inorg. Chem.* **1982**, *21*, 3173–3179.

[47] E. Bermejo, A. Castineiras, R. Dominguez, C. Schule, *J. Coord. Chem.* **1994**, *33*, 353–357.

[48] R. P. Alexander, H. Schroeder, *Inorg. Chem.* **1963**, *2*, 1107–1110.

[49] G. M. Sheldrick, *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Madison, WI, **1997**.

Received: July 20, 2006
Published Online: November 17, 2006