*Journal of Organometallic Chemistry*, 435 (1992) 29–35
Elsevier Sequoia S.A., Lausanne
JOM 22699

# Complexes of dibutyldihalotin(IV) with imidazole and pyrazole. The crystal structure of dibutyldichlorobis(pyrazole)tin(IV)

A. Sánchez González, J.S. Casas, J. Sordo
*Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15706 Santiago de Compostela (Spain)*

and G. Valle
*Centro di Studio sui Biopolimeri del C.N.R., Dipartimento di Chimica Organica, Università di Padova, Padova (Italy)*

(Received February 3, 1992)

## Abstract

Complexes of the type [$SnBu_2X_2L_2$] (X=Cl or Br; L=HIm or HPz) were obtained from the reaction of $SnBu_2X_2$ with imidazole (HIm) or pyrazole (HPz). The structure of dibutyldichlorobis (pyrazole)tin(IV) was determined by X-ray diffraction. The crystal consists of discrete all-*trans* $SnBu_2Cl_2(HPz)_2$ units with the metal atom octahedrally coordinated to two butyl carbons, two Cl atoms and two pyrazole rings. The pyrazole ligands are bound intra- and inter-molecularly to the chlorine atoms. IR data suggest similar *trans*-stereochemistry for the other compounds prepared. The $^{13}C$ NMR spectra indicate that [$SnBu_2X_2(HPz)_2$] dissociates completely in DMSO-$d_6$ but only partially in $CDCl_3$.

## Introduction

The coordination chemistry of dimethyl- and diethyl-tin(IV) dihalide compounds with imidazole and pyrazole has been studied previously [1–3]. Compounds of the type [$SnR_2X_2L_2$] have been prepared and the structures of these and other $SnR_2X_2$ adducts with *N*-donors have been compared. To investigate further the influence of the alkyl substituent on the structures of such compounds, we have now studied the interaction of imidazole (HIm) and pyrazole (HPz) with $SnBu_2X_2$. This paper describes the preparation of [$SnBu_2X_2L_2$] (X = Cl or Br; L=HIm or HPz) and the crystal structure of [$SnBu_2Cl_2(HPz)_2$].

---

Correspondence to: Professor J. Sordo, Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15706 Santiago de Compostela, Spain, or to Dr. G. Valle, Centro di Studio sui Biopolimeri del C.N.R., Dipartimento di Chimica Organica, Università di Padova, Padova, Italy.

## Experimental

### *Reagents and preparations*

Dibutyltin dichloride (Fluka), dibutyltin dibromide (Aldrich), pyrazole (Ega) and imidazole (Ega) were used as supplied. Solvents were purified by the usual methods. Adducts were prepared under dinitrogen by slow addition of a solution of the ligand in dichloromethane to a stirred solution of $SnBu_2X_2$ in the same solvent. Typically, a solution of HPz (7.2 mmol) in $CH_2Cl_2$ (20 $cm^3$) was added dropwise with continuous stirring to a solution of $SnBu_2Cl_2$ (3.6 mmol) in $CH_2Cl_2$ (20 $cm^3$), and the mixture was stirred for six days. The white powder obtained by slow evaporation of solvent was filtered and dried under vacuum. Crystals suitable for X-ray analysis were obtained by diffusion of cyclohexane into a solution of the complex in dichloromethane. Analytical data are listed in Table 1.

### *Measurements*

Elemental analyses were performed with a Carlo Erba 1108 apparatus. Melting points were determined with an Electrothermal apparatus. Infrared spectra were recorded in Nujol mulls or KBr discs on a Perkin–Elmer 1330 spectrometer. Conductivity measurements were made with a WTW-LF3 conductivity meter. $^{13}C$ NMR spectra were recorded with a Bruker WM 250 spectrometer.

### *Crystal structure determination*

A well-formed crystal of approximate dimension 0.4 × 0.3 × 0.4 mm mounted in a Philips PW 1100 diffractometer was used for determination of cell dimensions and measurement of intensity data. Crystal data: $C_{14}H_{26}Cl_2N_4Sn$, M=439.98, $C2/c$, $a = 22.864(2)$, $b = 12.082(2)$, $c = 17.071(2)$ Å, $\beta = 123.4(2)°$, $V = 3936.93$ Å$^3$, $Z = 8$, $D_c = 1.485$ g cm$^{-3}$, $F(000) = 1776.0$, $\mu$(Mo-$K_\alpha$) = 15.8 cm$^{-1}$, $R = 0.033$, $R_W = 0.039$.

### *Data collection*

4723 independent reflections in the range $4.2 < 2\theta < 56°$ were collected by the $\theta$–$2\theta$ step-scan method using Mo-$K_\alpha$ monochromatized radiation ($\lambda$=0.7107 Å). 3973 reflections with $F \geq 7\sigma(F)$ were considered as observed. The intensities were corrected for Lorentz and polarization effects, but not for absorption.

Table 1

Analytical and physical data of the compounds prepared

| Compound | Analysis: Found (calc.) (%) | | | m.p. | $\Lambda_M$ [a] |
|---|---|---|---|---|---|
| | C | N | H | (°C) | (ohm$^{-1}$ mol cm$^2$) |
| I [$SnBu_2Cl_2(HPz)_2$] | 38.1<br>(38.2) | 12.2<br>(12.7) | 6.0<br>(6.0) | 68 | 3.7 |
| II [$SnBu_2Br_2(HPz)_2$] | 31.7<br>(31.8) | 10.6<br>(10.6) | 5.0<br>(5.0) | 86 | 1.9 |
| III [$SnBu_2Cl_2(HIm)_2$] | 37.8<br>(38.2) | 12.6<br>(12.7) | 6.2<br>(6.0) | 77 | 18.4 |
| IV [$SnBu_2Br_2(HIm)_2$] | 31.9<br>(31.8) | 10.5<br>(10.6) | 5.1<br>(5.0) | 102 | 33.7 |

[a] $10^{-3}M$ in MeCN.

Table 2

Fractional coordinates for $[SnBu_2Cl_2(HPz)_2]$

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Sn | 0.70276(1) | 0.51589(2) | 0.31009(1) |
| Cl(1) | 0.77687(5) | 0.67640(7) | 0.42198(6) |
| Cl(2) | 0.62147(5) | 0.36077(7) | 0.19858(6) |
| N(1) | 0.6379(1) | 0.5264(2) | 0.3776(2) |
| N(2) | 0.6509(1) | 0.5950(2) | 0.4464(2) |
| N(3) | 0.7770(2) | 0.5142(2) | 0.2523(2) |
| N(4) | 0.8196(2) | 0.5960(3) | 0.2618(2) |
| C(1) | 0.5862(2) | 0.4620(3) | 0.3653(3) |
| C(2) | 0.5664(2) | 0.4912(3) | 0.4256(4) |
| C(3) | 0.6092(2) | 0.5769(4) | 0.4772(3) |
| C(4) | 0.7810(2) | 0.4291(3) | 0.1984(3) |
| C(5) | 0.8258(3) | 0.4718(4) | 0.1751(4) |
| C(6) | 0.8511(3) | 0.5718(5) | 0.2170(4) |
| C(7) | 0.6419(2) | 0.6344(3) | 0.2027(2) |
| C(8) | 0.5848(2) | 0.6933(3) | 0.2058(3) |
| C(9) | 0.5435(2) | 0.7722(4) | 0.1231(3) |
| C(10) | 0.4875(3) | 0.8366(6) | 0.1263(6) |
| C(11) | 0.7677(2) | 0.3878(3) | 0.4064(3) |
| C(12) | 0.8439(2) | 0.4129(3) | 0.4750(3) |
| C(13) | 0.8833(2) | 0.3117(4) | 0.5355(3) |
| C(14) | 0.9591(3) | 0.3366(5) | 0.6063(4) |

*Determination and refinement of the structure*

The positions of the chlorine and tin atoms were obtained by three-dimensional Patterson-Fourier synthesis. The remaining non-hydrogen atoms were located in a subsequent electron density map. The hydrogen atoms were located in a difference Fourier map and isotropically refined. Final refinements were carried out with anisotropic thermal parameters for all non-hydrogen atoms. $R$ and $R_W$ factors were 0.033 and 0.039 respectively. Scattering factors for all atoms were those incorporated in the SHELX program [4]. Positional parameters for the non-hydrogen atoms are listed in Table 2. Full lists of structure factors, atomic coordinates, bond lengths and angles, and thermal parameters are available from the authors.

## Results and discussion

Table 1 shows the elemental analyses, melting points and molar conductivities of the complexes. The conductivities show that the complexes remain non-ionized in MeCN.

*Description of the structure*

The structure of $[SnBu_2Cl_2(HPz)_2]$ is shown, with the atom numbering scheme, in Fig. 1. Bond distances and angles are listed in Table 3. The crystals consist of discrete $SnBu_2Cl_2(HPz)_2$ units in which the Sn atom is octahedrally coordinated to two Cl atoms, two butyl groups and two pyrazole rings in an all-*trans* configuration. The pyrazole ligands binds to the metal through the pyridine-like nitrogen, the bond distances and angles being similar to those found previously in other $SnR_2Br_2(HPz)_2$ complexes (R=Me, Et) [2,3]. The rings are essentially planar, with negligible deviation from the best least-squares plane, the values of the angles of both rings and of SnN(1)N(2), SnN(1)C(1), SnN(3)N(4) and SnN(3)C(4) being in keeping with the rules described for pyrazole adducts by Bonati [5]. The torsion angles about C(7)–C(8) and C(11)–C(12) are −177.8° and −177.5° respectively, and those about C(8)–C(9) and C(12)–C(13) are −177.6° and −178.3° respectively, showing that both butyl groups have the same extended form.

The presence of several intra- and inter-molecular hydrogen bonds in and between the discrete units is suggested by the following distances and angles: N(2)–Cl(1), 3.281 Å; H(N(2))–Cl(1), 2.736 Å; N(2)–H–Cl(1), 134.3°; N(4)–Cl(1), 3.510 Å; H(N(4))–Cl(1), 2.882 Å; N(4)–H–Cl(1), 122.8°; N(2)–Cl(1)$^a$, 3.364 Å; H(N(2))–Cl(1)$^a$, 2.847 Å; N(2)–H–Cl(1)$^a$, 130.9°; N(4)–Cl(2)$^b$, 3.391 Å; H(N(4))–Cl(2)$^b$, 2.672 Å; and N(4)–H–Cl(2)$^b$, 130.5° (symmetry codes: $^a -x+1/2+1, -y+1/2+1, -z+1$; $^b -x+1/2+1, +y+1/2, -z+1/2$). These three-centre bonds [6, and references therein] are slightly different; whereas the hydrogen bonds formed by H–N(2) are practically symmetrical, the bonds formed by H–N(4) are more asymmetric, the N(4)–Cl(1) distance being at the upper limit found for this bond in related compounds [7, and references therein]. As in other systems [6], the symmetric character increases the distance of the H atom from the plane formed by the other atoms involved (H–N(4) is located 0.023 Å from the N(4)Cl(1)Cl(2) $^b$ plane, whereas H–N(2) is 0.166 Å from the N(2)Cl(1)Cl(1) $^a$ plane). As a result of these hydrogen bonds, the structure can be described as

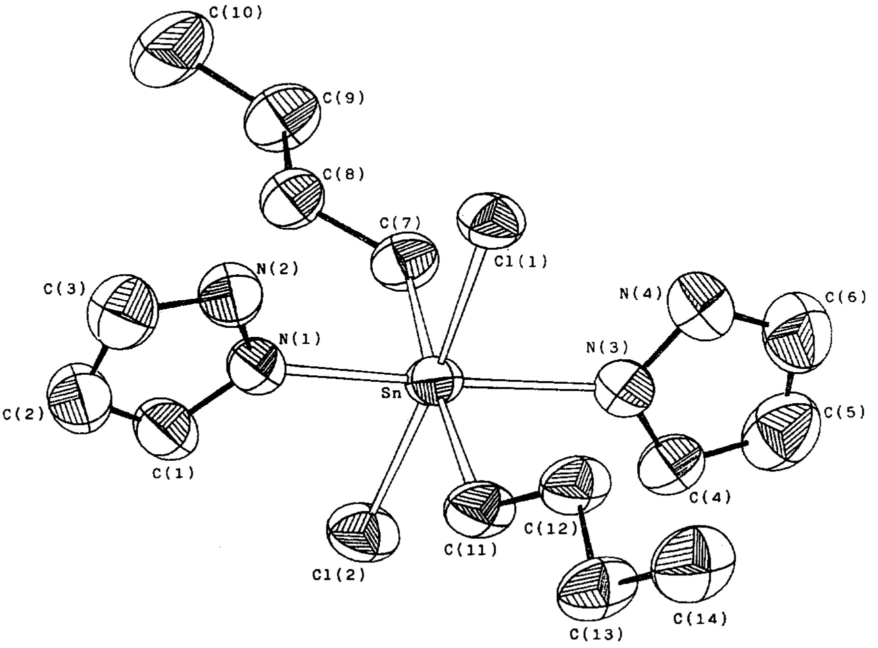

Fig. 1. The molecular structure of $[SnBu_2Cl_2(HPz)_2]$, with numbering scheme.

Table 3

Selected bond distances (Å) and angles (deg) for $[SnBu_2Cl_2(HPz)_2]$

| | | | |
|---|---|---|---|
| Sn-Cl(1) | 2.592(4) | Sn-Cl(2) | 2.587(4) |
| Sn-N(1) | 2.329(5) | Sn-N(3) | 2.388(5) |
| Sn-C(7) | 2.131(5) | Sn-C(11) | 2.149(5) |
| N(1)-N(2) | 1.331(5) | N(1)-C(1) | 1.332(6) |
| N(2)-C(3) | 1.335(7) | N(3)-N(4) | 1.334(5) |
| N(3)-C(4) | 1.331(6) | N(4)-C(6) | 1.340(9) |
| C(1)-C(2) | 1.379(9) | C(2)-C(3) | 1.363(6) |
| C(4)-C(5) | 1.35(1) | C(5)-C(6) | 1.360(8) |
| C(7)-C(8) | 1.513(6) | C(8)-C(9) | 1.525(6) |
| C(9)-C(10) | 1.53(1) | C(11)-C(12) | 1.500(6) |
| C(12)-C(13) | 1.531(6) | C(13)-C(14) | 1.499(7) |
| C(7)-Sn-C(11) | 172.6(2) | N(3)-Sn-C(11) | 87.8(3) |
| N(3)-Sn-C(7) | 85.8(2) | N(1)-Sn-C(11) | 91.2(3) |
| N(1)-Sn-C(7) | 95.6(2) | N(1)-Sn-N(3) | 175.0(1) |
| Cl(2)-Sn-C(11) | 87.4(1) | Cl(2)-Sn-C(7) | 89.4(2) |
| Cl(2)-Sn-N(3) | 94.4(2) | Cl(2)-Sn-N(1) | 90.5(2) |
| Cl(1)-Sn-C(11) | 94.5(2) | Cl(1)-Sn-C(7) | 89.07(9) |
| Cl(1)-Sn-N(3) | 89.2(2) | Cl(1)-Sn-N(1) | 86.0(2) |
| Cl(1)-Sn-Cl(2) | 176.02(9) | Sn-N(1)-C(1) | 130.0(3) |
| Sn-N(1)-N(2) | 125.3(4) | N(2)-N(1)-C(1) | 104.5(5) |
| N(1)-N(2)-C(3) | 112.6(4) | Sn-N(3)-C(4) | 128.8(3) |
| Sn-N(3)-N(4) | 125.6(3) | N(4)-N(3)-C(4) | 105.4(5) |
| N(3)-N(4)-C(6) | 110.8(4) | N(1)-C(1)-C(2) | 111.2(4) |
| C(1)-C(2)-C(3) | 105.2(7) | N(2)-C(3)-C(2) | 106.5(6) |
| N(3)-C(4)-C(5) | 110.9(4) | C(4)-C(5)-C(6) | 106.1(8) |
| N(4)-C(6)-C(5) | 106.7(7) | Sn-C(7)-C(8) | 117.0(4) |
| C(7)-C(8)-C(9) | 111.6(6) | C(8)-C(9)-C(10) | 113.0(6) |
| Sn-C(11)-C(12) | 117.9(3) | C(11)-C(12)-C(13) | 111.4(4) |
| C(12)-C(13)-C(14) | 111.9(4) | | |

monomeric $SnBu_2Cl_2(HPz)_2$ units held in pairs via N(2)-H-Cl(1)$^{a}$ bonds, these pairs being bound *via* N(4)-H-Cl(2)$^{b}$ bonds to form a polymeric structure. Figure 2 shows a simplified view of the structure.

Similar all-*trans* stereochemistry has previously been found in other pyrazole complexes of the type $[SnR_2X_2L_2]$ [2,3,7,8], in all of which the N-H groups were involved in hydrogen bonds. However, several structural analogies and differences deserve further comment.

Though the Sn-Cl, Sn-N and Sn-C bond distances are affected very little by whether R=Me, Et or Bu (the Sn-C distance, for example, is in all cases in the middle of the range for butyltin complexes [9-12]) and the coordination bond angles are near 90° in all these systems, there are significant differences as regards the mutual orientation of the two ligand rings. In $[SnBu_2Cl_2(HPz)_2]$, ring 1 [N(1)N(2)C(1)C(2)C(3)] makes an angle of 175.3° with the SnCl(1)N(1) plane, with which ring 2 [N(3)N(4)C(4)C(5)C(6)] makes an angle of 164.9°. In both rings the N-H group is directed towards Cl(1), allowing the formation of two intramolecular hydrogen bonds with the same chlorine atom. In the methyl and ethyl structures studied previously [2,3,7,8], each N-H group is directed towards a different halogen atom, so that all the X atoms are involved in intramolecular hydrogen bonds.

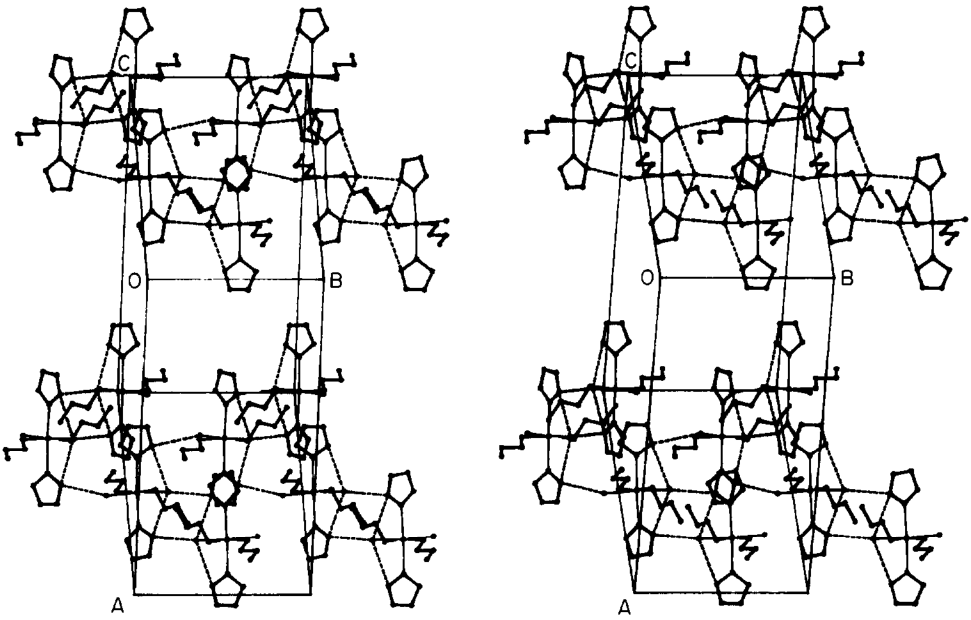

Fig. 2. A simplified stereoview of hydrogen bonding in $[SnBu_2Cl_2(PHz)_2]$.

*IR spectra*

The small shifts of the significant ring stretching frequencies upon coordination (in the range 1540–1360 $cm^{-1}$ for HPz and 1575–1325 $cm^{-1}$ for HIm) are similar to those detected in related systems [2,3] in keeping with coordination via the pyridine-like nitrogen atom. The position of the N–H stretching band agrees with the hydrogen bond observed in the crystal. The asymmetric Sn–C stretching bands at 590, 590, 610 and 620 $cm^{-1}$ for I, II, III and IV have frequencies close to those proposed for other butyl systems [13], and the asymmetric Sn–Cl stretching bands at 220 and 200 $cm^{-1}$ for I and III, respectively, are close to the positions of these bands in similar complexes with R=Me or Et [2,3]. The similarity of the data for II–IV with those observed for $[SnBu_2Cl_2(HPz)_2]$ (I) seems to indicate that all the compounds prepared have identical *trans* stereochemistry.

*NMR spectra*

The behaviour of the complexes in solution was explored through the $^{13}C$ NMR spectra of I in $CDCl_3$ and DMSO-$d_6$. The main parameters are listed in Table 4 together with the data for $SnBu_2Cl_2$ [14]. The chemical shifts and coupling constants of I in DMSO-$d_6$ are practically the same as those of the acceptor, showing that the HPz molecules have been displaced by the solvent from the coordination sphere of the tin atom, as has been observed in dimethyl- and diethyl-dihalotin(IV) adducts [2,3].

In $CDCl_3$ solution the spectral behaviour of the organometallic part of the adduct clearly differs from that of the acceptor. C(1) is strongly deshielded, and the coupling constants $^1J$ and $^3J$ are larger in the spectrum of I suggesting a change in the hybridisation of the tin atom. This indicates at least partial perseverance of

Table 4

$^{13}$C NMR parameters ($\delta$ in ppm from TMS and $J$ in Hz) for [$SnBu_2Cl_2(HPz)_2$]

| Compound | Solvent | C(1) | C(2) | C(3) | C(4) | $^nJ(^{119}Sn-^{13}C)$ | | | Ligand [a] |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $n = 1$ | $n = 2$ | $n = 3$ | |
| $SnBu_2Cl_2$ | $CDCl_3$ | 26.9 | 26.9 | 26.2 | 13.4 | 421.2 | 43.0 | 84.2 | |
| | DMSO-$d_6$ | 37.5 | 27.7 | 25.6 | 13.8 | 854.5 | 46.4 | 153.1 | |
| [$SnBu_2Cl_2(HPz)_2$] | $CDCl_3$ | 35.7 | 27.2 | 25.8 | 13.3 | 691.4 [b] | 43.0 [b] | 131.8 [b] | 105.9, 134.2 |
| | DMSO-$d_6$ | 37.7 | 27.7 | 25.7 | 13.8 | 858.3 | 44.8 | 151.6 | 104.4, 133.4 |

[a] Numbering scheme NC(3)C(4)C(5)N. Values for the free ligand in $CDCl_3$ solution are 105.1 [C(4)] and 133.8 [C(3) and C(5)]. [b] Under our experimental conditions $^{117}Sn-^{119}Sn$ satellites were not resolvable.

coordination to HPz. The same conclusion is suggested by the fact that pyrazole carbon atoms are slightly deshielded, probably due to the inductive effect of the tin–nitrogen donor–acceptor bond. However the value of $^1J(^{119}Sn-^{13}C)$ for I in $CDCl_3$ and its C(7)–Sn–C(11) angle in the solid state (see above) do not fit the relationship between these two parameters obtained by Holeček and Lyčka on the basis of data for tetra-, penta- and hexa-coordinated dibutyltin compounds [15]. As was suggested by these authors for [$SnBu_2Cl_2$dppoe] (dppoe = 1,2-bis(diphenylphosphoryl)ethane), this discrepancy may be due to partial dissociation of I, which reduces the coordination number of Sn to below the theoretical value of six. The same behaviour was observed for the analogous dimethyl- and diethyl-dihalotin(IV) compounds [2,3].

## Acknowledgments

We thank the Xunta de Galiuà (XUGA 20314 B91), Spain, and the Programa de Acciones Intègradas (59A) for financial support of this work.

## References

1 E. García Martínez, A. Sánchez González, A. Macías, M.V. Castaño, J.S. Casas and J. Sordo, J. Organomet. Chem., 385 (1990) 329.

2 B. Alberte, A. Sánchez González, E. García, J.S. Casas, J. Sordo and E.E. Castellano, J. Organomet. Chem., 338 (1988) 187.

3 A. Sánchez González, B. Alberte, J.S. Casas, J. Sordo, A. Castiñeiras, W. Hiller and J. Strähle, J. Organomet. Chem., 353 (1988) 169.

4 G.M. Sheldrick, SHELX-76 program for crystal structure determination, University of Cambridge, 1976.

5 F. Bonati, Gazz. Chim. Ital., 119 (1989) 291.

6 R. Taylor, O. Kennard, W. Versichel, J. Am. Chem. Soc., 106 (1984) 244.

7 G. Valle, R. Ettorre, V. Peruzzo and G. Plazzogna, J. Organomet. Chem., 326 (1987) 169.

8 R. Graziani, U. Casellato, R. Ettorre and G. Plazzogna, J. Chem. Soc., Dalton Trans. (1982) 805.

9 G. Domazetis, B.D. James, M.F. Mackay and R.J. Magee, J. Inorg. Nucl. Chem., 41 (1979) 1555.

10 P.G. Harrison, N.W. Sharpe, C. Pelizzi, G. Pelizzi and P. Tarasconi, J. Chem. Soc., Dalton Trans. (1983) 921.

11 G. Pelizzi, P. Tarasconi, F. Vitali and C. Pelizzi, Acta Crystallogr., C43 (1987) 1505.

12 C. Vatsa, V.K. Jain, T.K. Das and E.R.T. Tiekink, J. Organomet. Chem., 396 (1990) 59.

13 G. Domazetis, R.J. Magee and B.D. James, J. Inorg. Nucl. Chem., 43 (1981) 1351.

14 T.A.K. Al-Allaf, J. Organomet. Chem., 306 (1986) 337.

15 J. Holeček and A. Lyčka, Inorg. Chim. Acta, 118 (1986) L 15.