Journal of Organometallic Chemistry, 299 (1986) 251–258
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INSERTION OF MeNC INTO Pd–C_6Cl_5 BONDS. BRIDGED AND TERMINAL *N*-METHYLPENTACHLOROBENZIMIDOYLPALLADIUM(II) COMPLEXES

RAFAEL USÓN, JUAN FORNIÉS, PABLO ESPINET, LUIS PUEYO

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza (Spain)

and ELENA LALINDE

Colegio Universitario de la Rioja, Logroño (Spain)

(Received July 15th, 1985)

Summary

The synthesis of the complexes *trans*-$[Pd(C_6Cl_5)X(CNMe)_2]$ (X = Cl, Br, I, SCN) is described. These complexes undergo ready insertion of the CNMe ligand into the Pd—C_6Cl_5 bond to give pentachlorobenzimidoyl-bridged derivatives $[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2X_2(CNMe)_2]$. After addition of excess of CNR (R = Me, Bu^t) terminal pentachlorobenzimidoyl complexes $[Pd\{\mu\text{-}C(C_6Cl_5)=NMe\}X(CNR)_2]$ can be isolated.

Introduction

We recently described the synthesis of some complexes of the type $[Pd(C_6X_5)Cl(CNR)_2]$ (X = F, Cl; R = Bu^t, cyclohexyl, *p*-tolyl and observed that for R = *p*-tolyl the synthesis had to be carried out at 0°C in order to avoid subsequent reaction [1]. For X = F we found that this subsequent reaction involved insertion of a *p*-MeC_6H_4NC molecule into the Pd–C_6F_5 bond [2], and it was evident that a similar process took place for X = Cl.

Pentachlorophenyl derivatives have been less studied than C_6F_5 derivatives, partly because it is more difficult to gain information about their structures from IR studies and the valuable information provided by ^{19}F NMR spectroscopy in the C_6F_5 derivatives is not available for the C_6Cl_5 analogues. Thus, in order to make ^1H NMR spectroscopy more sensitive to structural changes we chose MeNC instead of *p*-MeC_6H_4NC to study isonitrile insertion into Pd–C_6Cl_5 bonds.

Results and discussion

(A) Synthesis of the complexes:

Whereas the relevant reaction for pentafluorobenzimidoylpalladium complexes

0022-328X/86/$03.50

[2–5] was that represented in eq. 1 ($R = Me$, p-MeC_6H_4) attempts to carry out the same process starting from *trans*-$[Pd(C_6Cl_5)_2(CNMe)_2]$ led, in several solvents, to extensive decomposition to metallic palladium; the rate of decomposition increased in the sequence acetone > benzene ≫ benzonitrile.

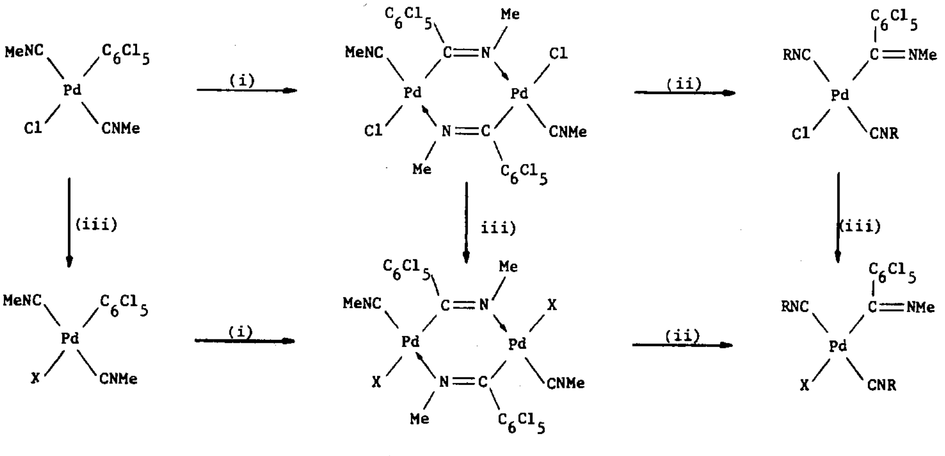
$$trans\text{-}[Pd(C_6F_5)_2(CNR)_2] + PdCl_2 \rightarrow [Pd_2(\mu\text{-}Cl)_2(C_6F_5)_2(CNR)_2] \rightarrow \{[Pd_2\{\mu\text{-}C(C_6F_5){=}NR\}_2](\mu\text{-}Cl)_2\}_2 \qquad (1)$$

Under various conditions neither $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_2(CNMe)_2]$ nor the expected final product $\{[Pd_2\{\mu\text{-}C(C_6Cl_5){=}NMe\}_2](\mu\text{-}Cl)_2\}_2$ could be detected. The fact that the insertion step proceeds quite easily for *trans*-$[Pd(C_6Cl_5)Cl(CNMe)_2]$ (see below) suggests that the absence of the expected reaction is the result of the non-occurrence of the first step of the reaction, i.e. $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_2(CNMe)_2]$ is not formed. Unfortunately, no alternative method for the preparation of this complex is at present available and the study had to be carried out with the less versatile precursor *trans*-$[Pd(C_6Cl_5)Cl(CNMe)_2]$ which is easily prepared by the reaction shown in eq. 2.

$$[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_2(tht)_2] + 4\ CNMe \rightarrow 2\ trans\text{-}[Pd(C_6Cl_5)Cl(CNMe)_2] + 2\ tht \qquad (2)$$

From this precursor several related derivatives can be prepared, as shown in Scheme 1. Thus, refluxing *trans*-$[Pd(C_6Cl_5)Cl(CNMe)_2]$ in benzene gave a yellow solution from which the imidoyl-bridged derivative $[Pd_2\{\mu\text{-}C(C_6Cl_5){=}N(Me)\}_2Cl_2(CNMe)_2]$ was isolated.

Upon addition of a stoicheiometric amount of CNMe (CNMe/Pd 1/1) to a yellow CH_2Cl_2 solution of $[Pd_2\{\mu\text{-}(C_6Cl_5){=}NMe\}_2Cl_2(CNMe)_2]$ the colour fades, and crystallisation yields a mixture of starting material and a white product, *trans*-$[Pd\{C(C_6Cl_5){=}N(Me)\}Cl(CNMe)_2]$. This terminal imidoyl complex can be prepared in almost quantitative yield by adding an excess of CNMe to a suspension of $[Pd_2\{\mu\text{-}C(C_6Cl_5){=}N(Me)\}_2Cl_2(CNMe)_2]$ in diethyl ether; under these conditions



SCHEME 1. X = Br, I, SCN; R = Me, Bu^t; (i) benzene, reflux; (ii) diethyl ether, RNC excess; (iii) MX, acetone.

trans-$[Pd\{C(C_6Cl_5)=N(Me)\}Cl(CNMe)_2]$ is obtained as a white precipitate which can be filtered off and stored in the freezer. The product shows a marked tendency to loose CNMe at room temperature, even in the solid state, to regenerate the imidoyl-bridged dimer.

When the bridge splitting is carried out with $CNBu^t$ in place of CNMe the need to use a large excess of $CNBu^t$ leads, in addition to the bridge splitting, to a displacement of the coordinated CNMe by the stronger nucleophile $CNBu^t$, to give *trans*-$[Pd\{C(C_6Cl_5)=N(Me)\}Cl(CNBu^t)_2]$.

The chloro ligand in *trans*-$[Pd(C_6Cl_5)Cl(CNMe)_2]$ can be replaced easily by other halide or pseudohalide ligands to give complexes of the type *trans*-$[Pd(C_6Cl_5)X(CNMe)_2]$ (X = Br, I, SCN), which, like the chloro derivative, upon heating give the imidoyl-bridged dimers $[Pd_2\{\mu\text{-}C(C_6Cl_5)=N(Me)\}_2X_2(CNMe)_2]$; these, upon treatment with an excess of CNR, give the terminal imidoyl complexes *trans*-

TABLE 1

ANALYTICAL DATA AND YIELDS

Compound		Analysis (Found(calcd.)(%))			Yield	Colour
		N	C	H		
I	$[Pd(C_6Cl_5)Cl(CNMe)_2]$	5.98	25.62	1.34	95	white
		(5.92)	(25.37)	(1.28)		
II	$[Pd(C_6Cl_5)Br(CNMe)_2]$	5.26	23.81	1.28	89	pale yellow
		(5.41)	(23.20)	(1.17)		
III	$[Pd(C_6Cl_5)I(CNMe)_2]$	5.04	21.80	1.10	72	yellow
		(4.96)	(21.27)	(1.07)		
IV	$[Pd(C_6Cl_5)(SCN)(CNMe)_2]$	8.20	26.58	1.02	65	pale yellow
		(8.47)	(26.64)	(1.22)		
V	$[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2Cl_2(CNMe)_2]$	5.61	25.45	1.33	74	yellow
		(5.92)	(25.37)	(1.28)		
VI	$[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2Br_2(CNMe)_2]$	5.26	23.84	1.27	70	yellow
		(5.41)	(23.20)	(1.17)		
VII	$[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2I_2(CNMe)_2]$	5.08	21.21	1.15	74	yellow
		(4.96)	(21.27)	(1.07)		
VIII	$[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2(SCN)_2(CNMe)_2]$	8.39	26.98	1.25	38	yellow
		(8.47)	(26.64)	(1.22)		
IX	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}Cl(CNMe)_2]$	8.23	28.30	1.72	74	white
		(8.17)	(28.02)	(1.76)		
X	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}Br(CNMe)_2]$	7.58	25.81	1.70	60	white
		(7.52)	(25.79)	(1.62)		
XI	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}I(CNMe)_2]$	7.04	23.94	1.45	38	white
		(6.94)	(23.79)	(1.50)		
XII	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}(SCN)(CNMe)_2]$	10.10	28.92	1.55	87	white
		(10.43)	(29.08)	(1.69)		
XIII	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}Cl(CNBu^t)_2]$	7.02	36.40	3.51	73	pale yellow
		(7.02)	(36.12)	(3.54)		
XIV	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}Br(CNBu^t)_2]$	6.28	33.40	3.27	92	yellow
		(6.54)	(33.62)	(3.29)		
XV	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}I(CNBu^t)_2]$	5.89	31.69	3.10	60	yellow
		(6.09)	(31.33)	(3.07)		
XVI	*trans*-$[Pd\{C(C_6Cl_5)=NMe\}(SCN)(CNBu^t)_2]$	9.05	36.48	3.10	80	white
		(9.02)	(36.74)	(3.41)		

$[Pd\{C(C_6Cl_5)=N(Me)\}X(CNR)_2]$ (R = Me, Bu^t). Alternatively both the imidoyl-bridged and the terminal imidoyl derivatives can be obtained from the corresponding chloro complexes via metathetical reactions with alkaline salts MX. For the terminal imidoyl complexes the reaction has to be carried out with free CNR in the solution in order to avoid loss of CNR and subsequent formation of the imidoyl bridged dimer. The reaction of *trans*-$[Pd\{C(C_6Cl_5)=N(Me)\}Cl(CNMe)_2]$ with an excess of KI in acetone in the presence of free CNMe does not give the expected white $[Pd\{C(C_6Cl_5)=N(Me)\}I(CNMe)_2]$ but instead an orange product, which has been identified as $[PdI_2(CNMe)_2]$.

Analytical results and yields for all the complexes are given in Table 1.

(B) ^1H NMR and IR spectra

The ^{1}H NMR data and relevant IR absorptions for the complexes are listed in Table 2.

The ^{1}H NMR spectra of the $[Pd(C_6Cl_5)X(CNMe)_2]$ derivatives I—IV show only one resonance for the methyl groups, as expected for a *trans* geometry. The imidoyl-bridged dimers $[Pd_2\{\mu\text{-}C(C_6Cl_5)=NMe\}_2X_2(CNMe)_2]$ (V–VIII) show only two methyl resonances, one for the methyl (isonitrile) group and one for the methyl (imidoyl) group indicating that only one isomer is formed, and their structure was assigned using the reasoning followed in interpreting our previous results on the related C_6F_5 derivatives [3]. The two methyl resonances are very close to each other and overlap almost completely for complex V; the assignments are based on the observation of a consistently larger $\nu_{1/2}$ (lower peaks for equal integrations) for the isonitrile than for the imidoyl signals, both in these and in the terminal imidoyl complexes IX–XII. In the latter, the observation of two signals (1/2 ratio) confirms the *trans* geometry of the complexes, and the different integrations for the signals allow clear distinction between the methyl(imidoyl) and the methyl(isonitrile) signal, even when both peaks have almost the same height. Finally, the terminal imidoyl complexes with CNBu^t XIII–XVI are also assigned a *trans* geometry on the basis of the observation of only one signal for the Bu^t groups.

The IR spectra give less information about the geometry. The $\nu(C\equiv N)$ absorptions are observed in the range 2300–2200 cm^{-1} for all the complexes, but fewer absorptions than predicted by group theory are generally observed. Thus for *trans*-$[Pd(C_6Cl_5)X(CNMe)_2]$ (C_{2v} symmetry) two $\nu(C\equiv N)$ absorptions ($A_1 + B_1$) are predicted but only one is observed; similarly, two absorptions ($A + B$) are predicted for the complex $[Pd_2\{\mu\text{-}C(C_6Cl_5)_2=NMe\}_2X_2(CNMe)_2]$ (C_2 symmetry) and only one is observed; for most of the complexes *trans*-$[Pd\{C(C_6Cl_5)=NMe\}X(CNR)_2]$ (C_s symmetry, provided that the imidoyl plane is orthogonal to the square plane, as observed in the X-ray structure [5]), two absorptions are observed in agreement with the prediction of two active IR modes ($A' + A''$), but the one at higher wavenumbers is noticeably weaker. We suggest that for most of the complexes considered, even when the two stretching modes are predicted to be IR active the symmetric one could possibly involve only very small changes in the dipole moment of the molecule, leading to a very low intensity of the corresponding absorption.

Imidoyl $\nu(C=N)$ absorptions are observed in the range 1660–1550 cm^{-1} as fairly broad bands. Two bands ($A + B$ modes) are generally observed for the imidoyl-bridged complexes and only one (A' mode) for the terminal imidoyl complexes, in good agreement with the predictions. It is notherworthy that the $\nu(C=N)$ absorption

TABLE 2

^{1}H NMR CHEMICAL SHIFTS [a] AND RELEVANT IR ABSORPTIONS (cm^{-1})

Compound	R(isoc.)	Me(imid.)	ν(C≡N)	ν(C=N)	ν(Pd–X) [b]	Other	
I	3.39	–	2251	–	312	942 830 672, 622	474
II	3.40	–	2251	–	255	942 830 672, 620	472
III	3.48	–	2245	–	–	942 830 672, 612	468
IV	3.50	–	2247	–	2119	940 830 672, 617	474, 467
V	3.34	3.33	2257	1628, 1590	294, 282	1015, 942 835 693, 662	542, 461, 442
VI	3.30	3.35	2251	1624, 1589	–	1010, 940 835 692, 661	538, 459, 441
VII	3.35	3.48	2247	1617, 1584	–	1008, 935 835 692, 661	536, 456, 439
VIII	3.45	3.22	2255	1591	2115, 2080	1008, 940 840 687, 658	533, 450, 435
IX	3.38	3.72	2240	1643	260	998, 945 800 657, 640, 595	522, 463, 448
X	3.39	3.72	2267, 2239	1632	–	990, 945 797 657, 640, 592	522, 462, 448
XI	3.42	3.74	2257, 2226	1632	–	990, 945 795 654, 640, 592	520, 462, 443
XII	3.44	3.72	2251	1650	2111	995, 960 795 655, 640, 590	522, 457, 440
XIII	1.51	3.77	2234, 2209	1654	273	995, 945 797 652, 638, 595	530, 515
XIV	1.56	3.84	2231, 2205	1653	–	996, 945 797 653, 639, 595	528, 513
XV	1.54	3.78	2205(br)	1630	–	990, 950 792 654, 647, 595	530, 512
XVI	1.51	3.71	2231, 2211	1652	2111	896, 945 795 656, 640, 585	525, 507

[a] In $CDCl_3$, δ, ref. TMS, all signals are singlets. [b] ν(C≡N) for X = SCN.

in all the complexes with terminal imidoyl groups appears at higher wavenumbers that any of the ν(C=N) absorptions in the parent complexes containing bridging imidoyl groups, supporting the criterion previously suggested for distinguishing between these two cases [5].

The low wavenumbers for the ν(Pd–Cl) modes in the imidoyl derivatives reflect the very high *trans* influence of the imidoyl group. On the other hand in the thiocyano derivatives the pseudo-halogen gives rise to absorptions near 2100 cm^{-1} related to the ν(C≡N) mode. In the mononuclear derivatives this absorption appears above 2100 cm^{-1}, and this has been suggested to indicate *S*-coordination [6,7]; the ratio of the area of the SCN absorption to that of the ν(C=O) absorption of salicylic acid as internal standard [8], gives "internal standard ratios" of ca. 0.75, which also points to *S*-coordination.

Bands appearing in ca. 950 cm^{-1} can be assigned to ν(N–C) of the isonitrile ligands according to previous reports on MeNC complexes of palladium [9]. It seems reasonable to assign the absorption in ca. 1000 cm^{-1}, observed only in the imidoyl derivatives, to ν(N–C) in the imidoyl group.

Absorptions in the range 840–580 are related to the C_6Cl_5 group [10]. Except for the absorption at ca. 670 cm^{-1} these bands are weak or very weak in the pentachlorophenyl derivatives I—IV, but medium to strong in the pentachlorobenzimidoyl complexes (V–XVI).

One or two bands in the range 475–435 cm^{-1} in the CNMe derivatives can be assigned to ν(Pd–C) vibrations of the Pd–CNMe bonds on the basis of previous analyses [9]. Thus the band in the range 542–525 cm^{-1} which is observed only in the pentachlorobenzimidoyl derivatives can be tentatively assigned to a Pd–C(imidoyl) stretching mode; the same band, but at wavenumbers about 20 cm^{-1} higher, is found in the spectra of related pentafluorbenzimidoyl complexes [2–5]. Finally, the medium intensity band at ca. 510 cm^{-1}, which appears only in the $CNBu^t$ derivatives, and is also found in related palladium complexes containing $CNBu^t$, can reasonably be assigned to a Pd–$CNBu^t$ stretching mode.

Experimental

The C, H and N analyses were carried out with a Perkin–Elmer 240B microanalyser. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer using Nujol mulls between polyethylene plates. ^1H NMR spectra were recorded on Varian XL-200 or Perkin–Elmer R12B instruments. $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_2(tht)_2]$ [11] CNMe and $CNBu^t$ [12] were prepared by published procedures.

trans-$[Pd(C_6Cl_5)Cl(CNMe)_2]$ (I)

A stoicheiometric amount of MeNC was added to 500 mg of $[Pd_2(\mu\text{-}Cl)_2(C_6Cl_5)_2(tht)_2]$ suspended in 20 ml of acetone and the mixture was stirred at 0°C for 2 h. Additional cold acetone was then added to dissolve the white precipitate, and the solution was filtered to remove traces of black Pd then evaporated without heating to small volume, to give a white precipitate. Precipitation was completed by addition of diethyl ether, and the white complex I was filtered off, washed with diethyl ether, and dried in the air.

The product must be stored in the freezer to avoid the insertion process which takes place during a few months at room temperature even in the solid state.

trans-[Pd(C_6Cl_5)X(CNMe)$_2$] (X = Br (II), I (III), SCN (IV))

Complex I (200 mg) in 5 ml of acetone was treated at 0°C with a slight excess of LiBr, NaI, or KSCN for 2 h. Then 30 ml of CH_2Cl_2 and 30 ml of water (both cold) were added, and the organic phase was separated, dried with $MgSO_4$, and evaporated without heating to small volume. Upon addition of cool n-hexane and stirring in an ice bath the desired product separated, and was filtered off, dried, and stored in the freezer to avoid the insertion, which takes place even in the solid state.

[Pd$_2${μ-C(C_6Cl_5)=NMe}$_2$X$_2$(CNMe)$_2$] (X = Cl (V), Br (VI), I (VII), SCN (VIIII))

Method 1. A mixture of 200 mg of *trans*-[Pd(C_6Cl_5)X(CNMe)$_2$] and benzene (20 ml) was refluxed for 12 h. The benzene was evaporated off and 20 ml of diethyl ether were added, to give a yellow precipitate. This was filtered off and dried.

Method 2. Complexes VI-VIII were also obtained from V by methathesis reactions with an excess of the corresponding alkaline salt in refluxing acetone for 2 h. The resulting solution was evaporated to dryness and the product was extracted with 30 ml of $CHCl_3$. Drying of the extract with $MgSO_4$, followed by evaporation and addition of diethyl ether gave the product.

trans-[Pd{C(C_6Cl_5)=NMe}X(CNMe)$_2$] (X = Cl (IX), Br (X), I (XI), SCN (XII))

An excess of CNMe (Pd/CNMe 2.5) was added to 500 ml of [Pd$_2${μ-C(C_6Cl_5)=NMe}$_2$X$_2$(CNMe)$_2$] suspended in 20 ml of diethyl ether. The solution was stirred for 2 h to give a white solid, which was filtered off, washed with cold diethyl ether, dried, and stored in the freezer.

trans-[Pd{C(C_6Cl_5)=NMe}X(CNBu^t)$_2$] (X = Cl (XIII), Br (XIV), I (XV), SCN (XVI)

An excess of CNBu^t (Pd/CNBu^t 2.5) was added to 500 mg of [Pd$_2${μ-C(C_6Cl_5)=NMe}$_2$X$_2$(CNMe)$_2$] suspended in 20 ml of diethyl ether and the mixture was stirred for 2 h to give a colorless solution. Addition of 20 ml of cyclohexane and evaporation of the diethyl ether gave a white product, which was filtered off, washed with cyclohexane, air dried, and stored in the freezer.

Acknowledgement

The authors thank the Comision Asesora de Investigación Científica y Técnica for financial support (Project 1522/82).

References

1 R. Usón, J. Forniés, P. Espinet and E. Lalinde, J. Organomet. Chem., 220 (1981) 393.
2 R. Usón, J. Forniés, P. Espinet and E. Lalinde, J. Organomet. Chem., 254 (1983) 371.
3 R. Usón, J. Forniés, P. Espinet and E. Lalinde, P.G. Jones and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., (1982) 2389.
4 R. Usón, J. Forniés, P. Espinet, E. Lalinde, A. Garcia, P.G. Jones, K. Meyer-Base and G.M. Sheldrick, J. Chem. Soc., Dalton Trans., in press.
5 R. Usón, J. Forniés, P. Espinet, E. Lalinde, P.G. Jones and G.M. Sheldrick, J. Organomet. Chem., 288 (1985) 249.
6 J.L. Burmeister and F. Basolo, Inorg. Chem., 3 (1964) 1587.
7 R.N. Keller, N.B. Johnson and L.L. Westmoreland, J. Am. Chem. Soc., 90 (1968) 2729.

8 R.A. Bailey, T.W. Michelsen and W.N. Hills, J. Inorg. Nucl. Chem., 33 (1971) 3206.
9 E. Garciafigeroa and C. Sourisseau, Nouv. J. Chim., 2 (1978) 593.
10 J. Casabó, J.M. Coronas and J. Sales, Inorg. Chim. Acta, 11 (1974) 5 and ref. therein.
11 R. Usón, J. Forniés, R. Navarro and M.P. García, Inorg. Chim. Acta, 33 (1979) 69.
12 W.P. Weber, G.W. Gokel and I.K. Ugi, Angew. Chem. Int. Ed. Eng., 11 (1972) 530.