Cyclometallated complexes of Pd(II) and Pt(II) with 2-phenylimidazoline

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Abstract

Cyclometallated complexes of Pd(II) and Pt(II) with 2-phenylimidazoline were synthesized. The complexes were characterized by ^1H and ^{13}C NMR spectroscopy, involving the use of COSY-45, HMQC and HMBC techniques, which allow unambiguous assignment of the NMR parameters. An X-ray diffraction study of $[Pd(C_6H_4-C_3H_5N_2)(\mu-OAc)]_2$ confirmed that cyclometallation of the 2-phenylimidazoline ligand had occurred.

1. Introduction

Recently we reported a series of cyclometallated compounds derived from α-benzoylbenzilidenimines [1], its biochemical properties and antiproliferative activity [2]. In continuation of our studies, we describe here the synthesis and characterization of cyclometallated compounds from 2-phenylimidazoline. Our interest in imidazole derivatives arises from the fact that the only reported cyclometallated complexes with imidazoles as ligands are those derived from *N*-substituted imidazole [3,4], and that planar compounds containing as minimum three fused rings belong to a class of compounds which can intercalate into DNA and show cytotoxic activity [5]. For these reasons, we thought that 2-phenylimidazoline, in which the NH group is not protected and the heterocyclic ring is not aromatic might give the desired cyclometallated compounds. The compounds obtained were characterized by ^1H and ^{13}C NMR spectroscopy involving COSY-45, HMQC and HMBC techniques and the μ-acetate compound $[Pd(C_6H_4-C_3H_5N_2)(\mu-OAc)]_2$, 2, was characterized by X-ray diffraction.

2. Results and discussion

The reaction of Pd(OAc)$_2$ with 2-phenylimidazoline (Imd) in glacial HOAc under N$_2$ at 60°C gives the cyclometallated complex $[Pd(C_6H_4-C_3H_5N_2)(\mu-OAc)]_2$, 2. The metathetical reaction of 2 with NaCl is reported to give $[Pd(C_6H_4-C_3H_5N_2)(\mu-Cl)]_2$, 3. This complex was also obtained by reaction of K$_2$PdCl$_4$ with Imd in H$_2$O at 70°C by refluxing a solution of the complex $[PdCl_2(C_6H_5-C_3H_5N_2)_2]$, 1, in MeOH. Compound 1 was previously obtained by reaction of Li$_2$PdCl$_4$ with Imd in MeOH at 20°C. The orthoplatinated compound $[Pt(C_6H_4-C_3H_5N_2)(\mu-Cl)]_2$, 4, could only be obtained by the reaction of K$_2$PtCl$_4$ with Imd in HOAc at 60°C, under N$_2$. When the reactions were carried out in other solvents or when the starting material was $[Pt(\eta^3-C_4H_7)(\mu-Cl)]_2$, a mixture of products was obtained. The cycloplatinated complex 4 was identified by ^1H NMR spectroscopy but attempts to separate it were unsuccessful.

The microanalytical data for the complexes (see Experimental section) are consistent with the proposed structures. The IR spectrum of complex 1 shows two stretching vibrations, at 348 and 306 cm^{-1}, assignable to ν_{as}(Pd–Cl) and ν_{as}(Pd–N), respectively, in the region expected for the *trans* isomer. Complex 2 showed two

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Table 1

^{1}H NMR data (ppm) for Imd, palladium and platinum complexes [a]
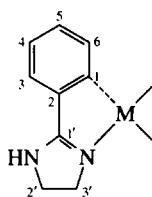
M = Pd, Pt

Atom	Imd [b]	Imd [c]	1 [c]	2 [d]	3 [c]	4 [c]
H1	7.75, m	7.83, m	8.49, d (7.2)			
H3	7.75, m	7.83, m	8.49, d (7.2)	7.07, m	7.39, dd (2.5, 7.1)	7.39, m
H4	7.39, m	7.45, m	7.57, m	6.85, m	7.13, m	7.11, m
H5	7.42, m	7.45, m	7.57, m	7.01, m	7.13, m	7.11, m
H6	7.39, m	7.45, m	7.57, m	7.00, m	7.99, dd (2.0, 6.9)	8.12 ,m
H2'	3.70, s	3.60, s	3.70, A_2B_2	[e]	3.72, m	3.81, m
H3'	3.70, s	3.60, s	3.70, A_2B_2	[e]	3.72, m	3.81, m
NH			7.98, s br	7.33, s br	8.66, s br	8.85, s br
CH_3				2.14, s		

[a] The numbers in parentheses correspond to $J(^1H-^1H)$ in Hz.
[b] $CDCl_3$ as solvent.
[c] DMSO-d_6 as solvent.
[d] $CDCl_3$ + HOAc-d_4 as solvent.
[e] H2'(a), H3'(a) at 2.55 ppm, 2H, and H2'(b), H3'(b) 3.29, m, 2H.

strong bands at 1573 and 1417 cm^{-1} corresponding to the ν_{as}COO and ν_sCOO stretching vibrations, respectively, of bridging of acetate [6]. Complex **3** showed two ν_{as}(Pd–Cl) bands, at 289 and 224 cm^{-1}. Since a carbon atom has a higher *trans* influence than a nitrogen atom, the higher frequency band is attributed to the stretching vibration ν_{as}(Pd–Cl) *trans* to the nitrogen atom and the lower frequency band ν_{as}(Pd–Cl) *trans* to the σ-bonded carbon [7]. The IR spectrum of complex **4** is similar to that of complex **3**, but the two ν_{as}(Pt–Cl) stretching vibrations are found at 308 and 228 cm^{-1}.

The ^{1}H and ^{13}C NMR parameters for the ligand and the Pd and Pt complexes are given in Tables 1 and 2.

The assignments of the parameters were based an unambiguous COSY-45, HMQC and HMBC data.

In the case of complex **1** these are downfield shifts of all protons relative to those of the free ligand as a result of the N coordination to palladium. The largest downfield shifts are found for the *ortho* protons of the aromatic ring, and are a consequence of conjugation with the double bond of the imidazoline ring.

The procedure used for the assignment of the signals from the cyclometallated complexes was as follows. In the case of complex **2**, for example, after an HMQC study had identified the quaternary carbons, an HMBC study allowed unambiguous assignment of C1' and H3,

Table 2

^{13}C NMR data (ppm) for Imd, palladium and platinum complexes (see carbon numbers in Table 1)

Atom	Imd [b]	Imd [c]	1 [c]	2 [d]	3 [c]	4 [c]
C1	126.8	127.2	128.6	148.0	152.0	140.5
C2	130.0	130.7	131.5	134.7	135.4	134.1
C3	126.8	127.2	128.6	123.3	125.1	124.9
C4	128.1	128.3	128.3	122.7	124.8	123.5
C5	130.3	130.3	128.3	128.6	130.3	131.2
C6	128.1	128.3	128.3	130.9	131.9	133.1
C1'	164.7	164.0	166.1	172.3	173.9	176.6
C2'	50.0	49.7	42.8	43.0	43.9	44.2
C3'	50.0	49.7	55.3	50.0	51.4	50.3
CH_3 [a]				19.3		
C7 [a]				191.2		

[a] Corresponding to acetate methyl group.
[b] $CDCl_3$ as solvent.
[c] DMSO-d_6 as solvent.
[d] $CDCl_3$ + HOAc-d_4 as solvent.

since C1' (172.3 ppm) is the only carbon that shows connectivity with a unique proton signal of the aromatic ring, H3 (7.07 ppm). Once H3 was determined, we could assign C1 (148.0 ppm). The connection of C1 allows the assignment of H5 (7.01 ppm). Assignments of H4 and H6, however, required additional COSY-45 experiments. In respect of the protons of the imidazoline ring, the carbons C2' at 43.0 ppm and C3' at 50.0 ppm show connectivity with the two proton signals at 2.55 and 3.29 ppm in HMQC. This indicates that the protons have different space positions. The signal at 2.55 ppm is assigned to H2' and H3', which are oriented to the inside of the structure, in an "open book" arrangement. These protons could experience anisotropic effects from the phenyl ring of the other Imd ligands of the dimer, and so be shifted towards higher field. Therefore, the signal at 3.29 ppm is assigned to protons H2' and H3' oriented to the outside of the "open book". Since the broad signal at 7.33 ppm disappears when D_2O is added, this signal is assigned to the proton of the NH group. The observed upfield shift for all hydrogen atoms relative to those in the free ligand, Imd, can be attributed to mutual shielding between the ligands that lie parallel to each other [8]. The signal at 2.14 ppm was attributed to the methyl group of the bridge acetate. The presence of only one signal from the methyl group is evidence for an *anti* disposition of the ligands.

The FAB mass spectrum of complex 2 shows peaks at m/z 622.0, 563.1 and 502.0 assigned to $[Pd(C_6H_4C_3H_5N_2)(\mu\text{-}OAc)]_2^+$, $[Pd_2(C_6H_4C_3H_5N_2)_2\text{-}(\mu\text{-}OAc)]^+$ and $[Pd(C_6H_4C_3H_5N_2)]_2^+$ ions, respectively (account being taken of the distribution of palladium isotopes).

The ^1H NMR spectral data for complexes 3 and 4 are listed in Table 1. The similarity between them suggests that the complexes have analogous structures. The deshielding of H2' and H3' can be attributed to the M–N coordination. The proton *ortho* to the Pd–C bond, H6, is strongly deshielded after cyclometallation (the effect is higher for the platinum complex 4). This can be attributed to the proximity to the metallated sites of the electron delocalization in the chelate ring [9] or to the increase in the C substitution [10]. However for complex 2 we observed a slight increase in the shielding upon cyclopalladation, and this can be attributed to the "open-book" conformation. Although the H3 protons, *meta* to palladium or platinum, should be less affected by cyclometallation, the large shielding observed could be due to cyclopalladation. The upfield shift observed for H4, *para* to palladium, clearly indicates that there is some metal–ligand back-bonding [11]. Signals at 8.66 ppm from complex 3 and at 8.85 ppm from complex 4 which disappear when D_2O is added, were assigned to NH protons.

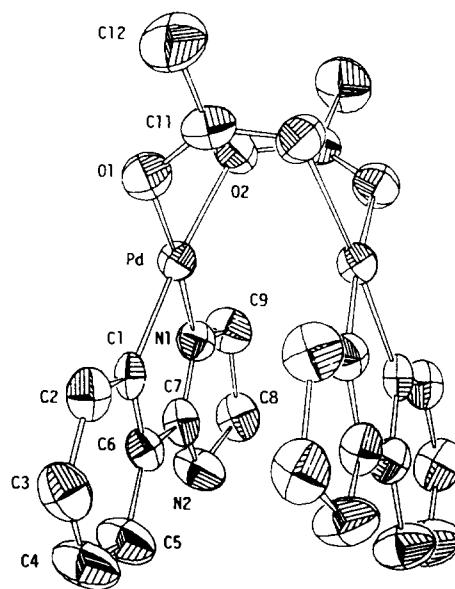The most significant differences between the ^{13}C NMR data for the palladium and platinum complexes

Fig. 1. Molecular structure of 2 showing the atom numbering scheme. H atoms have been omitted for clarity.

are in chemical shifts for C1 and C1', both directly involved in the cyclometallated ring. The high deshielding observed for C1 and C1' can be attributed to electronic perturbations due to the metal itself, and so different for palladium and platinum [12]. It is noteworthy that in these spectra all the signals appear further downfield, since the structure of the complexes is unfolded and planar. The proposed structures of complexes 3 and 4 could not be confirmed from the FAB mass spectra because they undergo significant decomposition under the conditions used for such spectra.

2.1. Crystal structure of $[Pd(C_6H_4C_3H_5N_2)(\mu\text{-}OAc)_2]_2$ (2)

For the X-ray diffraction study, a complex 2 was recrystallized from HOAc and the crystals contained two molecules of the acid for each molecule of the complex. The scheme used for atom labelling and an ORTEP drawing of the molecule on are shown in Fig. 1. Atomic parameters for the non-hydrogen atoms are listed in Table 3. Significant bond distances and bond angles are listed in Table 4.

In the crystal each ($\mu\text{-}OAc)_2$-bridged dimer is hydrogen bonded to two acetic acid molecules. Each palladium atom is bonded to four atoms (the nitrogen, the *ortho* carbon atom of the phenyl ring and one oxygen atom from each of the two bridging acetates) in a square-planar coordination slightly distorted towards tetrahedral geometry. The dihedral angle between the N–Pd–C and O–Pd–O planes is 5.3(3)°, the coordination planes of the palladium atom being tilted at an angle of 26.1(3)°. Although most crystal structures of cyclopalladated complexes show a square-planar coordi-

Table 3
Atomic parameters for the non-hydrogen atoms of 2

Atom	x/a	y/b	c/z
Pd	0.65820(8)	0.16740(7)	0.31530(4)
O1	0.78460(86)	0.08940(70)	0.36750(35)
O2	0.60000(81)	0.26410(73)	0.39000(35)
O3	0.49460(126)	0.23100(111)	0.53790(54)
O4	0.44340(141)	0.15200(127)	0.45490(69)
N1	0.53400(83)	0.23280(77)	0.26030(39)
N2	0.46860(111)	0.25880(93)	0.16760(41)
C1	0.70830(100)	0.09160(87)	0.24240(49)
C2	0.80060(107)	0.01530(101)	0.23440(57)
C3	0.82980(123)	−0.02020(98)	0.17760(63)
C4	0.77210(149)	0.01950(128)	0.12870(59)
C5	0.67780(139)	0.09550(117)	0.13490(55)
C6	0.64520(108)	0.12930(81)	0.19170(50)
C7	0.54950(106)	0.20810(90)	0.20470(52)
C8	0.39950(113)	0.33890(110)	0.20120(55)
C9	0.43350(111)	0.31300(103)	0.26570(58)
C11	0.87010(113)	0.13580(103)	0.39590(52)
C12	0.94000(150)	0.07160(126)	0.44150(69)
C13	0.43690(196)	0.16720(188)	0.51480(97)
C14	0.34470(274)	0.09220(207)	0.54030(111)

Fig. 2. ORTEP drawing of the packing cell of 2. Dashed lines represent hydrogens bonds.

nation geometry, there have been recent examples of tetrahedral distortion about the palladium atom [1a,1b,13], probably due to the folded open-book shape. The Pd–N and Pd–C bonds form the basis of a five-membered chelate ring. The Pd–N bond length of 1.990(9) Å is slightly shorter than the predicted value of 2.01 Å. The Pd–C bond distance of 1.96(1) Å is substantially shorter than the predicted value of 2.05 Å but similar to corresponding distances in other aryl complexes [1a,1b,13]. This suggests that there is some multiple-bond character in the Pd–C linkages as a result of metal-to-ligand back-bonding [1a,1b,13,14], a view that is supported by the NMR data.

The Pd–O bond *trans* to nitrogen is significantly shorter (2.036(9) Å) than that *trans* to the aromatic carbon (2.151(8) Å) as a consequence of the different *trans* influence.

The Pd–Pd distance of 2.832(1) Å is in the range observed for other Pd complexes for which metal–metal interactions have been suggested [15].

Hydrogen-bonding involving acetic acid gives rise to polymeric chains (see Fig. 2). The group O4–H41 bonds to the O2 of the acetate group (O2 · · · H41, 1.54(13) Å; O2 · · · O4, 2.62(1) Å; the O2–H41–O4 angle is 150(8)°) and atom O3 bonds to the group N2–H21 (O3 · · · H21, 1.99(1) Å; O3 · · · N2, 2.93(1) Å; the O3–H21–N2 angle is 153.0(7)°) (Fig. 2).

The potential of these compounds as antitumour drugs and the possibility of binding to DNA by intercalation are currently being investigated.

Table 4
Bond lengths (Å) and selected angles (°) in complex 2

Pd–O1	2.036(9)	C1–C2	1.38(2)	N1–Pd–C1	81.7(4)
Pd–O2	2.151(8)	C1–C6	1.40(1)	O2–Pd–C1	174.5(4)
Pd–N1	1.990(9)	C2–C3	1.39(2)	O2–Pd–N1	93.9(3)
Pd–C1	1.96 (1)	C3–C4	1.35(2)	O1–Pd–C1	94.3(4)
O1–C11	1.26 (1)	C4–C5	1.38(2)	O1–Pd–N1	175.4(4)
O3–C13	1.13 (2)	C5–C6	1.39(2)	O1–Pd–O2	90.2(3)
O4–C13	1.36 (3)	C6–C7	1.44(1)		
N1–C7	1.30 (1)	C8–C9	1.53(2)		
N1–C9	1.47 (1)	C11–C12	1.50(2)		
N2–C7	1.36 (1)	C13–C14	1.47(3)		
N2–C8	1.45 (2)				

3. Experimental section

Solvents were purified and dried by standard methods [16]. Palladium chloride, potassium tetrachloropalladate and potassium tetrachloroplatinate were purchased from Johnson-Mathey and palladium(II) acetate and 2-phenylimidazoline from Aldrich-Chemie.

Elemental analyses were carried out on a Perkin-Elmer 240B elemental analyser. The IR spectra in the 4000–200 cm^{-1} region were recorded as polyethylene or KBr pellets on a Perkin-Elmer 1650 spectrophotometer. The NMR spectra were obtained for solution in CDCl$_3$ (TMS as internal reference) or DMSO-d_6 (undeuterated residual DMSO as reference) and were recorded on a Bruker AC-200 or AMX-300 spectrometer. The assignments of the NMR data were based on the chemical shifts and by use of HMQC[17–19] (^{1}H-detected heteronuclear multiple-quantum coherence), HMBC [18,20] (heteronuclear multiple-bond connectivity) and COSY-45 methods when necessary. The mass spectra were obtained with a WG AutoSpec, under FAB conditions, with positive ions (3-nitrobenzyl alcohol as matrix).

3.1. X-ray structural study of 2

Recrystallization of complex 2 by slow evaporation of an acetic acid solution gave yellow air-stable crystals. A crystal data and details of data collection and refinement are given in Table 5. A prismatic crystal was coated with epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting to the values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for palladium were taken from the International Tables for X-Ray Crystallography [21]. The structure was solved by Patterson and Fourier methods. An empirical absorption correction [22] was applied at the end of the isotropic refinement.

An AcOH molecule of solvation was located. Final mixed refinement with unit weights and fixed isotropic factors and coordinates for H atoms, except for that of the acetic acid molecule (H41) whose position was located in a Fourier difference map as the higher peak, and its coordinates were refined. The final synthesis showed no significant electron density.

Most of the calculations were carried out with the X-RAY 80 system [23] and PARST [24], on a VAX 11/750 computer.

Tables of thermal parameters and of H-atom coordinates and a complete list of bond lengths and angles have been deposited at the Cambridge Crystallographic Data Control.

3.2. Synthesis of [PdCl$_2$(C$_6$H$_5$C$_3$H$_5$N$_2$)$_2$] (1)

To a solution of Li$_2$PdCl$_4$ prepared in situ from PdCl$_2$ (1 mmol) and LiCl (2 mmol) in 10 ml of methanol was added a solution of lmd (2 mmol) in 5 ml of methanol. The mixture was stirred for 3 days at 20°C and the yellow precipitate then filtered off, washed with methanol and dried under vacuum (66.2% yield). Anal. Found: C, 45.71; H, 4.23; N, 11.83. Calc. for PdCl$_2$C$_{18}$H$_{20}$N$_4$, C, 45.99; H, 4.26; N, 11.92%.

3.3. Synthesis of [Pd(C$_6$H$_4$C$_3$H$_5$N$_2$)(μ-OAc)]$_2$(2)

Method 1

Palladium(II) acetate (1 mmol) dissolved in 20 ml of glacial acetic acid under dinitrogen and a solution of lmd (1 mmol) in 5 ml of glacial acetic acid was added. The solution was stirred at 60°C for 2 h, the solvent then evaporated under vacuum and the residue extracted three times with 100 ml of CH$_2$Cl$_2$–H$_2$O (1:1). The combined extracts were dried over Na$_2$SO$_4$, filtered and concentrated on a rotary evaporator. Slow evaporation gave yellow crystals which were filtered off, washed with hexane and dried under vacuum (49.6% yield).

Method 2

To a suspension of complex 3 (0.5 mmol) in acetone (10 ml) was added silver acetate (1 mmol). The mixture

Table 5
Crystal data and details of data collection and refinement

Crystal data	
Formula	C$_{22}$H$_{24}$N$_4$O$_4$Pd$_2$·2C$_2$H$_4$O$_2$
Crystal system and space group	Orthorhombic, P$_{ccn}$
Unit cell dimensions: a, b, c (Å)	10.747(4), 12.295(7), 22.496(4)
Packing	
V (Å^3), Z	2972(2), 4
D$_c$ (g cm^{-3}), M, F(0, 0, 0)	0.83, 740.8, 1488
μ (cm^{-1})	24.3
Experimental data	
Diffractometer	
	Enraf–Nonius CAD-4
	Graphite-monochromated
	Mo K α (λ = 0.71069 Å)
Scan technique	Ω/2θ
Data collected	(0, 0, 0) to (13, 15, 28)
Reflections colected	3248
Unique data	1719
Unique data, I > 2σ(I)	1529
Std. reflections	3 reflections every 100 min, 10% decay
Solution and refinement	
Solution	Patterson
Refinement	Least squares on F$_{obs}$
W scheme	Unit
R, R$_w$	0.049, 0.056
Average shift/error	0.02

was stirred for 24 h and the yellow solution obtained was filtered and the solvent slowly evaporated. The precipitate was filtered off, washed with hexane and dried under vacuum (72.2% yield). Anal. Found: C, 42.81; H, 3.81; N, 8.91. Calc. for $Pd_2O_4C_{22}H_{24}N_4$, C, 42.50; H, 3.86; N, 9.02%.

3.4. Synthesis of $[Pd(C_6H_4C_3H_5N_2)(\mu-Cl)]_2$ (3)

Method 1

To a solution of Li_2PdCl_4 prepared in situ from $PdCl_2$ (1 mmol) and LiCl (2 mmol) in 10 ml of methanol was added a solution of lmd (1 mmol) in 5 ml of methanol. This solution was stirred and refluxed for 24 h. The dark-orange precipitate formed was filtered off, washed with methanol and dried under vacuum (47.8% yield).

Method 2

To a solution of K_2PdCl_4 (1.5 mmol) in 10 ml of water was added lmd (1.5 mmol). The mixture was stirred at 70°C for 2 h and the precipitated then filtered off, washed with water, acetone and diethyl ether and dried under vacuum (51.7% yield).

Method 3

To a stirred solution of complex 2 (0.5 mmol) in acetone (10 ml) was added an excess of a solution of sodium chloride in water (0.01 mol l^{-1}). The mixture was stirred for 24 h and the precipitate then filtered off, washed with water and acetone and dried under vacuum (48.3% yield). Found: C, 37.32; H, 3.10; N, 9.68. Calcd. for $Pd_2Cl_2C_{18}H_{18}N_4$, C, 37.62; H, 3.14; N, 9.75%.

3.5. Synthesis of $[Pt(C_6H_4C_3H_5N_2)(\mu-Cl)]_2$ (4)

To a suspension of K_2PtCl_4 (1.5 mmol) in 20 ml of acetic acid was added under dinitrogen a solution of lmd (1.5 mmol) in 15 ml of acetic acid. The mixture was stirred under dinitrogen at 60°C for 6 days, then the solid was filtered off, washed with acetic acid, water and acetone and dried under vacuum (48.3% yield). Anal. Found: C, 28.53; H, 2.23; N, 7.63. Calc. for $Pt_2Cl_2C_{18}H_{18}N_4$, C, 28.74; H, 2.41; N, 7.45%.

Acknowledgements

References

[1] (a) J.L. García-Ruano, I. López-Solera, J.R. Masaguer, C. Navarro-Ranninger, J.H. Rodríguez and S. Martínez-Carrera, *Organometallics*, 11 (1992) 3013; (b) J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger and J.H. Rodríguez, *Organometallics*, 12 (1993) 4104; (c) J.L. García-Ruano, I. López-Solera, J.R. Masaguer, M.A. Monge, C. Navarro-Ranninger and J.H. Rodríguez, *J. Organomet. Chem.*, 476 (1994) 111; (d) C. Navarro-Ranninger, I. López-Solera, A. Alvarez-Valdés, J.H. Rodríguez, J.R. Masaguer and J.L. García-Ruano, *J. Organomet. Chem.*, 476 (1994) 19.

[2] (a) C. Navarro-Ranninger, I. López-Solera, J.M. Pérez, J. Rodríguez, J.L. García-Ruano, P.R. Raithby, J.R. Masaguer and C. Alonso, *J. Med. Chem.*, 36 (1993) 3795; (b) C. Navarro-Ranninger, I. López-Solera, J.M. Pérez, J.R. Masaguer and C. Alonso, *Appl. Organomet. Chem.*, 7 (1993) 57.

[3] K. Hiraki, Y. Fuchita, H. Nakaya and S. Takakura, *Bull. Chem. Soc. Jpn.*, 52 (1979) 2531.

[4] A. Suárez, J.M. Vila, M.T. Pereira, E. Gayoso and M. Gayoso, *Synth. React. Inorg. Met.-Org. Chem.*, 20 (1990) 1425.

[5] M.V. Beusichem and N. Farrell, *Inorg. Chem.*, 31 (1992) 634.

[6] K. Nakamoto, *IR and Raman Spectra of Inorganic and Coordination Compounds*, Wiley-Interscience, New York, 4th edn., 1986.

[7] B. Crociani, T. Boshi, R. Pieetropaolo and U. Belluco, *J. Chem. Soc. A* (1970) 531.

[8] G. Balavoine, J.C. Clinet, P. Zerbib and K. Boubekeur, *J. Organomet. Chem.*, 389 (1990) 259.

[9] S. Chakladar, P. Paul, K. Venkatsubramanian and K. Nag, *J. Chem. Soc., Dalton Trans.* (1991) 2669.

[10] G.R. Newkome, K.J. Theriot, F.R. Fronczek and B. Villar, *Organometallics*, 8 (1989) 2513.

[11] M.A. Gutiérrez and G.R. Newkome, *J. Organomet. Chem.*, 202 (1980) 341.

[12] A. Albinati, S. Affolter and P.S. Pregosin, *Organometallics*, 9 (1990) 1953.

[13] (a) G.R. Newkome, W.E. Puckett, V.K. Grupta and G.E. Kiefer, *Chem. Rev.*, 86 (1986) 451; (b) I. Omae, *Coord. Chem. Rev.*, 83 (1988) 137.

[14] J. Selbin, K. Abbond, S.F. Watkins, M.A. Gutierrez and F.R. Fronczek, *J. Organomet. Chem.*, 241 (1983) 259.

[15] (a) J. Vicente, M.T. Chicote, J. Martín, M. Artiago, X. Solans, M. Font-Altaba and M. Aguiló, *J. Chem. Soc., Dalton Trans.* (1988) 141; (b) M.C. Etler and A.R. Siedle, *J. Am. Chem. Soc.*, 105 (1983) 641.

[16] D.D. Perin, W.L.F. Armarego and D.R. Perin, *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 2nd edn., 1980.

[17] A. Bax, R.H. Griffey and B.L. Hawhins, *J. Magn. Reson.*, 55 (1983) 301.

[18] M.F. Summers, L.G. Marzilli and A. Bax, *J. Am. Chem. Soc.*, 108 (1986) 4285.

[19] A. Bax and S. Subramanian, *J. Magn. Reson.*, 67 (1986) 565.

[20] A. Bax and M.F. Summers, *J. Am. Chem. Soc.*, 108 (1986) 2093.

[21] *International Tables of X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, 1972.

[22] N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 39 (1983) 158.

[23] J.M. Stewarts, G.S. Kruger, H.L. Amomon, C. Dichirson and S.R. Hall, *Technical Report TR 446*, University of Maryland, 1976.

[24] M. Nardelli, *Comput. Chem.*, 7 (1983) 96.