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# Synthesis and characterization of niobium(IV) and tantalum(V) guanidinates and benzamidinates Molecular structure of the first Nb(IV) guanidinate NbCl<sub>2</sub>{CyNC(N(SiMe<sub>3</sub>)<sub>2</sub>)NCy}<sub>2</sub>

Jean Manuel Decams<sup>a</sup>, Liliane G. Hubert-Pfalzgraf<sup>a,\*</sup>, Jacqueline Vaissermann<sup>b</sup>

<sup>a</sup>ESA CNRS 5079, Université Claude Bernard-Lyon 1, 43 boulevard du 11 novembre 1918, 69622 Villeurbanne Cedex, France <sup>b</sup>Laboratoire de Chimie des Métaux de Transition, URA-CNRS, 4, place Jussieu, 75230 Paris Cedex, France

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### Abstract

The reactions between niobium pentachloride or NbCl<sub>4</sub>(THF)<sub>2</sub> and  $[(Et_2N)_2TaCl_3]_2$  with various lithium guanidinates or benzamidinates were investigated. [NbCl<sub>2</sub>{RNCR'NR}<sub>2</sub>] [R=Cy (Cyclohexyl), R'=N(SiMe\_3)<sub>2</sub> (1); R=SiMe\_3, R'=p-tolyl (2)] [TaCl<sub>3</sub>{Me<sub>3</sub>SiNC(*p*-tolyl)NSiMe<sub>3</sub>]<sub>2</sub>] (3) and [(Et<sub>2</sub>N)<sub>2</sub>TaCl<sub>2</sub>{RNCR'NR}] [R=SiMe<sub>3</sub>, R'=p-tolyl (4) and R=Cy, R'=N(SiMe<sub>3</sub>)<sub>2</sub> (5)] were isolated and characterized by elemental analyses, FT-IR and <sup>1</sup>H NMR or ESR spectroscopy. The molecular structure of 1 corresponds to a centrosymmetric, monomeric [NbCl<sub>2</sub>{CyNC(N(SiMe<sub>3</sub>)<sub>2</sub>)NCy}<sub>2</sub>] species as established by X-ray diffraction studies with the chloride ligands in trans positions. The guanidinate ligand displays a symmetrical  $\sigma$ , $\sigma$ '-coordination behaviour (Nb-N 2.161(8) Å av.) © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Niobium; Tantalum; Benzamidinates; Guanidinates

# 1. Introduction

Amido ligands with various denticity have received increasing attention as ancillary ligands for the development of catalysts [1-3] especially for olefins polymerization or of precursors of nitrides for diffusion barriers [4-9]. Amidines RNHC(R')=NR and their deprotonated anions display a great variety of coordination modes with transition metals [10-12]. Moreover, amidinate and related type ligands, are accessible via a large range of synthetic routes such as metathesis reactions using metal halides, insertion of carbodimides into metal–hydrogen or metal– alkyl bonds, insertion of nitriles into M–N bonds. Such ligands have been extensively used recently especially for group 4 and 13 metals [13-19] and to, a lesser extent for niobium and tantalum [20-22]. Increasing interest has been promoted by their ability to stabilize labile bonds as shown by the bisbenzamidinate tantalum(V) methyl, methylidene and benzyl derivatives [23] and/or to undergo unusual reactivity as observed for multiple metal-metal species. Most group 5 derivatives correspond to species in oxidation state 5 and, if some dinuclear species in low oxidation state have been described [24,25], no species in oxidation state 4 has been reported. The steric and (to a lesser extent) electronic properties of amidinate type ligands can easily be tuned by the variation of C- and N-substituents. Steric analysis of this ligand system places it as intermediate between the Cp and Cp\* ligands [27,28].

We wish to report here the results of our investigations with niobium penta or tetrachloride and bis-N,N'-bisdiethylamidotantalum(V) trichloride. trimethylsilylbenzamidinato  $[p-tolylC(NSiMe_3)_2]$ and N,N'-bis(cyclohexyl)guanidinato { $R_2NC(NC_6H_{11})_2$ } ligands were chosen because of the ease of preparation of their lithium salts and the stabilizing properties they impart to their metallic derivatives. Various mono and bis amidinates derivatives have been isolated and were characterized by microanalyses, FT-IR, <sup>1</sup>H NMR or ESR spectroscopies.

<sup>\*</sup>Corresponding author. Tel.: +33-4-7243-1570; fax: +33-4-7243-1568.

E-mail address: hubert@univ-lyon1.fr (L.G. Hubert-Pfalzgraf)

The first niobium (IV) guanidinate  $[NbCl_2{RNCR'NR_2}]$ (R=Cy, R'=N(SiMe<sub>3</sub>)<sub>2</sub>**1**, and benzamidinate (R=SiMe<sub>3</sub>, R'=*p*-tolyl **2**) were obtained. The molecular structure of **1** was established by single crystal X-ray diffraction.

### 2. Experimental

All manipulations were routinely performed under a nitrogen atmosphere using Schlenk tubes and vacuum line techniques with dried and distilled solvents.  $NbCl_4(THF)_2$ , [29]  $[(NEt_2)_2TaCl_3]_2$  [30] and the lithium benzamidinates [10–19] were prepared as reported in the literature. LiCyNCR'NCy (R'=N(SiMe\_3)\_2) was generated by reacting 1 equivalent of LiN(SiMe\_3)\_2 and 1,3-dicyclohexylcarbodiimide. <sup>1</sup>H NMR spectra were recorded on solutions on a Bruker AC-200 spectrometer. Infrared spectra were registered with a Perkin Elmer Paraggon spectrometer as Nujol mulls between KBr plates. ESR spectra were obtained on a Bruker spectrometer. Analytical data were obtained from the Centre de Microanalyses du CNRS. The melting points as well as the decomposition temperatures were measured in capillaries and are given uncorrected.

# 2.1. Synthesis of $[{RNC(R')NR_{l_2}^{\uparrow}NbCl_2}]$ , R=Cy, $R'=N(SiMe_3)_2$ (1) and $R=SiMe_3$ , R'=p-tolyl (2)

solution of 2.8 g of А (7.54 mmol) Li[CyNC{N(SiMe<sub>3</sub>)<sub>2</sub>}NCy] in 40 ml of diethylether was added to a suspension of 1.02 g (3.77 mmol) of NbCl<sub>5</sub> in 20 ml of diethylether. Formation of a brown precipitate was observed while the reaction medium turned red. Filtration was achieved after decantation for 12 h, the filtrate was concentrated. Several crops of orange crystals of **1** were obtained at  $-20^{\circ}$ C (1.08 g, 32%). m.p. of 170°C, dec 220°C. Anal. calc. for C<sub>38</sub>H<sub>80</sub>N<sub>6</sub>Cl<sub>2</sub>Si<sub>4</sub>Nb C, 50.87; H, 8.99; N, 9.37; Cl, 7.5. Found: 50.75, H 8.75, N, 9.15, Cl, 7.9% IR (cm<sup>-1</sup>): 1660w, 1636w, 1605w  $\nu$  C=N; 1496m, 1447s, 1404s, 1360s, 1346s, 1310m, 1268m; 1258s vSi-Me; 1192s, 1186s, 1142m, 1082w, 1063m, 1047w, 1028w, 1010m, 970m, 935s, 887m, 859s, 839s, 804m, 759m, 728s, 694s, 660m, 642s, 620w; 525s, 487m, 465m, 453w, 435m  $\nu$ M–N. ESR (toluene, RT):  $\langle g \rangle$  1.913,  $\langle A \rangle$  110 G.

The same procedure applied to 1.14 g (2.9 mmol) of NbCl<sub>4</sub>(THF)<sub>2</sub> in toluene gave **1** (1.4 g, 54%). the compound was dried under vacuum for 12h and was solvent free (whereas the monocrystals were only briefly dried).

Compound **2** was obtained accordingly by using 0.611 g (1.61 mmol) of NbCl<sub>4</sub>(THF)<sub>2</sub> in hexane cooled to  $-78^{\circ}$ C and lithium benzamidinate complexed with TMEDA. Several crops of yellow crystals of **2** were obtained at  $-10^{\circ}$ C (0.44 g, 38%). m.p.=180^{\circ}C, dec 280°C; Anal. calc. for C<sub>28</sub>H<sub>50</sub>Cl<sub>2</sub>N<sub>4</sub>Si<sub>4</sub>Nb: C, 46.78, H, 7.01, N, 7.79, Cl, 9.86; Found: C, 46.25, H, 7.08, N, 7.80, Cl: 9.82% IR (cm<sup>-1</sup>): 1660w, 1612m, 1549w, 1521m  $\nu$ C=C, C=N; 1502m, 1406s, 1308s, 1298s; 1246s  $\nu$ Si–Me; 1210w,

118w, 1158w, 1143w, 1112w, 1025m, 1008m, 981s, 949m, 929s, 906m; 838s; 761s, 717s, 689m, 643s, 607w, 586w; 574w; 487m, 473s, 455m  $\nu$ M–N. ESR (hexane, RT): <g> 1.907, <A> 107G.

Compounds 1 and 2 were slightly soluble in hexane, more soluble in toluene, diethylether, THF and DME.

# 2.2. Synthesis of $[{Me_3SiNC(p-tolyl)NSiMe_3}_2TaCl_3](3)$

A solution of 2.00 g (4.88 mmol) of [{Me<sub>3</sub>SiNC(ptolyl)NSiMe<sub>3</sub>{Li(TMEDA)] in 40 ml of Et<sub>2</sub>O was added to TaCl<sub>5</sub> (0.874 g, 2.14 mmol) in 40 ml of Et<sub>2</sub>O cooled at -78°C. After stirring for 12 h at room temperature, filtration was achieved. The filtrate was concentrated, 3 was isolated as yellow crystals (0.85 g, 42%) at  $-20^{\circ}$ C. m.p. 140°C, dec 220°C. Anal. found: C, 40.68, H, 6.25; N, 6.94, Cl, 12.51; calc. for C<sub>28</sub>H<sub>50</sub>N<sub>4</sub>Si<sub>4</sub>Cl<sub>3</sub>Ta: C, 39.92, H, 5.98, N, 6.65, Cl, 12.6. IR (cm<sup>-1</sup>, Nujol): 1611 m, 1526m. v(C=C, C=N); 1491 m, 1481 s, 1444 s, 1311 m, 1244 s v(Si-Me); 1211 m, 1184 m, 1162 m, 1111 s, 1027 m, 1010 m, 990 vs; 842 s, 835 s, 821 s v(Si-C), 798 m, 765 s, 730 m, 717 m, 690 m, 649 m, 624 m, 617 m; 485 m, 481 m, 474 m  $\nu$ (M–N). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20°C, ppm): 7.25 (d, J=7 Hz, 2H, H(Ph), 6.73 [d, J=7Hz, 2H, H(Ph)], 1.95 [s, 3H, Me(Ph)], 0.31 (s, 18H, MeSi).

Compound 3 has solubility properties comparable to those of 1 and 2  $\,$ 

# 2.3. Synthesis of $[(Et_2N)_2TaCl_2\{RNC(R')NR\}]$ , $R=SiMe_3$ , R'=p-tolyl (4) and R=Cy, $R'=n(SiMe_3)_2$ (5)

Compound **4** was obtained as orange crystals (71%) by a similar procedure in toluene at  $-78^{\circ}$ C using lithium benzamidinate complexed with TMEDA and (Et<sub>2</sub>N)<sub>2</sub>TaCl<sub>3</sub> (1:1 stoichiometry). Anal. found: C, 39.42, H, 6.48, N, 8.07, Cl, 10.20; calc. for C<sub>22</sub>H<sub>45</sub>N<sub>4</sub>Si<sub>2</sub>Cl<sub>2</sub>Ta: C, 39.23; H, 6.73, N, 8.32, Cl 10.35%. IR (cm<sup>-1</sup>): 1613m, 1567w, 1517w vC=C, C=N; 1317m, 1308m, 1283m; 1248s vSi-Me; 1211s, 1186m, 1167m, 1131m, 1110m, 1094m, 1063m, 1043m, 1026m, 994s, 968m, 950m, 909m; 882m, 840s; 790m, 765m, 686m, 651m, 632m; 576m, 528m, 472s, 401w vM-N.<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, ppm): 7.1 d (J=7 Hz, CH, 2H), 6.75 d (J=7Hz, CH, 2H), 4.25 q (J=3Hz, CH<sub>2</sub>, 8H), 1.96 s [Me(tolyl), 3H], 1.16 t (J=3Hz, Me, 12H), 0.1 s [Me(Si), 18H]; m.p.=100°C, dec 160°C, sublimes at 110°C under 4.10<sup>-4</sup> mm of Hg.

A suspension of CyNC(N(SiMe<sub>3</sub>)<sub>2</sub>)NCyLi (0.8 g, 2.22 mmol) in 40 ml of toluene was added to a solution of  $(Et_2N)_2TaCl_3$  (0.96 g, 2.22 mmol) in 20 ml of toluene cooled at  $-78^{\circ}C$  similar workup as for **3**. Orange crystals of **5** (1.28 g, 76%) were obtained at  $-10^{\circ}C$ . m.p.=120°C, dec 140°C. Anal. found: C, 43.11, H, 7.60, N, 9.01, Cl, 9.21; calc. for  $C_{27}H_{60}N_5Si_2Cl_2Ta$  C, 42.51, H, 7.93, N, 9.18, Cl, 9.30% IR(cm<sup>-1</sup>): 1658w, 1641w, 1575w  $\nu$ C=N; 1450s, 1343s, 1311m; 1270m; 1256s  $\nu$ Si-Me; 1207s,

1185s, 1178s, 1142m, 1130m, 1092m, 1070m, 1062m, 1042m, 1013s, 996s, 929m, 906m, 897m; 881m, 873s, 860s, 835s, 802m; 788s, 767m, 755m, 708w, 694m, 651m, 645s, 620w; 577m, 548w, 525s, 489m, 476w, 465w, 438m  $\nu$ M–N. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub> ppm): 4.38q (J=6Hz, CH<sub>2</sub>, 8H), 3.91 (t, J=7Hz, 2H (Cy), 1.7 (m, Cy, 20H), 1.2 (t, J=6Hz, Me, 12H), 0.33 s (MeSi, 18H).

Compounds 5 and 4 are soluble in the usual solvents (hexane, toluene, ether,  $\ldots$ ).

2.4. X-ray structure determination of  $[NbCl_2{CyNCN(SiMe_3)_2NCy}_2, 2cC_6H_5CH_3]$ 

Suitable crystals of **1** were obtained directly from the reaction medium with  $NbCl_4(THF)_2$  as the starting material. The selected crystal was mounted in a Lindeman capillary. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. A decay of 50% was observed for the intensities of two checked reflections during data collection, the usual linear correction was applied. Complete crystallographic data and collection parameters are listed in Table 1. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [31]. Scattering factors and corrections factors for anomalous

Table 1

C <sub>52</sub> H <sub>96</sub> N <sub>6</sub> Si <sub>4</sub> Cl <sub>2</sub> Nb
1081.5
9.3418(9)
13.591(1)
13.799(1)
63.243(7)
79.934(8)
80.085(8)
1531.6(3)
1
Triclinic
PĪ
3.87
1.17
MACH3 Enraf-Nonius
Mo $K_{\alpha}$ ( $\lambda = 0.71069 \text{ Å}$ )
$\omega/2\theta$
$0.8 + 0.345 \ tg\theta$
1-25
Room temperature
0,11; -15,16; -16,16
5731
5369
$2240(Fo)^2 > 3\sigma(Fo)^2$
0.0474
0.0601
0.0689w = 1.0
No
261
-0.42
0.79

dispersion were taken from [32]. The structure was solved by standard Patterson-Fourrier techniques and refined by full-matrix least-squares. The asymmetric unit contains a molecule of solvent (toluene) together with half a molecular unit of the Nb compound. Refinements were performed using anisotropic thermal parameters for all non hydrogen atoms of the Nb compound. The toluene molecule was refined isotropically using restraints on the C–C bond lengths (1.40(2) Å) and bond angles (120(2)°). The solvent is disordered as shown by the high thermal factors of C(34) and C(37). Hydrogen atoms were introduced in calculated positions on the carbon atoms of the Nb compound and introduced in the last refinement with an overall refinable isotropic thermal parameter.

#### 3. Results and discussion

Niobium(IV) N, N', N''-trialkylguanidinates or bistrimethylsilylbenzamidinates [NbCl<sub>2</sub>{RNCR'NR}<sub>2</sub>] [R =Cy,  $R' = N(SiMe_3)_2$  (1) and  $R = SiMe_3$ , R' = p-tolyl) (2) were obtained by reacting an etheral suspension of NbCl<sub>5</sub> with 2 equivalents of Li(RNCR'NR) or of the TMEDA complex for the N,N'-bis(trimethylsilyl-p-tolyl benzamidi-(TMEDA = N, N, N', N'-tetramethylethylenediamine). nate Better yields ( $\simeq$ 50%) were obtained if the reactions were achieved with the metal halide in the appropriate oxidation state, namely with NbCl<sub>4</sub>(THF)<sub>2</sub> in toluene. By contrast, similar reactions applied to TaCl<sub>5</sub> in diethylether at low temperature proceeded without reduction affording a tantalum(V) disubstituted derivative 3. No tractable products could be isolated by using hexane as a solvent. The use of  $[(Et_2N)_2TaCl_3]_2$  as starting material allowed the isolation of  $[(Et_2N)_2TaCl_2(RNCR'NR)])$ ;  $[R=SiMe_3, R'=p-tolyl$ (4) and R=Cy,  $R'=N(SiMe_3)_2$  (5] (Eq. (1)) in good yields. The best yields (>70%) were obtained by using low temperature procedures. The various compounds including the niobium(IV) ones were soluble in organic media whereas 4 was also volatile (sublimation 110°C/  $4.10^{-4}$  mm of Hg). The different synthetic routes are summarized in Scheme 1.

The novel compounds were characterized by elemental analyses and FT-IR spectroscopy. IR spectra display mainly the absorption bands of the organic moieties. Sharp bands are observed between 1660 and 1600 cm<sup>-1</sup> for the  $\nu$ C=N and  $\nu$ C=C vibrations. The presence of metal-nitrogen bonds is illustrated by bands in the 550–400 cm<sup>-1</sup> region. This region is more complex for compounds 4 and 5 whose spectra show also absorption bands corresponding to the NEt<sub>2</sub> ligand. The presence of the trimethylsilyl substituents leads to a strong absorption band around 1250 cm<sup>-1</sup>, characteristic of the  $\nu$ Si-Me<sub>3</sub> vibration. The diamagnetic tantalum(V) derivatives were also characterized by <sup>1</sup>H NMR. The diethylamido ligands appear magnetically equivalent for 4 and 5 indicating a symmetrical and/or



fluxional structure The spectroscopic data thus support the structure represented in Eq. (1) based on a six-coordinated metal center. The most notable feature for the spectrum of **4** is the presence of a sharp resonance at 3.91 ppm attributed to the proton in  $\alpha$  position of the cyclohexyl groups. Only one type of SiMe3 groups is observed for compound **3** suggesting a fluxional behaviour for this species in which the metal is probably heptacoordinated. The tetravalent niobium species **1** and **2** display a characteristic ten line ESR pattern at room temperature ( $I_{Nb}=9/2$ ) suggesting the formation of monomeric species. This was confirmed by an X-ray diffraction study for **1**.



 $\begin{array}{c|cccc} The & molecular & structure & of \\ [NbCl_2 \{CyNC(N(SiMe_3)_2)NCy\}_{2]} & is depicted in Fig. 1. \\ Selected bond lengths and angles are collected in Table 2. \end{array}$ 

The structure is based on a centrosymmetric, monomeric species in which the metal is in a slightly distorted octahedral environment, the two chloride ligands being in trans position. The coordination sphere of the Nb(IV) center includes the four nitrogen atoms of the two chelating guanidinate anions. These display a  $\sigma, \sigma'$ -symmetrical coordination behaviour and the Nb-N bond lengths have identical values (2.161(8) Å av.). The Nb-Cl bond distances have values of 2.384(3) Å and are consistent with these reported in the literature for other Nb(IV) derivatives [33–38]. The four-membered Nb–N–C–N–Nb metallocycles are planar, the bite angles are small, namely  $60.7(3)^{\circ}$ but consistent with the value reported for similar ligands in  $cis-[SnCl_{2}{Me_{3}SiNC(Bu^{t})NSiMe_{3}}_{2}]$ or  $[{CyNC(NMe_2)CNCy}Ta(NMe_2)_4]$  [39]. The amido nitrogen atom N(3) is planar as well with a C(1)–N(3) bond distance of 1.40(1) Å. This C–N distance is longer than the C–N distances within the chelating ligand (1.335 Å av)but in agreement with the literature body [10-12,40,41]. Its value militates against conjugation of the N-C-N  $\pi$ -system and the exocyclic N(3) atom. Such a conjugation was observed for the dianionic guanidinato ligand in  $[{CyNC(NCy)CNCy}Ta(NMe_2)_3]$  giving an extra cyclic C-N distance of 1.28(2) Å and thus an imine character [26]. The cyclohexyl rings of 1 are orientated nearly parallel to each other, a situation which obviously minimizes the steric repulsion between these bulky substituents. No short intermolecular contacts were observed. The Nb....C(11)–H distance (>3.5 Å) is too long for



Fig. 1. Molecular structure of 1 showing the atom numbering scheme. Thermal ellipsoids at 30% probability.

effective interaction. The overall symmetry of **1** is comparable to that of the divalent vanadium derivatives  $[V{CyNC(R')NCy}_2(THF)_2]$  [42] but different to that of the zirconium analog,  $[ZrCl_2{CyNC(Me)NCy}_2]$ , for which the chlorine occupy cis positions [15]. Molecular modelling (Hyperchem V5) of **1** indicate comparable energies for the cis and trans isomers suggesting that solid state effects will govern. By contrast, for the bis benzamidinate derivative **2**, the cis isomer was found to display a much higher stability ( $\Delta E > 500$  kJ) than the trans isomer. X-ray data are in agreement with these observations since only cis-isomers have been structurally characterized so far for bis benzamidinato derivatives.

The reported N,N',N''-trialkylguanidinate or bis-(trimethylsilyl) benzamidinate ligands are able to function as supporting ligands for paramagnetic Nb(IV) species displaying high solubility as well as modest sensitivity to

Table 2 Interatomic	distances	(Å)	and	angles	(°)	for
$[NbCl_2{(CyN)_2C}]$	$2N(SiMe_3)_2$	$_{2}$ ],(C <sub>7</sub> H <sub>8</sub> )	) <sub>2</sub>			
Nb(1)-Cl(1)	2.38	4(3)				
Nb(1)–N(1)	2.16	52(8)				
Nb(1)–N(2)	2.15	9(7)				
Cl(1)-Nb(1)-N(	(1) 90.1	(2)	Cl(1)-N	Nb(1) - N(1')	89	.9(2)
Cl(1)-Nb(1)-N(	(2) 89.4	(2)	Cl(1)-N	Nb(1) - N(2')	90	.6(2)
N(1)-Nb(1)-N(	2) 60.7	(3)	N(1)-N	b(1) - N(2')	11	9.3(3)
Cl(1)-Nb(1)-N(	(2) 90.6	i(2)	Cl(1)-N	Nb(1) - N(2')	89	.4(2)
N(1)-Nb(1)-N(	2) 119	.3(3)	N(1)-N	b(1) - N(2')	60	.7(3)

ambient atmosphere. Compounds **1** and **2** are the first examples of Nb(IV) species based on such ligands. The thermal stability was higher for the benzamidinate derivatives since the guanidinates undergo easy decomposition via cleavage of the external C–N bond giving NH(SiMe<sub>3</sub>)<sub>2</sub>. Volatility could be achieved for a tantalum(V) species with an appropriate set of ligands including a trimethylsilylbenzamidinato one. The presence of dialkylamido ligands lead to a better volatility but reduced the stability toward ambient atmosphere.

### Supplementary data

Supplementary data (Tables of coordinates, thermal parameters, of non-essential bond lengths and angles) are available from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 101 725.

#### References

- V. Volkis, M. Shmulinson, C. Averbuj, A. Lisovskii, F.T. Edelmann, M.S. Eisen, Organometallics 17 (1998) 3155.
- [2] P. Mountford, Chem. Commun. (1997) 2127.
- [3] Y. Zhou, G.P.A. Yap, D.S. Richeson, Organometallics 17 (1998) 4387.
- [4] C.H. Han, K.N. Cho, J.E. Oh, S.H. Paek, C.S. Park, S.I. Lee, M.Y. Lee, J.G. Lee, Jpn. J. Appl. Phys. 37 (1998) 2646.

- [5] C.H. Han, K.N. Cho, J.E. Oh, S.H. Paek, C.S. Par, S.I. Lee, M.Y. Lee, J.G. Lee, Jpn. J. Appl. Phys. 8 (1996) 2468.
- [6] M.H. Tsai, S.C. Sun, H.T. Chiu, C.E. Tsai, S.H. Chuang, Appl. Phys. Lett. 67 (1995) 1128.
- [7] M.H. Tsai, S.C. Sun, H.T. Chiu, S.H. Chuang, Appl. Phys. Lett. 68 (1996) 1412.
- [8] A.L. Currie, K.E. Howard, J. Mater. Sci. 27 (1992) 3739.
- [9] N.A.K. Hansem, W.A. Herrmann, Chem. Mater. 10 (1998) 1577.
- [10] F.T. Edelman, Coord. Chem. Rev. 137 (1994) 403.
- [11] F.A. Cotton, Inorg. Chem. 37 (1998) 5710.
- [12] J. Barker, M. Kilner, Coord. Chem. Rev. 133 (1994) 219.
- [13] Y. Zhou, D.S. Richeson, Inorg. Chem. 35 (1996) 1423.
- [14] Y. Zhou, D.S. Richeson, Inorg. Chem. 36 (1996) 2448.
- [15] D. Herskovics-Korine, M.S. Eisen, J. Organometal. Chem. 503 (1995) 307.
- [16] S. K Hao, K. Feghali, S. Gambarotta, Inorg. Chem. 36 (1997) 1745.
- [17] A. Littke, N. Sleiman, C. Bensimon, D.S. Richeson, G.P.A. Yap, S.J. Brown, Organometallics 17 (1998) 446.
- [18] M.P. Coles, D.C. Swenson, R.J. Jordan, V.G. Young, Organometallics 16 (1997) 5183.
- [19] M.P.M. Westerhausen, M.H. Digeser, W. Schwartz, Inorg. Chem. 36 (1997) 521.
- [20] P.J. Stewart, A.J. Blake, P. Mountford, Inorg. Chem. 36 (1997) 1982.
- [21] M.G.B. Drew, J.D. Wilkins, J. Chem. Soc., (A) (1973) 2611.
- [22] K. Merzweiler, D. Fenske, E. Hartmann, K. Denicke, Z. Naturforsch. B 44 (1989) 1003.
- [23] D.Y. Dawson, J. Arnold, Organometallics 16 (1997) 1111.
- [24] F.A. Cotton, L.M. Daniels, C.A. Murillo, Y. Wang, J. Am. Chem. Soc. 118 (1996) 4830.
- [25] F.A. Cotton, J.H. Matonic, C.A. Murillo, X. Wang, Bull. Soc. Chim. Fr. 133 (1996) 711.

- [26] K.T. Ma, G.P.A. Tin, D.S. Yap, A. Richeson, Inorg. Chem. 38 (1999) 998.
- [27] R. Duchateau, C.T. van Wee, P.T. van Duijnen, J.H. Teuben, Organometallics 15 (1996) 2279.
- [28] A. Kasani, R.P. Kamalesh Babu, K. Feghali, S. Gambarotta, G.P.A. Yap, L.K. Thompson, R. Herbst-Irmer, Chem. Eur. J. 5 (1999) 577.
- [29] L.E. Manzer, Inorg. Chem. 16 (1977) 525.
- [30] Y.W. Chao, P.A. Wexter, D.E. Wigley, Inorg. Chem. 28 (1989) 3860.
- [31] D.J. Watkin, C.K. Prout, R.J. Carruthers, P.W. Betteridge, CRYS-TALS, Issue 10, Chemical Crystallography Laboratory, Oxford, UK, 1996.
- [32] D.T. Cromer, International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, UK, 1974.
- [33] L.G. Hubert-Pfalzgraf, M. Postel, J.G. Riess, in: Comprehensive Coordination Chemistry, Pergamon Press, London, 1987, Chap. 34.
- [34] L.G. Hubert-Pfalzgraf, B. King (Eds.), in Encyclopedia of Inorganic Chemistry, M. Dekker, New York, 1994, p. 2444.
- [35] C.E. Holloway, M. Melnik, J. Organometal. Chem. 303 (1986) 1.
- [36] L.G. Hubert-Pfalzgraf, M. Tsunoda, G. Le Borgne, J. Chem. Soc., Dalton Trans. (1988) 533.
- [37] L.G. Hubert-Pfalzgraf, A. Zaki, L. Toupet, Acta Crystallogr. 49 (1993) 1609.
- [38] Y. Zhou, D.S. Richeson, Inorg. Chem. 36 (1997) 501.
- [39] M.K.T. Tin, G.P.A. Yap, D.S. Richeson, Inorg. Chem. 37 (1998) 6728.
- [40] F.H. Allen, J.E. Davis, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, E.M. Mitchell, G.F. Mitchell, J.M. Smith, D.G. Watson, J. Chem. Inf. Comput. Sci. 31 (1991) 187.
- [41] J.R. da S. Maia, P.A. Gazard, M. Kilner, A.S. Batsanov, J.A.K. Howard, J. Chem. Soc., Dalton Trans. (1997) 4625.
- [42] P. Berno, S.K. Hao, R. Minhas, S. Gambarotta, J. Am. Chem. Soc. 116 (1994) 7417.