

Phosphane coordination to rare earth metal centers: monomeric, solvent-free complexes of type $\text{Cp}'_2\text{LnX}$ with phosphanoethyl substituted cyclopentadienyl ligands

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Abstract

The reaction of phosphanoethyl substituted cyclopentadienides $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PR}_2]\text{M}$, $\text{R} = \text{Me}$, Cy , $t\text{-Bu}$, Ph , $\text{M} = \text{Li}$, K with LnX_3 ($\text{Ln} = \text{rare earth metal}$, $\text{X} = \text{Cl}^-$, CF_3SO_3^-) afforded twofold substituted metal complexes of the type $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PR}_2]_2\text{LnX}$. Using the dianionic ligand $\text{Li}_2[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]$ phosphano bridged *ansa* metallocene derivatives $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]\text{LnX}$ ($\text{Ln} = \text{Y}$, Lu ; $\text{X} = \text{Cl}^-$, CF_3SO_3^-) were isolated. The complexes are soluble in toluene, monomeric and free of solvent. According to X-ray studies on $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PMe}_2]_2\text{YCl}$, a distorted trigonal bipyramid with two axial phosphano groups and two equatorial cyclopentadienyl moieties is the structural motif, the third equatorial site being occupied by the halide ligand. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Anionic phosphane ligands; Rare earth metal complexes; Cyclopentadienyl complexes

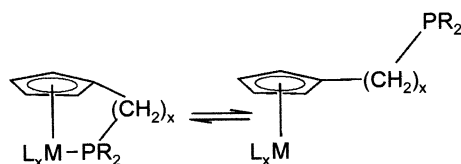
1. Introduction

Because of the very weak interaction of the ‘hard’ lanthanoid cation and the ‘soft’ phosphorus atom only a few examples of lanthanoid complexes with neutral phosphane ligands are known so far [1]. In order to achieve more stable complexes the concept of anionic phosphane ligands was introduced in rare earth metal chemistry. Complexes are known with phosphanides [2], phosphanoalkoxides [3], amidophosphanes [4] and phosphanomethanides [5]. Whereas cyclopentadienides are the most important class of ligands in organometal-

lic chemistry of rare earth elements, in particular for catalytic reactions a combination of a ‘stable’ (Cp^-) with a ‘labile’ (PR_3) ligand is desired. Therefore phosphanoalkyl cyclopentadienide ligands seem to provide an attractive potential in this field by a reversible phosphane donor capacity (‘hemilabile ligand’) (Scheme 1).

The phosphane functionality should also prevent the system from oligomerisation reactions as well as from coordination of donor solvent molecules, as do some cyclopentadienyl based ligands with donor functionalized side chains, but exhibiting a less reversible coordination to the metal center [6–8].

By varying the organic substituents at the phosphorus atom the solubility and the donor strength of the phosphane can be influenced and thus adjusted to the respective needs. Apart from a foregoing preliminary account from our laboratory [9], rare earth metal complexes with phosphanoalkyl substituted cyclopentadienides have not been described as yet. Indeed, cyclopentadienyl ligands with a directly attached phosphane moiety have successfully been introduced in rare earth metal chemistry, i.e. $\text{CpLa}(\text{C}_5\text{H}_4\text{PPh}_2)_2\cdot\text{THF}$ [10], $\text{Yb}(\text{C}_5\text{H}_4\text{PPh}_2)_2\cdot\text{THF}$ [11], $(\text{COT})\text{SmC}_5\text{Me}_4\text{PR}_2(\text{THF})_2$



Scheme 1. Reversible coordination of phosphanoalkyl substituted cyclopentadienyl ligands.

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[12], however, it is important to realize that in all these compounds phosphorus is not coordinated to the metal center.

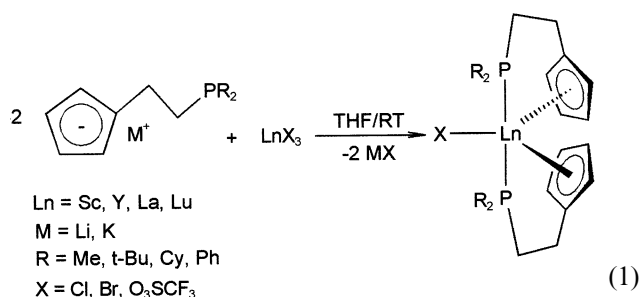
There are several routes to synthesize phosphanoalkyl substituted cyclopentadienides [13]. Most of these procedures are tedious and proceed in low yield. However, mono- and dianionic phosphanoethyl substituted cyclopentadienides can be prepared by the reaction of the corresponding mono- and dimetallated phosphanes with spiro[2.4]hepta-4,6-diene [14] in satisfying yields [9,15–17] (Scheme 2).

Monoanionic alkali cyclopentadienides of the type $M[C_5H_4(CH_2)_2PR_2]$ ($M = Li, K$) with $R = Ph$ [15,16], Me [9], $i\text{-Pr}$ [15], $t\text{-Bu}$ [15] and the dianionic derivative $Li_2[(C_5H_4CH_2CH_2)_2PPh]$ [17] are known. An X-ray structure determination of $K[C_5H_4(CH_2)_2PPh_2]$ [16] has been reported. The lithium cyclopentadienides $Li[C_5H_4(CH_2)_2PCy_2]$ and $Li_2[(C_5H_4CH_2CH_2)_2PMe]$ were newly synthesized using the nucleophilic ring opening reaction mentioned above.

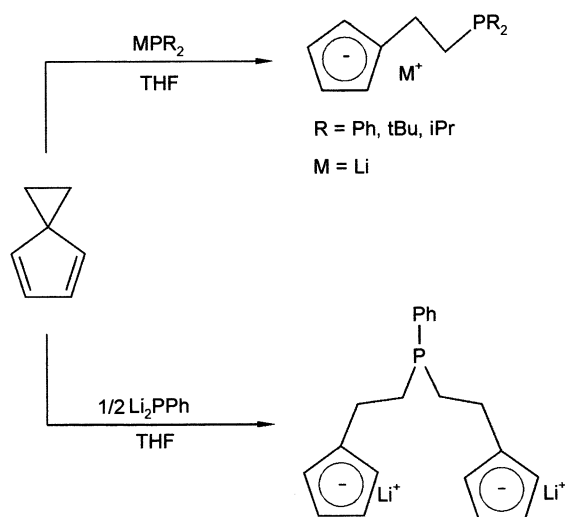
2. Results and discussion

2.1. Complexes of the type $[(C_5H_4CH_2CH_2PMe_2)_2]LnX$

Complexes of type Cp_2LnX normally are not readily obtained due to ligand scrambling. Furthermore, donor solvent molecules (e.g. THF) and/or metal halides (e.g. $LiCl$) are additionally coordinated or dimerisation is observed [18]. Hence, on attempted syntheses, complex mixtures often are encountered, and only in cases, where crystalline products are obtained or diamagnetic metal nuclei are involved, a structural characterization is possible. In an attempt to get clear-cut results and to obtain compounds Cp_2LnX free of solvent and alkali halides, we therefore reacted the diamagnetic metal nuclei are involved, a structural characterization is possible. In an attempt to get clear-cut results and to obtain compounds Cp_2LnX free of solvent and alkali halides, we therefore reacted the diamagnetic salts LnX_3 ($Ln = Sc, Y, La, Lu$; $X = Cl, O_3SCF_3$) with two equivalents of $[C_5H_4CH_2CH_2PR_2]Li$ ($R = Me, Cy, t\text{-Bu}, Ph$) in THF as solvent Eq. (1).

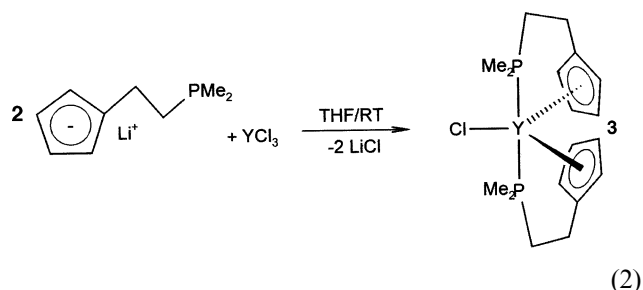


In all cases, products with the desired composition were obtained, but depending on the metal, the anionic group X and the size of the phosphane substituent R , not in all cases in a pure state and with different coordination mode and behavior of the ligands. The



Scheme 2. Synthetic route to phosphanoethyl cyclopentadienyl lithium derivatives according to [9,15–17].

results were as follows: The yttrium complex **1**, as obtained from the reaction according Eq. (2), is a colorless crystalline solid, monomeric and soluble in hydrocarbons. It is isomorphous to the bromine analogue $[(C_5H_4CH_2CH_2PMe_2)_2]YBr$ (**2**), which was described previously [9].



In the $^{31}P\{^1H\}$ -NMR spectrum of **1** a doublet at $\delta -34.65$ with a $^1J_{PY}$ coupling constant of 74.0 Hz (cf.: **2**, $^1J_{PY} = 72.8$ Hz [9]; $Y[N(SiMe_2CHPMe_2)(SiMe_2CH_2PMe_2)] [N(SiMe_2CH_2PMe_2)_2]$, $^1J_{PY} = 70.0$ Hz [19]), which is invariant with temperature (+60 to $-80^\circ C$) and solvent (C_6D_6 or $[d_8]THF$), is detected. Thus the two $Y-P$ bonds remain retained within this range of temperature. The coordination of both phosphane functionalities is also evident from the $^{13}C\{^1H\}$ -NMR signals of the methylene and C_{ipso} carbon atoms, which each appear as a 'pseudotriplet' [20]. However, 1H - and $^{13}C\{^1H\}$ -NMR spectra, in contrast to the $^{31}P\{^1H\}$ -NMR spectrum, are clearly temperature dependent: whereas the methyl and methylene protons at r.t. appear as broad singlets, at $-80^\circ C$ these signals each split into signals of equal intensity. As well, whereas the ring carbon nuclei and the methyl groups each give rise to a single broad line, at $-80^\circ C$ these signals are split into two singlets for the methyl carbon atoms and four

signals for the ring carbon atoms (besides the separate signal for the C_{ipso} ring carbon atom, vide supra). Thus a dynamic process is evident, which is not due to a dissociative Y–P bond cleavage but should involve some kind of pseudorotation, probably analogously to

Table 1

Selected bond distances (Å) and angles (°) for **1** (left column) and **2** (right column) [9] for comparison

Bond length			
Y–X1a ^a	2.3917(11)	Y–X1a ^a	2.392
Y–X1b ^a	2.3953(15)	Y–X1b ^a	2.386
Y–Cl	2.6248(6)	Y–Br	2.794(1)
Y–P1	2.9417(7)	Y–P1	2.960(1)
Y–P2	2.9754(7)	Y–P2	2.933(1)
Bond angles			
X1a–Y–X1b	126.30(5)	X1a–Y–X1b	129.9
P1–Y–P2	153.55(2)	P1–Y–P2	154.8(1)
Cl–Y–X1a	116.86(3)	Br–Y–X1a	117.1
Cl–Y–X1b	116.84(4)	Br–Y–X1b	113.0

^a X1a, b: center of the Cp rings.

Table 2

Crystallographic data for $(C_5H_4CH_2CH_2PMe_2)_2YCl$ (**1**)

Crystal data	
Chemical formula	$C_{18}H_{28}ClP_2Y$
f_w (g mol ^{−1})	430.70
Color	White
Crystal size (mm)	0.25 × 0.3 × 0.5
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.8217(2)
b (Å)	15.6988(3)
c (Å)	12.3731(2)
β (°)	108.3363(9)
V (Å ³)	1995.31(6)
Z	4
T (K)	193
$\rho_{calc.}$ (g cm ^{−3})	1.434
μ (cm ^{−1})	32.1
$F(000)$	888
Data collection	
λ (Å)	0.71073
Scan method	ϕ -scan
θ range (°)	4.0–26.4
Data collected (h, k, l)	$\pm 13, \pm 19,$ $-15-+14$
Refinement	
Reflections collected	15 344
Independent reflections	4049
Observed reflections with $[I > 2\sigma(I)]$	3849
R_{int}	0.035
R_1^a	0.029
$wR_2^{b,d}$	0.081
Goodness-of-fit ^c	1.05
$\Delta\rho_{max/min}$ (e Å ^{−3})	+0.56, −0.46

^a $R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|$.

^b $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$.

^c GOF = $[\Sigma w(F_o^2 - F_c^2)^2 / (NO - NV)]^{1/2}$.

^d $w = 1/[\sigma^2(F_o^2) + (0.0442P)^2 + 1.90P]$ where $P = (F_o^2 + 2F_c^2)/3$.

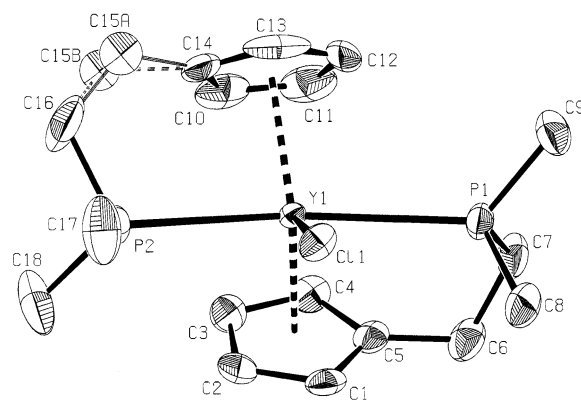


Fig. 1. PLATON representation of $ClY(C_5H_4CH_2CH_2PMe_2)_2$ (**1**). Thermal ellipsoids are given at the 50% probability level; hydrogen atoms are omitted for clarity.

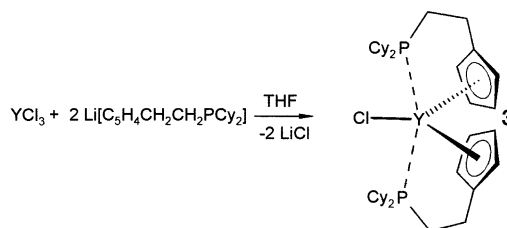
the Berry process as established for many other penta-coordinated species [21]. Alternatively, but much less likely, dissociation of the anionic groups (Cl, C_5H_4) would occur, while the Y–P bond remains intact.

Indeed, the solid state structure of **1** confirms a structural geometry around the metal, which best can be described as distorted trigonal bipyramid.

Crystals suitable for X-ray analysis of **1** were obtained by slowly removing the solvent of the filtered solution. Selected bond distances and angles are given in Table 1 and were compared with those of **2** [9]. Crystallographic data are given in Table 2 and Fig. 1.

In line with the spectroscopic findings, **1** displays a distorted trigonal bipyramidal geometry with the yttrium center coordinated by both phosphorus atoms in axial positions. The Y–P bond lengths of 2.9417(7) and 2.9754(7) Å are only slightly longer than in $\{Y[N(SiMe_2CHPMe_2)(SiMe_2CH_2PMe_2)[N(SiMe_2CH_2PMe_2)_2]\}$ [19] [2.871(1), 2.896(1) and 2.903(1) Å]. The Y–Cl bond distance [2.6248(6) Å] in **1** lies between that found in $(Me_5C_5)_2YCl(THF)$ [2.576(1) Å] [22] and in $[(C_5H_5)_2YCl]_2$ [2.674(1) and 2.689(1) Å] [22] and close to that found in $[(C_5H_4CH_2CH_2SeEt)_2YCl]$ [2.6071(6) Å] [8c]. The average Y–Cp(center) distance of 2.393 Å agrees well with that of other yttrium cyclopentadienyl complexes [6–8,23].

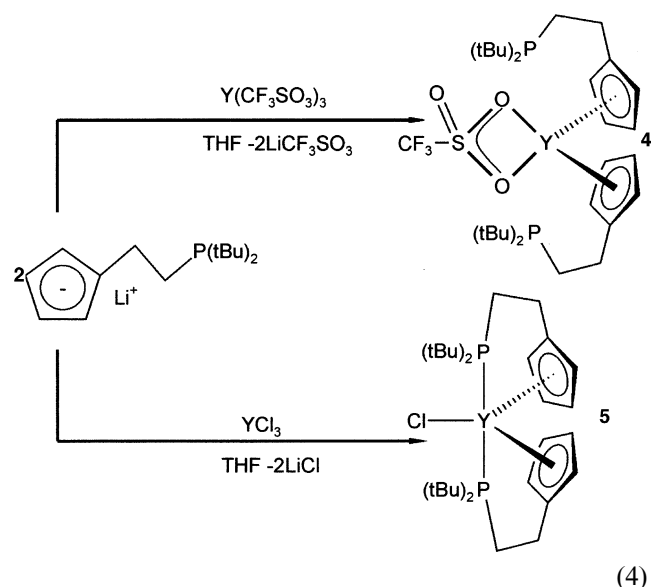
The influence of increasing steric bulk of the phosphane substituents is demonstrated by the reaction of YCl_3 with $[C_5H_4CH_2CH_2PR_2]Li$ (R = Cy, tBu) (Eq. (3) and (4)).



(3)

Compound **3** thus obtained forms a colorless foam and is easily soluble in aromatic hydrocarbons. The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum consists of a doublet at $\delta -2.30$ with a P–Y coupling constant of 29.4 Hz, which is not temperature dependent. The ^1H -NMR spectrum is very complex, because of superpositions of the cyclohexyl proton signals. For the ring protons an uncompletely resolved A_2B_2 spin system at $\delta 5.84$ is observed. In the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum each a singlet is observed for the methylene carbon atoms (no pseudotriplet splitting as in the case of **1**). This indicates a markedly weaker coordination of the phosphane functionality in **3** compared to **1** due to the sterical demand of the cyclohexyl substituents.

The influence of the remaining anionic functionality X (the leaving group) on the coordination of the phosphanoalkyl cyclopentadienyl ligand to rare earth metal centers is evident from Eq. (4). Both **4** and **5** were obtained as colorless solids from toluene in good yields.

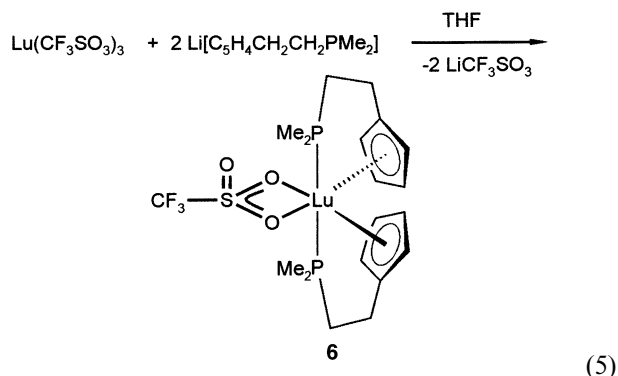


NMR spectroscopic studies confirm both complexes **4** and **5** are monomeric and do not contain additional solvent molecules.

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P}(\text{tBu})_2]_2\text{Y}(\text{CF}_3\text{SO}_3)$ (**4**) consists of a doublet at $\delta 31.94$ with a P–Y coupling constant of only 7.1 Hz, whereas for complex $[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{P}(\text{tBu})_2]_2\text{YCl}$ (**5**) a doublet at $\delta 32.56$ with a P–Y coupling constant of 48.5 Hz is observed. Obviously the $\delta^{31}\text{P}$ shift is not an adequate indicator for the type of coordination of the phosphane moiety. The small P–Y coupling constant for **4** indicates that the ‘phosphane arms’ are not effectively bonded to the metal center. The ^1H -NMR signal of the ring protons in compound **4** appears as an uncompletely resolved A_2B_2 pattern, whereas for **5** a singlet is detected. These findings indicate that complex **5** might be involved in faster exchange processes of the anionic groups than **4** and **3**. This process would increase the

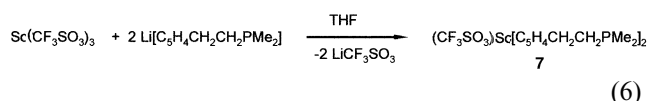
positive charge at yttrium and thus also might explain the increasing value of the P–Y coupling constant in going from **3** to **5**.

Comparable in size to Y^{3+} (0.90 Å) is Lu^{3+} (0.86 Å). The lutetium complex **6** obtained according to Eq. (5) is a colorless solid, soluble in aromatic hydrocarbons.



The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum consists of one singlet at $\delta -26.27$. This signal remains unchanged over a temperature range from r.t. to -90°C : no dynamic behavior can be observed in solution. Similar to **1** the $^{13}\text{C}\{^1\text{H}\}$ resonances of the CH_3 groups, the CpCH_2 groups, the CH_2P groups and the C_{ipso} atom of **6** each show a ‘pseudo triplet’ splitting indicating likewise a bis-phosphane coordination [20]. In the case of **6**, also the ^1H -NMR signals indicate this kind of coordination by the triplet nature of the PCH_3 , PCH_2 and $\text{CH}_2\text{C}_5\text{H}_4$ resonances. No temperature dependence of the ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR signals is observed, as it was the case with **1**. This might be taken as an indication of a higher coordination number in **6** (‘pseudo-octahedral’).

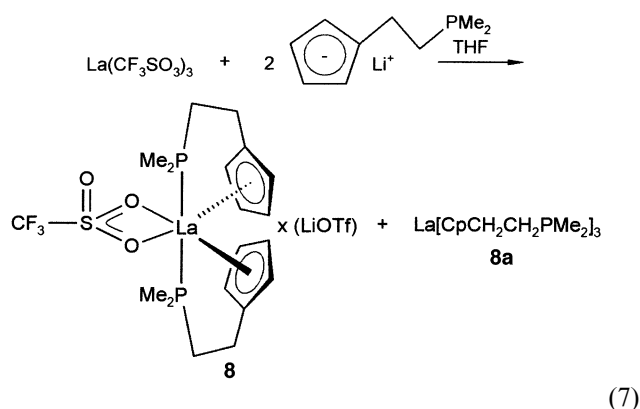
With scandium as the smallest rare earth metal element a bis-substitution product was even observed when a 3:1 stoichiometry of $\text{Li}[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PMe}_2]$ and $\text{Sc}(\text{CF}_3\text{SO}_3)_3$ was used Eq. (6).



Some unidentified by-products (ca. 1%) were also found and complicate the identification and characterization of **7**. However, the spectroscopic data seem to indicate a coordination of both P-atoms to the scandium center: the complex pattern of the ^1H -NMR signals is indicative for a bis-phosphane coordination. Nevertheless the exact mode of coordination in **7** remains uncertain.

With the large La^{3+} cation distinct difficulties in the synthesis of twofold complexes occur. The reaction of LaCl_3 with two equivalents $\text{Li}[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PMe}_2]$ or $\text{K}[\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PPh}_2]$ proceeded under the formation of a precipitate which was insoluble in THF, whereas

the reaction of $\text{La}(\text{CF}_3\text{SO}_3)_3$ with $\text{Li}[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{PMe}_2)]$ yielded a colorless solid, which was completely soluble in toluene Eq. (7).



Two signals in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum at δ -43.58 and -30.31 , respectively, show that a mixture of the twofold and the threefold substituted lanthanum complexes **8** and **8a** [9] was obtained. Therefore ^1H -NMR data could not be attributed conclusively and constitutional assignments for **8** therefore are not feasible. According to the ^7Li -NMR spectrum of the mixture, the monotriflate compound **8** contains LiCF_3SO_3 .

2.2. Complexes of the type $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]\text{LnX}$

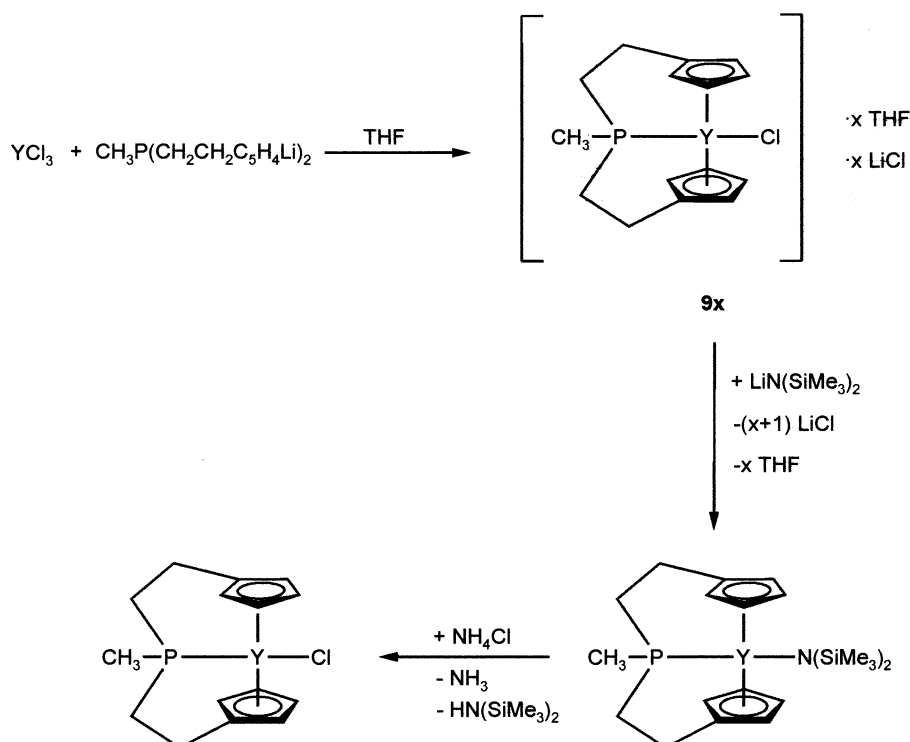
To increase the reactivity of the biscyclopentadienyl complexes towards substitution reactions the ligand

$\text{Li}_2[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]$ is introduced into rare earth chemistry.

The reaction of one equivalent of $\text{Li}_2[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]$ with one equivalent of YCl_3 in THF proceeded under formation of the $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]\text{YCl}$ (**9x**) which obviously contains LiCl and THF, from which it could not be separated because of the insolubility of the product in toluene (Scheme 3).

Nevertheless, $^{31}\text{P}\{^1\text{H}\}$ - and $^{13}\text{C}\{^1\text{H}\}$ -NMR measurements of the reaction mixture confirm the presence of the desired product: after 12 h reaction time the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum consists of a doublet at δ -21.29 with a $^1J_{\text{PY}}$ coupling constant of 84.3 Hz.

The ^1H -NMR spectrum exhibits a doublet for the methyl group at δ 1.06 with a $^2J_{\text{HP}}$ coupling constant of 5.9 Hz. For the methylene protons very complex signals are detected. The CH_2P groups are observed at δ 1.30 – 1.38 and the CpCH_2 -groups at δ 2.45 – 2.59 . The signals are complex because of the formation of the chelate ring. Within this ring system all protons are diastereotopic. For the ring protons of the cyclopentadienyl fragment an uncompletely resolved ABCD spin system is observed (δ_{A} , 5.54 ; δ_{B} , 5.60 ; δ_{C} , 5.78 ; δ_{D} , 5.98 ; cf.: $\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PPh}$ [17]). Since separation and purification of **9** from the mixture was not possible, an alternative strategy was employed. Compound **9x** was converted into the corresponding hexamethyl disylazide derivative $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]\text{YN}(\text{SiMe}_3)_2$



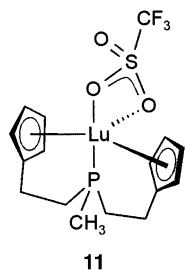
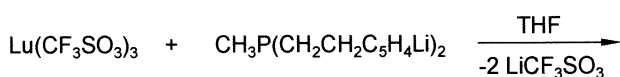
Scheme 3. Preparation of pure $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PMe}]\text{YCl}$ (**9**).

(10), which could be separated from LiCl by extraction with toluene. Reaction of **10** with NH_4Cl in toluene finally led to the pure chlorine compound **9** (Scheme 3).

As it was the case with product **9x**, pure **9** likewise is insoluble in toluene and the ^1H -NMR spectra of both materials are identical.

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum of **10** consists of a doublet at $\delta -19.95$ with a P–Y coupling constant of 110.8 Hz. The value of the coupling constant is remarkable high and may indicate a strengthening of the yttrium to phosphorus bond. (Note that the spectrum of **10** was recorded in C_6D_6 , whereas the spectrum of **9** was recorded in $\text{C}_6\text{D}_6 + \text{THF}$. It might be concluded, that THF coordinates (reversible) to **9**, while **10** is free of THF). In the ^1H -NMR spectrum of **10**, two signals for the methyl protons of the silyl groups (δ 0.14, 1.38) are observed. Accordingly two signals are observed for these groups in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum (δ 5.54, 6.27). Due to this result rotation about the Y–N bond seems to be hindered even at r.t.

The monotriflate complex $[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{P-Me}]\text{Lu}(\text{CF}_3\text{SO}_3)$ (**11**) on the other hand is easily soluble in aromatic hydrocarbons like toluene. It is accessible as a colorless solid by reaction of the ligand $\text{Li}_2[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PCH}_3]$ with one equivalent $\text{Lu}(\text{CF}_3\text{SO}_3)_3$ in excellent yield Eq. (8).



(8)

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum consists of a singlet at $\delta -8.86$ (cf.: $\text{Li}_2[(\text{C}_5\text{H}_4\text{CH}_2\text{CH}_2)_2\text{PCH}_3]$: -47.56). The methyl group at the phosphorus appears as a doublet as well in the ^1H - [δ 0.92 (6.2 Hz)] and in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum. ABCDX (for $\text{CH}_2\text{CH}_2\text{P}$) and ABCD (for C_5H_4) spin systems in the ^1H -NMR spectrum correspond to five separate signals for the C_5H_4 rings in the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum at r.t. and indicate a rigid coordination of the dianionic ligand to the metal center. However, whereas for **9** and **10** a distorted pseudotetrahedral geometry is most likely adopted, for **11** a higher coordination number due to a bidentate triflate coordination can not be ruled out. It should be mentioned, that comparable *ansa*-lanthanoidocene complexes with other heteroelements than phosphorus in the *ansa*-backbone have been described [24].

3. Conclusions

Using the diamagnetic rare earth metal centers Sc, Y, La and Lu a coordination of the phosphane functionality of phosphanoethyl cyclopentadienyl ligands is feasible. The strength of the metal–phosphorus bond strongly may be influenced by the nature of the ligand (monoanionic or dianionic), the phosphorus substituents and the residual anionic group X present at the metal (Cl^- , O_3SCF_3^-). The nature of the metal–X bond likewise is tunable by the specific phosphorus substituents. Indeed, it is this anionic functionality, which makes the compounds described in this paper, valuable precursors for reactions and derivatisations in this field of chemistry. Quite remarkably, most of the compounds $\text{Cp}'_2\text{LnX}$ with additional phosphanoalkyl side chains are obtained in good to excellent yields as monomeric, salt and solvent free compounds, in marked contrast to other bis-cyclopentadienyl rare earth metal derivatives and thus enhance the synthetic value of the compounds described here considerably. In contrast to comparable cyclopentadienyl ligands with donor functionalized side chains (OR, SR, NR_2 donors) [6–8], the coordination of the R_2P donor functionality to the metal is more labile and strongly dependent on the P substituents. Moreover, this functionality offers the possibility of further derivatisation at phosphorus and thus changing the ligation property considerably [25].

4. Experimental

4.1. General considerations

All operations were performed under an atmosphere of dry, oxygen free nitrogen and with thoroughly dried glassware by use of standard high-vacuum-line techniques. Pentane, toluene and THF were distilled under nitrogen from K–Na alloy. Elemental analyses were obtained with a Vario EL CHN analyzer of the Mikroanalytisches Laboratorium der TU München. Due to the high air and moisture sensitivity of all compounds, not all analyses were completely satisfactory. Mass spectra were conclusive in all cases, however. Chemical ionization (CI) mass spectral data were obtained employing a Varian Mat 311A spectrometer; peaks are reported as m/z (assignment, relative intensity). NMR spectra were recorded on a JEOL GX 270 spectrometer (^1H 270.17 MHz, $^{13}\text{C}\{^1\text{H}\}$ 67.94 MHz, $^{31}\text{P}\{^1\text{H}\}$ 109.4 MHz), a JEOL GX 400 (^1H 399.65 MHz, ^7Li , $^{13}\text{C}\{^1\text{H}\}$ 100.40 MHz, $^{31}\text{P}\{^1\text{H}\}$ 161.7 MHz) and a JEOL JNM-Lambda 400 (^{19}F 376.10 MHz) spectrometer. Chemical shifts refer to TMS ($\delta = 0$) as internal (^1H , ^{13}C) standard, to 80% H_3PO_4 (^{31}P) and to CF_3COOH (^{19}F) and LiBr 20% in D_2O (^7Li) as external standard. All chemi-

cal shifts are reported in ppm and coupling constants J in Hz. In case of high order spin systems, the distance N between the two outermost lines of a symmetrical multiplet t or q is given. The symbol m^* denotes a superposition of an A_2B_2 spin system ($X-CH_2CH_2-Y$) with an $A_nXX'A'_n$ spin system. All measurements were carried out at 25°C in C_6D_6 . Exceptions were given separately. Temperature dependent-NMR spectra were recorded with $[D_8]$ toluene as solvent.

$Sc(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, $La(CF_3SO_3)_3$, $Lu(CF_3SO_3)_3$ [26], Cy_2PH [27a], Cy_2PLi [27a], Li_2PMe [27b], $Li[C_5H_4CH_2CH_2PMe_2]$ [9], $Li[C_5H_4CH_2CH_2P(t-Bu)_2]$ [15b] and spiro[2,4]hepta-4,6-diene [14] were prepared according to literature procedures. YCl_3 was prepared from the hexahydrate by drying in vacuo (140°C 10^{-3} Torr) for 5 days. The lanthanoid hexahydrate chlorides were purchased from commercial sources.

4.2. $Li[C_5H_4CH_2CH_2PCy_2]$

To a solution of 4.36 mmol (0.89 g) $LiPCy_2$ in 50 ml of THF 4.36 mmol (0.4 g) spiro[2,4]hepta-4,6-diene in 20 ml of THF were added by means of a pipette. After stirring the reaction mixture for 12 h at r.t. the solvent was removed and the product was washed three times with pentane. After removing the solvent and drying a colorless solid is obtained. Yield: 0.72 g (56%). 1H -NMR ($[d_8]$ dioxane, r.t.): δ 1.23–1.76 [m, 24 H, Cy, CH_2PCy_2 : superposition], 2.64 [dtr, $^3J_{HH} = 7.8$, $^3J_{HP} = 2.9$, 2 H, $C_5H_4CH_2CH_2P(CH_3)_2$], 5.53 [A₂B₂ spin system, δ_A , 5.49; δ_B , 5.58; $J_{AB} = 2.4$, 4 H C_5H_4]. $^{13}C\{^1H\}$ -NMR ($[d_8]$ dioxane, r.t.): δ 25.35 [d, $^2J_{CP} = 6.6$, $C_5H_4CH_2$], 27.23 [m, C3,4, Cy], 29.96 [d, $^1J_{CP} = 7.7$, CH_2PCy_2], 31.21 [d, $^2J_{CP} = 13.2$, C2, Cy], 33.63 [d, $^1J_{CP} = 9.4$, C1, Cy], 102.85 [s, CH, C_5H_4], 103.25 [s, CH, C_5H_4], 120.75 [d, $^3J_{CP} = 9.9$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR ($[d_8]$ dioxane, r.t.): δ -8.76 (s). Anal. Calc. for $C_{19}H_{30}PLi$: C, 77.00; H, 10.20; P, 10.45. Found: C, 75.91; H, 10.32; P, 10.74%.

4.3. $Li_2[(C_5H_4CH_2CH_2)_2PMe]$

To a suspension of 0.068 mol (4.07 g) Li_2PMe in 50 ml of THF 0.14 mol (12.90 g) spiro[2,4]hepta-4,6-diene in 20 ml of THF were added by means of a pipette. After stirring the reaction mixture for 12 h at r.t. the solvent was removed and the product was washed three times with pentane. After evaporation of the solvent and drying a colorless solid is obtained. Yield: 7.23 g (44%). 1H -NMR ($[d_8]$ THF, r.t.): δ 0.98 [s, 3H, CH_3P], 1.67 [m, 4 H, $CH_2C_5H_4$], 2.57 [m, 4 H, $MePCH_2$], 5.41 [m, 8 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR ($[d_8]$ THF, r.t.): δ 10.05 [d, $^1J_{CP} = 13.8$, CH_3P], 25.79 [d, $^2J_{PC} = 12.3$, PCH_2], 32.57 [d, $^1J_{CP} = 6.1$, $CH_2(C_5H_4)_2$], 101.68 [s, CH, (C_5H_4)], 101.84 [s, CH, (C_5H_4)], 119.54 [d, $^3J_{CP} = 10.8$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR ($[d_8]$ THF, r.t.): δ -47.56. Anal.

Calc. for $C_{15}H_{19}Li_2P$: C, 73.79; H, 7.84; Li, 5.69; P, 12.69. Found: C, 74.10; H, 8.00; Li, 5.71; P, 12.80%.

4.4. $[C_5H_4CH_2CH_2P(CH_3)_2]YCl$ (1)

To a mixture of 14.4 mmol (2.3 g) of $Li[C_5H_4CH_2CH_2PMe_2]$ and 7.0 mmol (1.38 g) YCl_3 , 40 ml of THF was added at -78°C. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. The toluene extract was concentrated and **1** was isolated as colorless crystals. Yield: 1.1 g (97%). 1H -NMR (C_6D_6 , r.t.): δ 0.86 [d, $^2J_{HP} = 1.7$, 12 H, $P(CH_3)_2$], 1.60 [br, 4H, $C_5H_4CH_2CH_2P(CH_3)_2$], 2.39 [br, 4 H, $C_5H_4CH_2CH_2P(CH_3)_2$], 5.58 [br, 4 H, $C_5H_4CH_2CH_2$], 5.69 [br, 4 H, $C_5H_4CH_2CH_2$]. 1H -NMR ($[d_8]$ toluene, -80°C): δ 0.67 [s, br, PMe], 1.18 [s, br, PMe], 1.23 [br, CH_2P], 1.18 [br, $CH_2C_5H_4$], 2.07 [br, CH_2P], 2.77 [br, $CH_2C_5H_4$], 5.61, 6.14, 6.29 [br, C_5H_4]. $^{13}C\{^1H\}$ -NMR ($[d_8]$ toluene, -80°C): δ 9.61 [br, CH_3], 10.20 [br, CH_3], 24.39 [br, CH_2P], 33.42 [br, $CH_2C_5H_4$], 101.83, 106.52, 108.06, 110.20 [br, C_5H_4], 131.84 [br, C_{ipso}].

$^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 10.22 [s, CH_3], 24.39 [t, $N = 12.3$, CH_2PMe_2], 33.45 [t, $N = 13.1$, $C_5H_4CH_2$], 107.20 [s, br, CH (C_5H_4)], 129.45 [t, $N = 6.1$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -34.65 [d, $^1J_{P-Y} = 74.0$]. $^{31}P\{^1H\}$ -NMR ($[d_8]$ THF, r.t.): δ -33.90 [d, $^1J_{P-Y} = 74.0$]. $^{31}P\{^1H\}$ -NMR ($[d_8]$ toluene, -80°C): δ -34.65 [d, $^1J_{P-Y} = 74.0$]. Mass spectrum (CI); m/z (%): 430 (49) [M], 395 (100) [$M-C_5H_4(CH_2)_2P(CH_3)_2$], 154 (12) [$C_5H_5(CH_2)_2P(CH_3)_2$]. Anal. Calc. for $C_{18}H_{28}ClP_2Y$: C, 50.19; H, 6.55. Found: C, 51.22; H, 6.84%.

4.5. $[C_5H_4CH_2CH_2PCy_2]_2YCl$ (3)

To a mixture of 4.05 mmol (1.2 g) of $Li[C_5H_4CH_2CH_2PCy_2]$ and 2.05 mmol (0.4 g) YCl_3 , 40 ml of THF was added at -78°C. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. The toluene extract was concentrated and **3** was isolated as colorless crystals. Yield: 1.13 g (78%). 1H -NMR (C_6D_6 , r.t.): δ 1.02–1.90 [m, 48 H, $CH_2P(C_6H_{11})_2$], 2.80 [q, $N = 28.7$, $CH_2C_5H_4$], 5.84 [A₂B₂ Spin system, uncompletely resolved δ_A , 5.79; δ_B , 5.88; 8 H, $C_5H_4CH_2CH_2PCy_2$]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 26.20 [d, $^2J_{CP} = 9.3$, $C_5H_4CH_2$], 27.58 [d, $^4J_{CP} = 8.3$, C4, Cy], 28.15 [d, $^3J_{CP} = 18.7$, C3, Cy], 29.65 [d, $^1J_{CP} = 6.7$, CH_2P], 30.22 [d, $^2J_{CP} = 9.3$, C2, Cy], 34.30 [d, $^1J_{CP} = 9.9$, C1, Cy], 106.33 [s, C_5H_4], 111.49 [s, C_5H_4], 126.50 [d, $^3J_{CP} = 10.9$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -2.30 [d, $J_{PY} = 29.4$]. $^{31}P\{^1H\}$ -NMR ($[d_8]$ toluene, -80°C): δ -2.30 [d, $J_{PY} = 29.4$]. Anal. Calc. for $C_{38}H_{60}ClP_2Y$: C, 64.91; H, 8.60. Found: C, 65.20; H, 9.11%.

4.6. $[C_5H_4CH_2CH_2P(t-Bu)_2]_2Y(CF_3SO_3)$ (**4**)

To a mixture of 5.48 mmol (1.34 g) of $Li[C_5H_4CH_2CH_2P(t-Bu)_2]$ and 1.77 mmol (0.95 g) $Y(CF_3SO_3)_3$, 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. The toluene extract was evaporated and **4** was isolated as a colorless foam. Yield: 0.72 g (98%). 1H -NMR (C_6D_6 , r.t.): δ 1.12 [d, $^3J_{HP} = 10.8$, 18 H, $PC(CH_3)_3$], 1.73 [m*, $N = 14.1$, 2 H, $CH_2CH_2P(tBu)_2$], 2.93 [m*, $N = 20.2$, 2 H, $CH_2CH_2P(tBu)_2$], 5.98 [A_2B_2 spin system, uncompletely resolved δ_A , 5.93; δ_B , 6.04; 4 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 25.41 [d, $^2J_{CP} = 26.4$, $CH_2C_5H_4$], 30.08 [d, $^2J_{CP} = 12.7$, $C(CH_3)_3$], 31.19 [d, $^1J_{CP} = 33.6$, $C(CH_3)_3$], 31.71 [s, $CH_2P(t-Bu)_2$], 108.17 [s, C_5H_4], 113.477 [s, C_5H_4], 120.03 [q, $^1J_{CF} = 318.4$, CF_3], 133.39 [d, $^3J_{CP} = 10.5$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 31.94 [d, $J_{PY} = 7.1$]. $^{31}P\{^1H\}$ -NMR ($[d_8]toluene$, $-80^\circ C$): δ 31.94 [d, $J_{PY} = 7.1$]. Mass spectrum (CI); m/z (%): 713 (12.53) [M^+], 563 (8.11) [$M^+ - C_5H_4CH_2CH_2(t-Bu)_2$], 477 (100) [$C_5H_4CH_2CH_2P(t-Bu)_2$].

4.7. $[C_5H_4CH_2CH_2P(t-Bu)_2]_2YCl$ (**5**)

To a mixture of 5.48 mmol (1.34 g) of $Li[C_5H_4CH_2CH_2Pt-Bu_2]$ and 1.77 mmol (0.95 g) YCl_3 , 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. On concentration of the solvent, **5** was isolated as colorless crystals. Yield: 0.72 g (51%). 1H -NMR (C_6D_6 , r.t.): δ 1.06 [d, $^3J_{HP} = 11.2$, 36 H, $PC(CH_3)_3$], 1.74 [m*, $N = 21.5$, 4 H, $CH_2C_5H_4$], 2.87 [dtr, $^3J_{HH} = 7.8$, $^2J_{HP} = 12.2$, 4 H, $CH_2P(t-Bu)_2$], 6.11 [s, 8 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 24.33 [d, $^2J_{CP} = 8.8$, $CH_2C_5H_4$], 29.01 [d, $^1J_{CP} = 20.2$, $C(CH_3)_3$], 29.42 [d, $^2J_{CP} = 10.4$, $C(CH_3)_3$], 31.82 [d, $^1J_{CP} = 10.4$, $CH_2P(t-Bu)_2$], 108.70 [s, C_5H_4], 111.42 [s, C_5H_4], 131.80 [d, $^3J_{CP} = 9.9$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 32.56 [d, $J_{PY} = 48.5$]. $^{31}P\{^1H\}$ -NMR ($[d_8]toluene$, $-80^\circ C$): δ 32.56 [d, $J_{PY} = 48.5$]. Mass spectrum (CI); m/z (%): 599 (12.91) [M^+], 563 (6.27) [$M^+ - Cl$], 541 (27.76) [$M^+ - C_4H_{10}$], 238 (100) [$C_5H_4CH_2CH_2P(t-Bu)_2$]. Anal. Calc. for $C_{30}H_{52}ClP_2Y$: C, 60.15; H, 8.75. Found: C, 58.21; H, 8.53%.

4.8. $[C_5H_4CH_2CH_2PMe_2]_2Lu(CF_3SO_3)$ (**6**)

To a mixture of 3.37 mmol (0.54 g) of $Li[C_5H_4CH_2CH_2PMe_2]$ and 1.69 mmol (1.05 g) $Lu(CF_3SO_3)_3$, 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. The

toluene extract was concentrated and **6** was isolated as colorless crystals. Yield: 0.83 g (78%). 1H -NMR (C_6D_6 , r.t.): δ 0.94 [m*, $N = 4.7$, 12 H, $P(CH_3)_2$], 1.58 [m*, $N = 37.6$, 4 H, CH_2PMe_2], 2.36 [m*, $N = 30.9$, 4 H, $C_5H_4CH_2$], 5.63 [s, 4 H, C_5H_4], 5.70 [s, 4 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 10.34 [t, $N = 7.3$, $P(CH_3)_2$], 23.7 [t, $N = 11.4$, $C_5H_4CH_2$], 33.25 [t, $N = 16.1$, CH_2PMe_2], 106.62 [s, C_5H_4], 131.37 [t, $N = 7.8$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -26.27(s). $^{31}P\{^1H\}$ -NMR ($[d_8]toluene$, $-80^\circ C$): δ -26.27(s). Mass spectrum (CI); m/z (%): 630 (48.02) [M^+], 562 (3.85) [$M^+ - CF_3$], 477 (100) [$M^+ - C_5H_4(CH_2)_2P(CH_3)_2$]. Anal. Calc. for $C_{19}H_{28}P_2O_3SF_3Lu$: C, 36.20; H, 4.48. Found: C, 34.56; H, 4.28%.

4.9. $[C_5H_4CH_2CH_2PMe_2]_2La(CF_3SO_3)$ (**8**)

To a mixture of 5.06 mmol (0.81 g) of $Li[C_5H_4CH_2CH_2PMe_2]$ and 2.53 mmol (1.48 g) $La(CF_3SO_3)_3$, 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and a colorless solid was isolated by extraction with 50 ml of toluene and evaporation of the solvent. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -43.58 [br, $La(C_5H_4CH_2CH_2PMe_2)_3$], 50%, -30.31 [br, $[C_5H_4CH_2CH_2PMe_2]_2LaCF_3SO_3$], 50%. $^7Li\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -0.75 (s). Mass spectrum (CI); m/z (%): 593 (37.6) [$M^+ + 1$], 440 (53.92) [$M^+ - CF_3SO_3$], 154 (100) [$C_5H_5CH_2CH_2PMe_2$].

4.10. Reaction of $Li[C_5H_4CH_2CH_2PMe_2]$ with $Sc(CF_3SO_3)_3$

To a mixture of 5.99 mmol (0.96 g) of $Li[C_5H_4CH_2CH_2PMe_2]$ and 1.99 mmol (0.98 g) $Sc(CF_3SO_3)_3$, 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and a colorless solid was isolated by extraction with 50 ml of toluene and evaporation. Yield: 0.80 g. 1H -NMR (C_6D_6 , r.t.): δ 1.05 [s, 12 H, PMe_2], 1.78 [m*, $N = 48.0$, CH_2PMe_2], 2.57 [m*, $N = 30.21$, $C_5H_4CH_2$], 6.03 [A_2B_2 spin system uncompletely resolved, δ_A , 5.96; δ_B , 6.09; 8 H, $C_5H_4CH_2CH_2PMe_2$]. $^{13}C\{^1H\}$ -NMR ($[d_8]toluene$, r.t.): δ 11.71 [s, PMe_2], 25.05 [d, $^2J_{CP} = 13.0$, $CH_2C_5H_4$], 34.66 [d, $^1J_{CP} = 5.2$, CH_2PMe_2], 110.70 [s, $C_5H_4CH_2$], 111.78 [s, $C_5H_4CH_2$], 120.15 [q, $^1J_{CF} = 318.3$, CF_3], 133.77 [d, $^3J_{CP} = 9.3$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR ($[d_8]toluene$, r.t.): δ -31.94 [s, br, 40%], -37.66 [s, br, 60%]. $^{31}P\{^1H\}$ -NMR ($[d_8]toluene$, $-80^\circ C$): δ -31.25 [s, $(C_5H_4CH_2CH_2PMe_2)_2ScCF_3SO_3$, 90%], -26.07 [$(C_5H_4CH_2CH_2PMe_2)_3Sc$, 5%], -25.49 [$(C_5H_4CH_2CH_2PMe_2)_3Sc$, 5%]. $^{19}F\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -78.6 [s, CF_3]. Mass spectrum (CI); m/z (%): 501 (5.25) [$M^+ + 1$], 351 (100) [$M^+ - CF_3SO_3$], 154 [34.03] [$C_5H_5CH_2CH_2PMe_2$].

4.11. Reaction of YCl_3 with $Li_2[(C_5H_4CH_2CH_2)_2PCH_3]$

To a suspension of 4.06 mmol (0.79 g) YCl_3 in 40 ml THF were added 4.06 mmol (0.99 g) $Li_2(C_5H_4CH_2CH_2)_2PCH_3$ at $-78^\circ C$ and then allowed to warm up to r.t. The reaction mixture shows signals of compound **9** (vide infra). On evaporation of the solvent, a colorless solid remains, which is insoluble in hydrocarbons.

4.12. $(Me_3Si)_2NY[(C_5H_4CH_2CH_2)_2PCH_3]$ (**10**)

To a suspension of 3.99 mmol (0.78 g) YCl_3 in 40 ml THF were added with stirring 4.02 mmol (0.98 g) $Li_2(C_5H_4CH_2CH_2)_2PCH_3$ at $-78^\circ C$ and then allowed to warm up to r.t.. To the reaction mixture 4.1 mmol (0.69 g) $LiN(SiMe_3)_2$ were added. After 12 h reaction time the solvent was removed and the residue was extracted three times with 30 ml of toluene. The toluene was removed and a colorless solid remained. Yield: 1.56 g (81%). 1H -NMR (C_6D_6 , r.t.): δ 0.14 [s, br, 9 H, $SiMe_3$], 0.38 [s, br, 9 H, $SiMe_3$], 0.72 [d, $^2J_{HP} = 5.5$, CH_3P , 3 H], 1.37 [m*, $N = 23.1$, 4 H, CH_2Cp], 2.32 [m*, $N = 94.1$, 4 H, CH_2PMe], 5.53 [m*, $N = 7.7$, 1 H, CH (C_5H_4)], 5.90 [m*, $N = 8.1$, 1 H, CH (C_5H_4)], 6.07 [m*, $N = 7.7$, 1 H, CH (C_5H_4)], 6.41 [m*, $N = 7.7$, 1 H, CH (C_5H_4)]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 5.54 [s, br, $SiMe_3$], 6.27 [s, br, $SiMe_3$], 9.57 [dd, $^1J_{CP} = 9.2$, $^2J_{CY} = 1.5$, CH_3P], 24.05 [d, $^2J_{CP} = 10.0$, CH_2Cp], 30.57 [d, $^1J_{CP} = 16.1$, CH_2PMe], 104.01 [d, $J_{CY} = 1.5$, C_5H_4], 109.28 [s, C_5H_4], 110.75 [s, C_5H_4], 114.79 [d, $J_{CY} = 1.5$, C_5H_4], 128.91 [d, $^3J_{CP} = 6.9$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -19.95 [d, $^1J_{PY} = 110.8$]. Mass spectrum (CI); m/z (%): 479 (19.48) [$M + 1$], 464 (42.77) [$M^+ - CH_3$], 319 (100) [$M^+ - N(SiMe_3)_2$]. Anal. Calc. for $C_{21}H_{37}NPYSi_2$: C, 52.59; H, 7.78; N, 2.92. Found: C, 49.90; H, 7.63; N, 2.41%.

4.13. $ClY[(C_5H_4CH_2CH_2)_2PCH_3]$ (**9**)

To a solution of 1.65 mmol (0.79 g) **10** in 40 ml toluene were added with stirring 1.50 mmol (0.08 g) NH_4Cl at $-78^\circ C$ and then allowed to warm up to room temperature. The formation of a colorless solid is observed. After filtration the solid was washed with toluene and dried in vacuo. Yield: 0.45 g (84%). 1H -NMR (THF + C_6D_6 , r.t.): δ 1.06 [d, $^2J_{HP} = 5.9$, 3H, CH_3], 1.30–1.38 [m, 4H, CH_2 C_5H_4], 2.45–2.59 [m, 4H PCH_2], 5.54 [m, 2 H C_5H_4], 5.60 [m, 2 H, C_5H_4], 5.78 [m, 2 H, C_5H_4], 5.98 [m, 2 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR (THF + C_6D_6 , r.t.): δ 8.40 [d, $^1J_{CP} = 4.7$, PCH_3], 24.65 [d, $^2J_{CP} = 15.6$, CH_2 C_5H_4], 29.53 [d, $^1J_{CP} = 11.9$, PCH_2], 103.07 [s, CH, (C_5H_4)], 107.07 [s, CH, (C_5H_4)], 107.52 [s, CH (C_5H_4)], 115.71 [s, CH (C_5H_4)], 129.9 [d, $^3J_{CP} = 8.3$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (THF + C_6D_6 , r.t.): δ -21.29 [d, $J_{YP} = 84.3$]. Anal. Calc. for $C_{15}H_{19}PYCl$: C,

50.80; H, 5.40; Cl, 10.00. Found: C, 49.92; H, 6.00; Cl, 11.5%.

4.14. $(CF_3SO_3)Lu[(C_5H_4CH_2CH_2)_2PCH_3]$ (**11**)

To a mixture of 2.05 mmol (0.50 g) of $Li_2(C_5H_4CH_2CH_2)_2PCH_3$ and 2.04 mmol (1.27 g) $Lu(CF_3SO_3)_3$, 40 ml of THF was added at $-78^\circ C$. The reaction mixture was slowly warmed up to r.t. and stirred for another 12 h. The solvent was removed and the product was extracted with 50 ml of toluene. The toluene extract was evaporated and **11** was isolated as a colorless solid. Yield: 1.10 g (97%). 1H -NMR (C_6D_6 , r.t.): δ 0.92 [d, $^2J_{HP} = 6.2$, 3 H, CH_3P], 1.34 [m*, $N = 48.3$, 4 H, CH_2 C_5H_4], 2.29 [m*, $N = 137.7$, 4 H, $MePCH_2$], 5.47 [m, 2 H C_5H_4], 5.94 [m, 2 H, C_5H_4], 6.20 [m, 2 H, C_5H_4], 6.49 [m, 2 H, C_5H_4]. $^{13}C\{^1H\}$ -NMR (C_6D_6 , r.t.): δ 7.52 [d, $^1J_{CP} = 7.3$, CH_3P], 24.18 [d, $^2J_{PC} = 13.0$, $CH_2C_5H_4$], 29.90 [d, $^1J_{CP} = 17.6$, PCH_2], 102.55 [s, CH, (C_5H_4)], 107.19 [s, CH, (C_5H_4)], 108.49 [s, CH (C_5H_4)], 115.18 [s, CH (C_5H_4)], 128.76 [d, $^3J_{CP} = 8.1$, C_{ipso}]. $^{31}P\{^1H\}$ -NMR (C_6D_6 , r.t.): δ -8.86 (s). ^{19}F -NMR (C_6D_6 , r.t.): δ 0.46 [s, CF_3]. Mass spectrum (CI); m/z (%): 553 (32) [$M - 1$], 404.9 (100) [$M - CF_3SO_3$], 232 (63) [$CH_3P(CH_2CH_2C_5H_5)_2$].

4.15. X-ray crystallography

Suitable single crystals of complex **1** for a X-ray diffraction study were obtained by slowly removing the solvent. The structure was solved by a combination of direct methods, difference-Fourier syntheses and least-squares methods. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray Crystallography [28]. All calculations were performed on a Linux PC using the programs PLATON [29], SIR-92 [30], and SHELX-93 [31].

4.15.1. Data collection, structure solution and refinement

A summary of the collection and refinement data are reported in Table 2. Single crystal data for **1** were collected on a kappa-CCD system from Nonius with a rotating anode generator (Nonius FR591; Mo- K_α , $\lambda = 0.71073$ Å) in rotation mode (φ -scans) using Mo- K_α radiation (graphite monochromator). The data collection was performed at 193 K within the θ -range of $4 < \theta < 26.4^\circ$ ($\varphi = 0.0$ – 360° with $\Delta\varphi = 1^\circ$). A total number of 15 344 reflections were collected. After merging 4049 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for intensity decay and/or absorption effects with the program Scalepack [32] were applied. All 'heavy' atoms of the asymmetric unit were anisotropically refined. Only car-

bon atom C15 was refined isotropically with two split positions due to disorder in the ethylene backbone of the second phosphine ligand and all hydrogen atoms were calculated in ideal positions (riding model). Full-matrix least-squares refinements of 193 parameters were carried out by minimizing $\Delta w(F_o^2 - F_c^2)^2$ with SHELXL weighting scheme and stopped at shift/err < 0.001.

4.16. Supplementary material

Crystallography data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC no. 139688. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). A listing (25 pages) can also be ordered from the ACS, and can be downloaded from the internet; see any current masthead page for ordering and Internet access instructions.

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References

- [1] (a) D.R. Cary, G.E. Ball, J. Arnold, J. Am. Chem. Soc. 117 (1995) 3492. (b) P.J. Shapiro, E. Bunel, W.P. Schaefer, J.E. Bercaw, Organometallics 9 (1990) 867. (c) T.D. Tilley, R.A. Anderson, A. Zalkin, J. Am. Chem. Soc. 104 (1982) 3725. (d) T.D. Tilley, R.A. Anderson, A. Zalkin, Inorg. Chem. 22 (1983) 856. (e) S. Stults, A. Zalkin, Acta Crystallogr. C 43 (1987) 430.
- [2] See for example: (a) G. Bielang, R.D. Fischer, J. Organomet. Chem. 161 (1978) 335. (b) G.W. Rabe, J.W. Ziller, Inorg. Chem. 34 (1995) 5378. (c) H. Schumann, G.M. Frisch, Z. Naturforsch. 34b (1979) 784. (d) W.J. Evans, I. Bloom, W.E. Hunter, J.L. Atwood, Organometallics 2 (1983) 709. (e) M. Westerhausen, M. Hartmann, W. Schwarz, Inorg. Chim. Acta 269 (1998) 91. (f) H.C. Aspinall, S.R. Moore, A.K. Smith, J. Chem. Soc. Dalton Trans. (1993) 993.
- [3] P.B. Hitchcock, M.F. Lappert, I.A. MacKinnon, J. Chem. Soc. Chem. Commun. (1988) 1557.
- [4] M.D. Fryzuk, T.S. Haddad, J. Am. Chem. Soc. 110 (1988) 8263.
- [5] H.H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman, A. Schier, P. Bissinger, W. Hiller, J. Organomet. Chem. 482 (1994) 151.
- [6] Selected examples for complexes with alkyl–OR donor functionalized cyclopentadienyl ligands: (a) W.T. Scroggins, M.F. Rettig, R.M. Wing, Inorg. Chem. 15 (1976) 1381. (b) P. Van de Weghe, C. Bied, J. Collin, J. Organomet. Chem. 475 (1994) 121. (c) C. Qian, B. Wang, D. Deng, J. Sun, F.E. Hahn, J. Chen, P. Zheng, J. Chem. Soc. Dalton Trans. (1996) 955. (d) D. Deng, C. Qian, G. Wu, P. Zheng, J. Chem. Soc. Chem. Commun. (1990) 880. (e) D. Deng, B. Li, C. Qian, Polyhedron 9 (1990) 1453. (f) C. Qian, B. Wang, D. Deng, G. Wu, P. Zheng, J. Organomet. Chem. 427 (1992) C29. (g) D. Deng, F. Song, Z. Wang, C. Qian, G. Wu, P. Zheng, Polyhedron 11 (1992) 2883. (h) J. Chen, G. Wu, P. Zheng, D. Deng, J. Hu, C. Qian, Jiegou Huaxe (Chin. J. Struct. Chem.) 12 (1993) 254. (i) D. Deng, C. Qian, F. Song, Z. Wang, P. Zheng, S. Jin, Y. Lin, J. Organomet. Chem. 458 (1993) 83. (j) D.A. Laske, R. Duchateau, J.H. Teuben, A.L. Spek, J. Organomet. Chem. 462 (1993) 149. (k) C. Qian, B. Wang, D. Deng, J. Hu, J. Chen, G. Wu, P. Zheng, Inorg. Chem. 33 (1994) 3382. (l) D. Deng, Y. Jiang, C. Qian, G. Wu, P. Zheng, J. Organomet. Chem. 470 (1994) 99. (m) D. Deng, X. Zheng, C. Qian, J. Sun, L. Zhang, J. Organomet. Chem. 470 (1994) 95. (n) D. Deng, X. Zheng, C. Qian, J. Sun, A. Dormond, D. Baudry, M. Visseaux, J. Chem. Soc. Dalton Trans. (1994) 1665. (o) B. Wang, D. Deng, C. Qian, New J. Chem. 19 (1995) 515.
- [7] Selected examples for complexes with alkyl–NR₂ donor functionalized cyclopentadienyl ligands: (a) T.F. Wang, T.Y. Lee, J. Organomet. Chem. 423 (1992) 31. (b) W.A. Herrmann, R. Anwender, F.C. Munck, W. Scherer, Chem. Ber. 126 (1993) 331. (c) R. Anwender, W.A. Herrmann, W. Scherer, F.C. Munck, J. Organomet. Chem. 462 (1993) 163. (d) P. Jutzi, J. Dahlhaus, M.O. Kristen, J. Organomet. Chem. 450 (1993) C1. (e) G.A. Molander, H. Schumann, E.C. Rosenthal, J. Demtschuk, Organometallics 15 (1996) 3817. (f) H. Schumann, F. Erbstein, K. Herrmann, J. Demtschuk, R. Weimann, J. Organomet. Chem. 526 (1998) 255. (g) J.R. van den Hende, P.B. Hitchcock, M.F. Lappert, T.A. Nile, J. Organomet. Chem. 472 (1994) 79.
- [8] Selected examples for complexes with Alkyl–SR donor functionalized cyclopentadienyl ligands: (a) M. Graganjac, C. Ruffig, T.B. Rauchfuss, Organometallics 4 (1985) 1909. (b) B. Henri, G. Günther, M. Walter, J. Organomet. Chem. 493 (1995) 163. (c) H. Schumann, K. Herrmann, J. Demtschuk, S.H. Mühle, Z. Anorg. Allg. Chem. 625 (1999) 1107.
- [9] H.H. Karsch, V.W. Graf, M. Reisky, E. Witt, Eur. J. Inorg. Chem. (1998) 1403.
- [10] H. Schumann, J.A. Meese-Marktscheffel, B. Gorella, F.H. Görlitz, J. Organomet. Chem. (1992) C27.
- [11] G.B. Deacon, A. Dietrich, C.M. Forsyth, H. Schumann, Angew. Chem. Int. Ed. Engl. 28 (1989) 1370.
- [12] M. Visseaux, A. Dormond, M.M. Kubicki, C. Moise, D. Baudry, M. Ephritikhine, J. Organomet. Chem. 433 (1992) 95.
- [13] (a) T. Kauffmann, J. Ennen, H. Lhotak, A. Rensing, F. Steinseifer, A. Woltermann, Angew. Chem. 92 (1980) 321; Angew. Chem. Int. Ed. Engl. 19 (1980) 328. (b) C. Charrier, F. Mathey, J. Organomet. Chem. 170 (1979) C41. (c) C. Charrier, F. Mathey, Tetrahedron Lett. (1978) 2407. (d) S.O. Grim, R.C. Barth, J. Organomet. Chem. 94 (1975) 327. (e) R. Uriate, T.J. Mazanec, K.D. Tau, D.W. Meek, Inorg. Chem. 19 (1980) 79.
- [14] C.F. Wilcox, R.R. Craig, J. Am. Chem. Soc. 83 (1961) 3866.
- [15] (a) A.H. Cowley, C.S. King, A. Decken, Organometallics 14 (1995) 20. (b) R.T. Kettenbach, W. Bonrath, H. Butenschön, Chem. Ber. 126 (1993) 1657. (c) A.M. Slawin, D.L. Williams, J. Crosby, J.A. Ramsden, C. White, J. Chem. Soc. Dalton Trans. (1988) 2491.
- [16] H.H. Karsch, V.W. Graf, M. Reisky, J. Chem. Soc. Chem. Commun. (1999) 1695.
- [17] O.J. Curnow, G. Huttner, S.J. Smail, M.M. Turnbull, J. Organomet. Chem. 524 (1996) 267.
- [18] See e.g.: G. Yang, Y. Fan, J. Organomet. Chem. 322 (1987) 57. Further reading: R. Anwender, W.A. Herrmann, Top. Curr. Chem. 179 (1996) 1.
- [19] D. Fryzuk, T.S. Haddad, S.J. Rettig, Organometallics 10 (1991) 2026.
- [20] (a) D.A. Redfield, L.W. Cary, J.H. Nelson, Inorg. Chem. 14, 1975, 50. (b) D.A. Redfield, L.W. Cary, J.H. Nelson, Inorg. Nucl. Chem. Lett. 10 (1974) 727. (c) P.S. Pregosin, W.R. Kunz, ³¹P and ¹³C-NMR of Transition Metal Phosphine Complexes, in: P. Diehl, E. Fluck, R. Kosfeld, (Eds.), NMR Basic Principles and Progress, vol. 16. Springer-Verlag, Berlin, 1979, p. 65.

- [21] (a) R. Poilblanc, M. Lenzi, R. Mathieu, *Inorg. Chem.* 9 (1970) 2030. (b) R.R. Holmes, *Acc. Chem. Res.* 12 (1979) 257. (c) R.R. Holmes, Pentacoordinated phosphorus, in: *Structure and Spectroscopy*, ACS Monograph 175, vol. I, American Chemical Society, Washington DC, 1980. (c) R. Luckenbach, *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*, Thieme, Stuttgart, 1973.
- [22] E.B. Lobkovskii, G.L. Soloveichik, B.M. Bulichev, A.B. Erofeev, *Zh. Struct. Khim.* 25 (1984) 170.
- [23] C. Qian, X. Zheng, B. Wang, D. Deng, J. Sun, *J. Organomet. Chem.* 466 (1994) 101.
- [24] (a) C. Qian, C. Zhu, Y. Lin, Y. Xing, *J. Organomet. Chem.* 507 (1996) 41. (b) C. Qian, D. Zhu, *J. Organomet. Chem.* 445 (1993) 79.
- [25] H.H. Karsch, V. Graf, to be published.
- [26] (a) H.M. Hamidi, J.L. Pascal, *Polyhedron* 13 (1994) 1787. (b) R.D. Howells, J.D. McCrow, *Chem. Rev.* 77 (1977) 69.
- [27] (a) G. Hanika, Thesis, TU München, 1988. (b) K.H. Lundberg, R.J. Rowatt, W.E. Miller, *Inorg. Chem.* 8 (1969) 1336.
- [28] A.J.C. Wilson (Ed.), *International Tables for Crystallography*, vol. C, Tables 6.1.1.4 (pp. 500–502), 4.2.6.8 (pp. 219–222), and 4.2.4.2 (pp. 193–199), Kluwer Academic, Dordrecht, The Netherlands, 1992.
- [29] A.L. Spek, PLATON-92–PLUTON-92 An integrated tool for the analysis of the results of a single crystal structure determination, *Acta Crystallogr. Sect. A* 46 (1990) C34.
- [30] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR-92, University Bari, Italy, 1992.
- [31] G.M. Sheldrick, SHELXL-93, in: G.M. Sheldrick, C. Krüger, R. Goddard (Eds.), *Crystallographic Computing 3*, Oxford University, England, 1993, pp. 175–189.
- [32] C.E. Housecroft, in: P. Braunstein, L. Oro, P.R. Raithby (Eds.), *Metal Clusters in Chemistry*, 276, Wiley–VCH, Weinheim, 1999, p. 9.