Dimethylphosphanylethylcyclopentadienyl Complexes of Lanthanum and Yttrium

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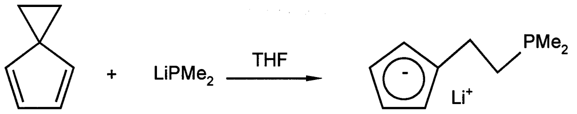
The reactions of Li[$C_5H_4(CH_2)_2P(CH_3)_2$] (**1**) with La(CF_3SO_3)$_3$ and Y(CF_3SO_3)$_3$ are described. Three equivalents of **1** reacted with La(CF_3SO_3)$_3$ under formation of La[$C_5H_4(CH_2)_2P(CH_3)_2$]$_3$ (**2**). Two equivalents of **1** with one equivalent of Y(CF_3SO_3)$_3$ in the presence of LiBr yielded BrY[$C_5H_4(CH_2)_2P(CH_3)_2$]$_2$ (**3**). Both complexes **2** and **3** have been characterized by X-ray structure analysis. In both cases an intramolecular coordination of the phosphanoethyl chain is established in the solid state by X-ray crystallography as well as in solution by NMR spectroscopy.

In general, neutral phosphane ligands do not form stable donor complexes with rare earth metals. Only a few complexes with neutral phosphane ligands are found in the literature: La[TeSi(SiMe$_3$)$_3$]$_3$(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$[1], [(C$_5$Me$_4$SiMe$_2$N*t*Bu)Sc(PMe$_3$)μ-H]$_2$[2], [N(SiMe$_3$)$_2$]$_2$Yb(Me$_2$PCH$_2$CH$_2$PMe$_2$)[3], (C$_5$Me$_5$)$_2$YbCl(Me$_2$PCH$_2$PMe$_2$)[4], and (C$_5$H$_4$Me)$_3$CePMe$_3$[5]. Stable complexes are known with anionic phosphane ligands like phosphanides[6], phosphanomethanides[7], phosphanoalkoxides[8], and amidophosphanes[9]. Phosphanomethanides were found to stabilize even high phosphane coordination numbers (up to 8 P−Ln bonds).

Continuing our investigations on phosphane compounds of rare earth metals we now focus on phosphanoalkylcyclopentadienide ligands. The characteristic feature of this ligand system is the linkage of a cyclopentadienyl and a phosphane moiety by means of an alkyl chain. Similar cyclopentadienyl-based ligands with amino- or alkoxyalkyl side chains coordinated to lanthanoide centers have been described[10][11][12][13][14][15]. However, the strong coordination of the heteroatom to the metal center normally is irreversible in these cases.

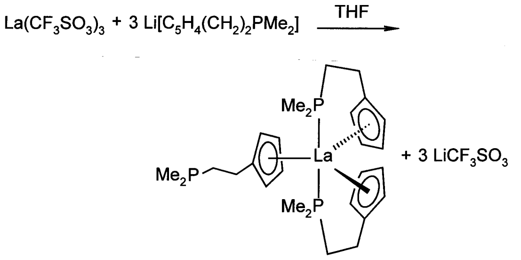
The additional phosphane functionality, in contrast, should provide a more labile and hence reversible coordination to the metal center which should enable enhanced reactivity and in particular is of great interest for catalytic reactions.

Only a restricted number of phosphanylcyclopentadienyl complexes have been reported so far and only a few are characterized by X-ray structure determinations[16][17][18][19][20]. Several independent routes have been applied for the synthesis of phosphanoalkyl-substituted cyclopentadienyl ligands, depending on the length of the alkyl chain connecting the cyclopentadienyl and the phosphane functionality.[21][22][23][24][25]. Phosphanoethyl-substituted cyclopentadienides {M[$C_5H_4(CH_2)_2PR_2$], M = Li, Na, K} best are prepared by reaction of the corresponding phosphanide with spiro[2.4]hepta-4,6-diene[26] and anionic ligands with R = Ph, *i*Pr, *t*Bu are known[18]. The ligand Li[$C_5H_4(CH_2)_2P(CH_3)_2$] (**1**) was newly synthesized using this method (Eq. 1).



(1)

The reaction of three equivalents of Li[$C_5H_4(CH_2)_2P(CH_3)_2$] with one equivalent of La(CF_3SO_3)$_3$ led to the homoleptic compound La[$C_5H_4(CH_2)_2P(CH_3)_2$]$_3$ (**2**) in good yield (Eq. 2).



(2)

Colorless crystals were obtained from a concentrated solution of **2** in toluene. The complex is soluble in THF and aromatic hydrocarbons. At −90°C the $^{31}P\{^1H\}$-NMR shows two signals at $\delta = -39.91$ and $\delta = -51.24$ of intensity 2:1 which coalesce at −50°C, and at room temperature only one broad singlet at $\delta = -43.62$ is observed. This is explained by a fast exchange of two coordinated and one “dangling“ phosphano groups with the low-field signal being assigned to the coordinating phosphane ligands and the signal at $\delta = -51.24$ being assigned to the noncoordinating phosphorus nucleus. This latter chemical shift corresponds to that of the neutral phosphane [$C_5H_5(CH_2)_2P(CH_3)_2$]

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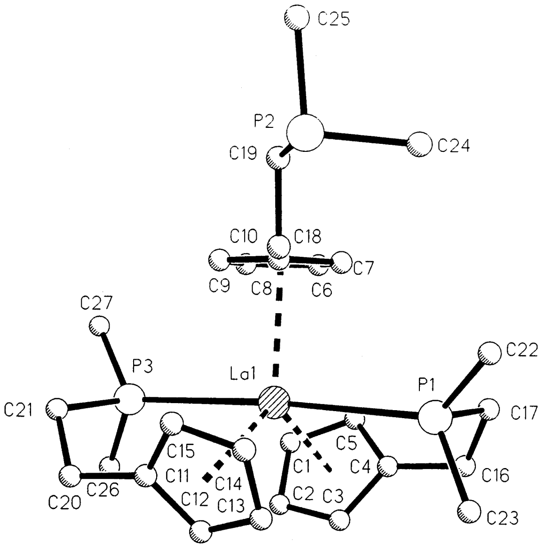
($\delta = -51.42$; -51.54). Careful analysis of the spectra at various temperatures led to the conclusion that two phosphano groups throughout remain coordinated to the metal center during the exchange process, i. e. a dissociative pathway is unlikely. The ^{139}La NMR ($I = 7/2$, 99.1%) resonance of **2** is observed at $\delta = -509.92$ (cf.: $Cp_3LaNCCH_3$, $\delta = -578$[27]) as a broad singlet. These spectroscopic findings are also consistent with the result of an X-ray structure determination (Figure 1).

Figure 1. Molecular structure of **2**



Lanthanum is trigonal planar, surrounded by three cyclopentadienyl rings, as it is the case in other cyclopentadienyllanthanum compounds[28]. Additionally, two phosphorus atoms complete the coordination sphere to a trigonal bipyramid by occupying the axial positions.

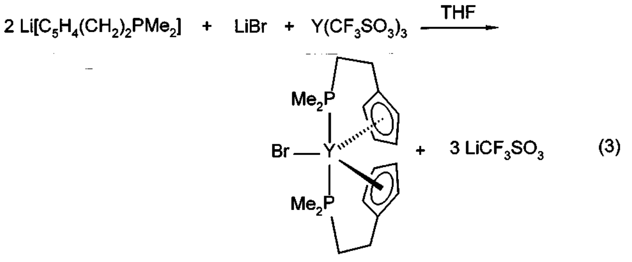
The lanthanum−phosphorus bond lengths [La−P1 = 3.211(5), La−P3 = 3.186(5) Å] are in the expected range for a lanthanum interaction with a phosphorus atom of covalency 3[1][7]. The molecular geometry and atom numbering scheme are shown in Figure 1, selected bond lengths [Å] and angles [°] are listed in Table 1.

Table 1. Selected bond lengths [Å] and angles [°] of compounds **2** and **3**

	1		2
La−X1a[a]	2.622(1)	Y−X1a[b]	2.386(1)
La−X1b	2.621(1)	Y−X1b	2.392(1)
La−X1c	2.621(1)	Y−P1	2.960(1)
La−P1	3.211(5)	Y−P2	2.933(1)
La−P3	3.186(5),	Y−Br	2.7939(5)
P1−La−P3	176.17(1)	X1a−Y−X1b	129.9(1)
X1a−La−X1c	118.7(1)	X1a−Y−Br	117.1(1)
X1b−La−X1a	121.6(1)	X1b−Y−Br	113.0(1)
X1c−La−X1a	119.7(1)	X1a−Y−P1	91.6(1)
X1a−La−P1	85.3(1)	X1a−Y−P2	99.9(1)
X1a−La−P3	91.6(1)		

[a] X1a, b, c: centroids of the Cp rings (C1 to C5, C6 to C10, C11 to C15). − [b] X1a, b: centroids of the Cp rings (C111 to C115 and C211 to C215).

The reaction of two equivalents of $Li[C_5H_4(CH_2)_2P(CH_3)_2]$ with one equivalent of $Y(CF_3SO_3)_3$ in the presence of LiBr proceeds under formation of the disubstituted yttrium bromide derivative **3** (Eq. 3).



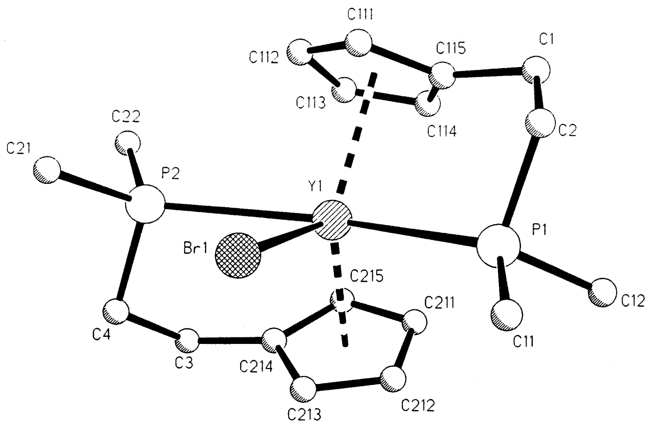
The product is obtained as colorless solid, soluble in aromatic solvents. The stabilisation by intramolecular coordination of the two phosphano functionalities is a dominant feature: this additional coordination prevents the dimerisation of the system and also the coordination of donor solvents, which otherwise are common features of bis(cyclopentadienyl)lanthanoid halides[29]. The $^{31}P\{^1H\}$-NMR spectrum shows a doublet at $\delta = -36.53$ with a $^1J_{PY}$ coupling constant of 72.8 Hz (^{89}Y, $I = 1/2$, 100%)[30] which remains unchanged over a temperature range from +30 to −100°C. This indicates that the system is not involved in dynamic processes.

Single crystals for an X-ray study were grown by slowly cooling a solution of **3** in toluene to low temperature. The compound crystallizes with one molecule of toluene in the formular unit. Both phosphano groups are bonded to the yttrium center (Figure 2) which confirms the spectroscopic findings. Similar to compound **2**, the two phosphorus atoms occupy the apical positions of a slightly distorted trigonal bipyramid. The Y−P bond lengths [2.960(1) and 2.933(1) Å] are only slightly longer than in $\{Y[N(SiMe_3CHPMe_2)(SiMe_2CH_2PMe_2)][N(SiMe_2CH_2PMe_2)_2]\}$ (2.817, 2.896, and 2.903 Å)[30]. Compound **3** represents the second hitherto known (and the first mononuclear) yttrium bromide featuring a terminal Y−Br bond, which is slightly longer [2.7939(5) Å] than that in $Y_3(OCMe_3)_7Br_2(THF)_2$ (Y−Br = 2.782 Å)[31]. Together with two cyclopentadienyl moieties of the $CpCH_2CH_2PMe_2$ ligands, the bromine completes the trigonal plane of the tbp molecular skeleton. With regard to the center of the Cp rings, the Cp(1)−Y−Cp(2) angle amounts to 129.9°, which gives an indication for the steric demand of the terminal bromine ligand. The average Y−Cp(center) distance (2.39 Å) agrees well with that found in other Y^{III} cyclopentadienyl complexes[32]. The molecular geometry and atom numbering scheme are shown in Figure 2, selected bond lengths [Å] and angles [°] are listed in Table 1.

Experimental Section

All operations were performed under dry, oxygen free nitrogen and with thoroughly dried solvents and glassware. Standard high-vacuum-line techniques were used. − Elemental analyses were ob-

Figure 2. Molecular structure of **3**



tained with a Vario EL CHN elemental analyzer of the microanalytical laboratory of the TU München. No attempts were made to further ameliorate the analytical data, which were not satisfying in all cases due to the high sensitivity of the compounds. − MS: Varian MAT 70 eV, CI. − NMR: Jeol GX 270 (^{1}H 270.17 MHz, ^{13}C 67.94 MHz, ^{31}P 109.4 MHz), Jeol GX 400 (^{1}H 399.65 MHz, ^{31}P 161.7 MHz, ^{13}C 100.40 MHz, ^{139}La 56.35 MHz), Jeol JNM Lambda 400 (^{7}Li 155.40 MHz). Chemical shifts (^{1}H, ^{13}C) refer to TMS (δ = 0) as internal standard. For ^{31}P, 80% H_3PO_4, for ^{139}La, $LaCl_3$ (0.1 M in D_2O, δ = 0) and for ^{7}Li, LiBr (20% in D_2O, δ = 0) as external standards. All chemical shifts are reported in ppm and coupling constants *J* in Hz. In case of high-order spin systems, the distance "*N*" [Hz] between the two outermost lines of the multiplet is given. All measurements were carried out at 25°C in C_6D_6 as solvent. Temperature-dependent NMR spectra were recorded with [D$_8$]toluene as solvent. $LiPMe_2 \cdot 0.5\ Et_2O$[33], $La(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$[34], and spiro[2.4]hepta-4,6-diene[26] were prepared according to literature procedures.

Li[C$_5$H$_4$(CH$_2$)$_2$P(CH$_3$)$_2$] (**1**): To a solution of 0.024 mol (2.5 g) of $LiPMe_2 \cdot 0.5\ Et_2O$ in 50 ml of THF, 0.024 mol (2.19 g) of spiro[2.4]hepta-4,6-diene in 20 ml of THF was added by pipette. After stirring the reaction mixture for 12 h at room temperature, the solvent was removed and the product was washed three times with pentane. After drying the residue, 3.15 g (82%) of a colorless solid was obtained. − ^{1}H NMR ([D$_8$]dioxane, 293 K): 1.06 [d, $^2J_{HP}$ = 1.24, 6 H, P(C*H*$_3$)$_2$], 1.75 [dt, $^2J_{HP}$ = 1.95, $^3J_{HH}$ = 7.32, 2 H, CpCH$_2$C*H*$_2$P(CH$_3$)$_2$], 2.75 [dt, $^3J_{HP}$ = 12.21, $^3J_{HH}$ = 7.32, 2 H, CpC*H*$_2$CH$_2$P(CH$_3$)$_2$], 5.65 [A$_2$B$_2$: δ_A = 5.68, δ_B = 5.61, J_{AB} = 2.44, 4 H, C$_5$*H*$_4$CH$_2$CH$_2$]. − ^{13}C {^{1}H} NMR ([D$_8$]dioxane, 293 K): δ = 12.07 (d, $^1J_{CP}$ = 2.59, CH$_3$), 25.10 (d, $^2J_{CP}$ = 11.92 *C*H$_2$P), 39.32 (s, Cp*C*H$_2$), 101.62 (s, CH$_2$C*C*H), 101.90 (s, CCH*C*H), 119.84 (d, $^3J_{CP}$ = 9.33, C-*ipso*). − ^{31}P{^{1}H} NMR ([D$_8$]dioxane, 293 K): δ = −56.34 (s). − ^{7}Li NMR ([D$_8$]dioxane, 293 K): δ = −8.21 (s). − $C_9H_{14}LiP$ (160.13): calcd. C 67.51, H 8.81, Li 4.33, P 19.35; found C 65.67, H 8.74, Li 4.35, P 18.37.

La[C$_5$H$_4$(CH$_2$)$_2$P(CH$_3$)$_2$]$_3$ (**2**): To a mixture of 6.2 mmol (1.0 g) of **1** and 2.05 mmol (1.2 g) of $La(CF_3SO_3)_3$, 40 ml of THF was added at −78°C. The reaction mixture was slowly warmed up to room temperature and stirred for another 12 h. The solvent was removed and the product was extracted with 40 ml of toluene. The toluene extract was concentrated and **2** was isolated as colorless crystals, 1.14 g, (92%), dec. 138°C. − ^{1}H NMR (C$_6$D$_6$, 293 K): δ = 0.92 [s, 18 H, P(C*H*$_3$)$_2$], 1.56 ["t", *N* = 14.29, 6 H, CpCH$_2$C*H*$_2$P(CH$_3$)$_2$], 2.60 [m, *N* = 30.27, 6 H, CpC*H*$_2$CH$_2$P(CH$_3$)$_2$], 5.76 [A$_2$B$_2$ spin system, uncompletely resolved, δ_A = 5.72, δ_B = 5.79, 12 H, C$_5$*H*$_4$CH$_2$CH$_2$]. − ^{13}C{^{1}H} NMR (C$_6$D$_6$, 293 K): δ = 12.99 (s, *C*H$_3$), 25.68 (s, *C*H$_2$P), 35.05 (s, Cp*C*H$_2$), 109.03 (s, CH$_2$C*C*H), 110.12 (s, CCH*C*H), 128.90 (s, C-*ipso*). − ^{31}P{^{1}H} NMR (C$_6$D$_6$, 293 K): δ = −43.62 (s, br). − ^{31}P{^{1}H} NMR ([D$_8$]toluene, 203 K): δ = −39.91 (s, br, 2P, La-*P*Me$_2$), −51.24 [s, br 1P, C$_5$H$_4$(CH$_2$)$_2$*P*Me$_2$]. − ^{139}La NMR (C$_6$D$_6$ 293 K): δ = −509.92. − MS (70 eV); *m/z* (%): 445 (100) [M$^+$ − C$_5$H$_4$(CH$_2$)$_2$P(CH$_3$)$_2$], 384 (50) [M$^+$ − C$_5$H$_4$(CH$_2$)$_2$P(CH$_3$)$_2$ − P(CH$_3$)$_2$], 154 (13.9)

Table 2. Crystal data of compounds **2** and **3**

Empirical formula	$C_{27}H_{42}LaP_3$ (**2**)	$C_{25}H_{36}BrP_2Y$ (**3**)
Molecular mass	598.431 g/mol	567.301 g/mol
Crystal dimensions [mm]	0.11 × 0.45 × 0.5	0.5 × 0.4 × 0.3
Crystal System	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	8.555(1)	12.357(1)
b [Å]	25.003(1)	14.249(1)
c [Å]	13.080(1)	15.206(2)
β [°]	92.03(1)	101.48(1)
V [Å^3]	2796.1(4)	2623.8(4)
Z	4	4
Diffractometer	Enraf Nonius CAD4-Turbo	Enraf Nonius CAD4-Turbo
Radiation	Mo-K_α (λ = 0.71073 A)	Mo-K_α (λ = 0.71073 A)
Density (calculated) [Mg/m^3]	1.422	1.436
Absorption coefficient [mm^{-1}]	1.712	3.877
F (000)	1224	1160
θ range for data collection [°]	3 to 27	3 to 27
Limiting indices	$-10 \le h \le 10$, $0 \le k \le 31$, $0 \le l \le 16$	$-15 \le h \le 15$, $0 \le k \le 18$, $0 \le l \le 19$
Reflexions collected	6048	5901
Independent reflexions	6047	5697
Absorption correction	DIFABS[29]	Empir.
Data/restraints/parameters	5348/0/280	4134/0/267
Goodness-of-fit on F^2	1.054	1.007
Final *R* indices [$F_o > 4\ \sigma(F_o)$]	*R*1 = 0.0185, *wR*2 = 0.0439	*R*1 = 0.0356, *wR*2 = 0.0788
R indices (all data)	*R*1 = 0.0258, *wR*2 = 0.0462	*R*1 = 0.0722, *wR*2 = 0.0906
Largest diff. peak and hole	0.370 and −0.463 e × A^{-3}	0.681 and −0.422 e × A^{-3}

$[C_5H_5(CH_2)_2P(CH_3)_2]$. − $C_{27}H_{42}LaP_3$ (598.43): calcd. C 54.2, H 7.07; found C 51.56, H 7.13.

$BrY[C_5H_4(CH_2)_2P(CH_3)_2]_2$ (**3**): To a mixture of 3.73 mmol (0.6 g) of **1**, 1.86 mmol (1 g) of $Y(CF_3SO_3)_3$ and 1.86 mmol (0.16 g) of LiBr, 40 ml of THF was added at −78°C. The reaction mixture was slowly warmed up to room temperature and stirred for another 12 h. The solvent was removed and the product was extracted with 40 ml of toluene. The toluene extract was concentrated and **3** was isolated as colorless crystals 0.8 g, (75%), dec. 135°C. − ^1H NMR (C_6D_6, 293 K): δ = 0.91[s, 12 H, $P(CH_3)_2$], 1.65 [s, br, 4 H, $CpCH_2CH_2P(CH_3)_2$], 2.43 [m, 4 H, $CpCH_2CH_2P(CH_3)_2$], 5.80 [s, br, 8 H, $C_5H_4CH_2CH_2$]. − $^{13}C\{^1H\}$ NMR (C_6D_6, 293 K): δ = 10.73 (s, CH_3), 24.61 ("t", N = 12.12, CH_2PMe_2), 33.86 ("t", N = 12.67, $CpCH_2$), 107.81 [s, br, CH (Cp)], 131.85 ("t", N = 4.42 C-*ipso*). − $^{31}P\{^1H\}$ NMR (C_6D_6, 293 K): δ = −36.53 (d, $^1J_{P\text{-}Y}$ = 72.8). − MS (70 eV); *m/z* (%): 476 (40) $[M^+ + 1]$, 395 (100) $[M^+ - C_5H_4(CH_2)_2P(CH_3)_2]$, 154 (71) $[C_5H_5(CH_2)_2P(CH_3)_2]$. − $C_{18}H_{28}P_2BrY$ (475.19): calcd. C 45.50, H 5.94, Br 16.81; found C 44.81, H 6.0, Br 15.64.

Crystal Structure Determination: Suitable crystals of **2** and **3** were sealed into glass capillaries. The structures were solved by direct methods and refined by full-matrix least-squares calculations against F^2 (SHELXL-93)[35][36]. Crystal data and numerical data of the structure determinations are given in Table 2. The thermal motion of all non-hydrogen atoms was treated anisotropically. All hydrogen atoms were calculated in ideal positions. Further informations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-408608 (**2**) and CSD-408609 (**3**).

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