Bis-(2-diphenylphosphinoethyl)cyclopentadienylchlorolutetium: synthesis and dynamic behavior in solution

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The new biscyclopentadienyl lutetium complex $(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2LuCl$ was synthesized by the reaction of $LuCl_3(THF)_3$ with lithium (2-diphenylphosphinoethyl)cyclopentadienide. Its behavior in solution was investigated by dynamic NMR spectroscopy. It was shown that the coordination of both phosphino groups to the lutetium center is retained over the whole temperature range studied. The barrier to pseudo-rotation for the trigonal bipyramid, which governs the intramolecular dynamics of this complex, was determined.

Key words: phosphinoethyl substituted cyclopenadienes, cyclopentadienyl lutetium complexes, dynamic NMR spectroscopy, trigonal bipyramid pseudo-rotation.

Metals of the lanthanide subgroup normally do not tend to form stable complexes with neutral phosphine ligands. Only a few compounds of this type are known.[1—7] For the preparation of phosphine complexes of lanthanides, a different approach is promising, namely, the use of phosphine ligands capable of being coordinatied to lanthanide through not only the P atom but also chelating ligands. Phosphinoethylcyclopentadienyl ligands, capable of forming a chelating pseudo-five-membered metallacycle $Cp'—CH_2—CH_2—P(Ph_2)—Lu$ are interesting in this respect.

Results and Discussion

We prepared the heteroligand complex $[(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2LuCl]$ (**1**) by the reaction of 2 equiv. of $Li[C_5H_4(CH_2)_2PPh_2]$ with lutetium chloride tetrahydrofuranate in THF (Scheme 1).

Scheme 1

$$LuCl_3(THF)_3 + 2\ Li[C_5H_4(CH_2)_2PPh_2] \xrightarrow[2)\ Toluene]{1)\ THF} \mathbf{1}$$

Unlike the unsubstituted analog Cp_2LuCl, complex **1** (Fig. 1) is highly soluble in toluene; thus it can be easily separated from lithium chloride formed in the reaction.

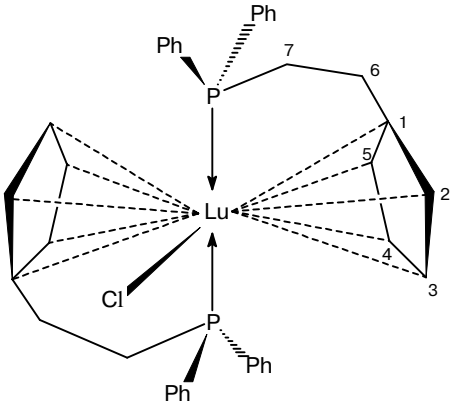

Fig. 1. Atom numbering in complex **1**.

It appears of interest to investigate the coordination of the diphenylphosphino groups to the central Lu atom. We were unable to prepare single crystals of complex **1** suitable for X-ray diffraction analysis; however, the structure of **1** in solution was studied in detail by NMR spectroscopy.

The NMR spectra of complex **1** change with temperature. The NMR study of the dynamic behavior of complex **1** was carried out over a broad temperature range in a non-solvating solvent, toluene-d_8. The temperature dependence of the NMR spectra could have resulted from two different dynamic processes, namely,

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(1) dissociation—coordination of the phosphino group (groups) and (2) intramolecular conformational dynamics of the complex not accompanied by bond rupture.

The results obtained point unambiguously that the coordination of both phosphino groups to the Lu atom is retained throughout the whole temperature range. This is indicated by the downfield shift of the signal of the PPh_2 groups (by ~20 ppm) with respect to those for the free ligand ($\delta_P \approx -15$); this is consistent with published data.[8] The chemical shift displays a weak temperature dependence ($\delta_P = -6.4$ and -4.5 at -59 and +55 °C, respectively). Moreover, the direction of the change is opposite to that expected to accompany dissociation of the phosphine ligand upon an increase in the temperature. The second unambugious proof for the coordination of both PPh_2 groups is the fact that the signals of all the carbon atoms having a detectable spin coupling constant with the ^{31}P nucleus are manifested in the ^{13}C NMR spectrum (even at 55 °C) as virtual triplets, which represent the X part of the AA′X spin system. This type of multiplicity is observed when there is a strong spin-spin coupling between the nuclei A and A′ (the P nuclei in this particular case) compared with the AX and A′X couplings. For transition metal phosphine complexes, this condition is almost always fulfilled because the through-metal $^2J_{PP}$ value (especially for the *trans*-arrangement of phosphine ligands) is, as a rule, an order of magnitude higher than the $^{1-3}J_{PC}$ value in phosphines.[9]

At room temperature, the ^1H and ^{13}C NMR spectra contain, despite some broadening, only one set of signals corresponding to the substituted Cp ligand, the Cp protons, the C(2)—C(5) atoms, and the bridging protons are equivalent in pairs. When the temperature increases to 55 °C, all the broadened signals in the ^1H and ^{13}C NMR spectra narrow down, *i.e.*, the fast exchange limit is practically attained. When the temperature decreases to −59 °C, the signals of all four protons of the Cp rings and the bridging protons become nonequivalent in the ^1H NMR spectrum (Fig. 2 and Table 1). The assignment of signals of cyclopentadienyl protons is based on the fact that for slow exchange, the greater the distance from the protons to the substituent, the greater the difference of chemical shifts in the H(2), H(5) and H(3), H(4) pairs. The ^{31}P NMR signal of the PPh_2 groups remains narrow over the whole temperature range.

Table 1. Temperature dependence of the chemical shifts in the ^1H NMR spectrum of complex **1** in toluene-d_8

T/°C	δ			
	Cp′C<u>H</u>$_2$	Cp′CH$_2$C<u>H</u>$_2$	H(2), H(5)	H(3), H(4)
+55	2.57	2.39	6.03	5.85
+25	2.53	2.38	6.10	5.86
−59	2.55, 2.65	1.90, 2.26	5.80, 6.56	5.96, 6.00

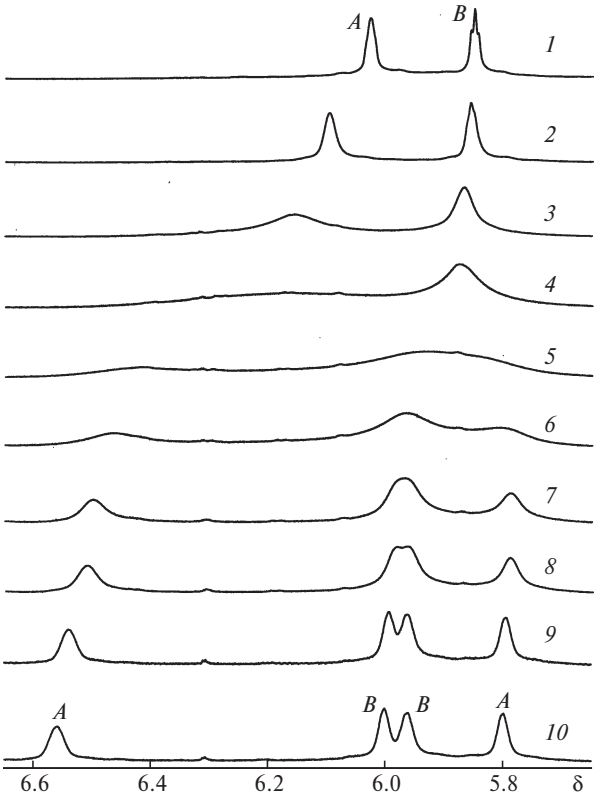


Fig. 2. ^1H NMR spectra of complex **1** in toluene-d_8 (the region of cyclopentadienyl protons is shown) at 55 (*1*), 25 (*2*), 5 (*3*), −5 (*4*), −16 (*5*), −21 (*6*), −31 (*7*), −35 (*8*), −48 (*9*), and −59 °C (*10*). *A* are the signals of H(2), H(5); *B* are the signals of H(3), H(4).

According to known X-ray diffraction data, lanthanide complexes of this type have a structure of a distorted trigonal bipyramid in which two heteroatomic ligands occupy the apical positions and the Cp rings and the halogen atom lie in the equatorial plane. This geometry is found, for example, in the dicyclopentadienyl complexes

$(C_5H_4CH_2CH_2PMe_2)_2YBr$;[10]
$[C_5H_4CH(Ph)CH_2NMe_2]_2LuCl$,
$[C_5H_4CH_2CH(Me)OMe]_2SmCl$;[11]
$(C_5H_4CH_2CH_2OMe)_2LaI$;[12]
and $(C_5H_4CH_2CH_2OMe)_2Y(\mu\text{-}H)_2BH_2$.[13]

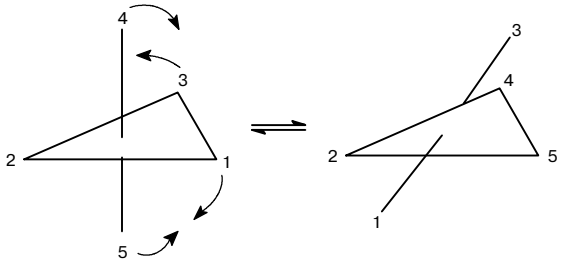
There are no reasons for suggesting that the geometry of complex **1** would differ in kind from the geometry of the above-mentioned compounds. However, the symmetry of a trigonal bipyramid, even that having a C_2 axis (which is quite possible in solution) implies nonequivalence of all protons as well as C(2)—C(5) atoms and substituents at the P atom at any temperature because the metal atom forms an asymmetric center. The P atoms are equivalent in this case (see Fig. 1). Nevertheless, neither complex **1** nor all known complexes of this type including those mentioned above show diastereotopism in the NMR spectra at room temperature; exceptions are

compounds having an asymmetric center in the bridge, for example, $[C_5H_4CH(Ph)CH_2NMe_2]_2LuCl$ and $[C_5H_4CH_2CH(Me)OMe]_2SmCl$.[11] No adequate interpretation of these findings can be found in the literature.

When interpreting the dynamic behavior of this complex, the isomerization mechanism *via* elimination—addition of the Cl anion should apparently be rejected straight away. This process is hardly possible in a nonpolar solvent. This is all the more impossible in the case of the complex $(C_5H_4CH_2CH_2OMe)_2Y(\mu\text{-}H)_2BH_2$,[13] in which no diastereotopism is observed either, according to the NMR spectra at room temperature. Elimination of the diastereotopism at higher temperatures should imply fast equilibrium between two enantiomers. We observed a similar situation for the half-sandwich $(C_5Me_4CH_2CH_2SCH_3)ZrCl_3$ complex,[14] in which fast exchange between the two mirror conformations takes place upon an increase in temperature due to inversion of the pseudo-five-membered metallacycle. However, mere inversion of the Cp′—CH_2—CH_2—$P(Ph_2)$—Lu metallacycles in complex **1** would not remove the asymmetric center on the metal atom.

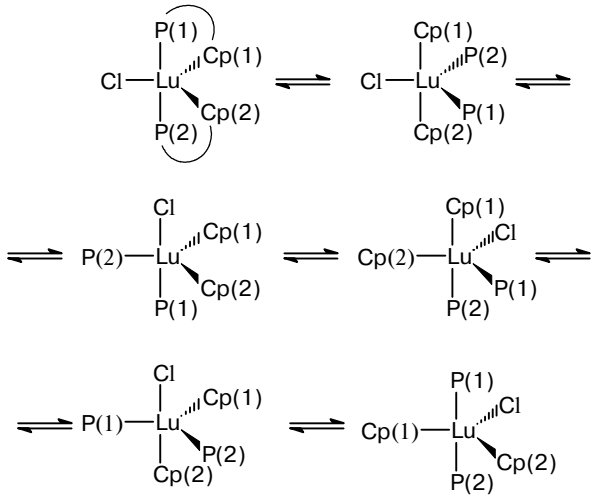
In our opinion, the only mechanism that explains adequately the intramolecular dynamics of complexes of this type is pseudo-rotation of the trigonal bipyramid, first proposed by Berry.[15] This isomerization mechanism includes simultaneous position exchange of two equatorial and two apical ligands *via* the intermediate formation of a tetragonal bipyramid (Scheme 2), the barrier to this process being relatively low. Trigonal-bipyramidal complexes differ dramatically in intramolecular lability from four- and six-coordinate complexes in which nothing of the kind has been observed.

Scheme 2



The Berry pseudo-rotation mechanism makes it possible to exchange positions of any two ligands *via* several steps. Scheme 3 shows the five-step isomerization of complex **1**, in which two cyclopentadienyl (or two phosphine) ligands exchange places (for simplicity, the bridges are shown only for the starting isomer). It can be readily seen that the initial and final isomers are enantiomers. It can also be seen that in neither of the isomers, the Cp ring and the phosphino group belonging to one ligand are located simultaneously in the apical positions; this is precluded by the small length of the bridge linking them. Thus, this mechanism can account for the seeming disappearance of the asymmetric center on the metal at elevated temperatures.

Scheme 3



The barrier to the pseudo-rotation in complex **1** estimated from the temperatures of coalescence of the H(3), H(4) ($T_c = -34$ °C) and Cp′C$\underline{H}_2$ ($T_c = -21$ °C) signals amounts to $\Delta G^{\#} = 12.3 \pm 0.2$ kcal mol^{-1}. This value is somewhat greater than the value that we measured previously for the $(C_5Me_4CH_2CH_2SCH_3)ZrCl_3$ complex (10.5 kcal mol^{-1}).[14] This can be easily explained by assuming that each isomerization step is accompanied by conformational transformations in both metallacycles and that the overall height of the energy barrier to the whole process cannot be lower than that for a single step, in particular, because of the different stabilities of the intermediate isomers.

Thus, the data of NMR spectroscopy demonstrate convincingly that both phosphino groups in the five-coordinate $[(\eta^5{:}\eta^1\text{-}C_5H_4CH_2CH_2PPh_2)_2LuCl]$ complex are coordinated to the Lu atom and that the dynamic behavior of the complex in solution is determined by intramolecular pseudo-rotation of the trigonal bipyramid by the Berry mechanism.

Experimental

All the synthetic operations and the preparation of samples for physicochemical studies were performed in all-sealed evacuated Schlenk type vessels. The methods of solvent preparation were described previously.[16] The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in toluene-d_8 on a Varian VXR-400 spectrometer (400, 100, and 162 MHz, respectively, 25 °C); mass spectrum was run on a Kratos-MS-890 spectrometer.

The lutetium content was determined by direct complexometric titration with the Xylylene Organge indicator.

Bis-(2-diphenylphosphinoethylcyclopentadienyl)chlorolutetium. A 0.6 *M* solution of lithium 2-diphenylphosphinoethylcyclopentadienide[18] (11.1 mL, 6.7 mmol) was added to a

suspension of $LuCl_3(THF)_3$ [17] (1.660 g, 3.3 mmol) in 40 mL of absolute THF. The reaction mixture was stirred for 2 days at ~20 °C, then THF was removed *in vacuo*, and 20 mL of absolute toluene was added. The mixture was heated to reflux with stirring and the solvent was removed *in vacuo*. The dry residue was extracted with toluene. The extract was concentrated and the resulting light-yellow substance was stirred with pentane for 2 weeks. The suspension of the powdered product in pentane was separated from the oily precipitate. The resulting white powder was recrystallized from pentane (2×30 mL) and dried *in vacuo* to give 2.280 g (86%) of complex **1**. Found (%): Lu, 23.04. $C_{38}H_{36}ClLuP_2$. Calculated (%): Lu, 22.87. ^{1}H NMR, δ: 2.38 (br.s, 4 H, CH_2P); 2.53 (br.m, 4 H, $C\underline{H}_2CH_2P$); 5.86 (br.s, 4 H, H(3), H(4)); 6.10 (br.s, 4 H, H(2), H(5)); 7.09 (m, 12 H, H_m, H_p); 7.55 (m, 8 H, H_o). ^{13}C NMR, δ: 24.18 (virt.t, $\underline{C}H_2CH_2P$, $|J_{CP} + J_{CP'}| = 14.1$ Hz); 31.57 (virt.t, CH_2P, $|J_{CP} + J_{CP'}| = 9.9$ Hz); 107.6, 109.1 (both br.s, C(2), C(3), C(4), C(5)); 128.59 (br.s, C_m); 129.33 (s, C_p); 129.99 (virt.t, C(1), $|J_{CP} + J_{CP'}| = 8.4$ Hz); 133.71 (virt.t, C_o, $|J_{CP} + J_{CP'}| = 12.7$ Hz); 136.29 (virt.t, C_{ipso}, $|J_{CP} + J_{CP'}| = 10.0$ Hz). ^{31}P NMR, δ: −5.6 (s). MS (EI, 70 eV), m/z (I_{rel} (%)): 764 $[M]^+$ (2.8), 578 $[M - HPPh_2]^+$ (0.4), 487 $[M - C_5H_4CH_2CH_2PPh_2]^+$ (34.7), 393 $[M - HPPh_2 - PPh_2]^+$ (2.7), 278 $[C_5H_5CH_2CH_2PPh_2]^+$ (97.1), 277 $[C_5H_4CH_2CH_2PPh_2]^+$ (88.8), 250 $[C_5H_5PPh_2]^+$ (87.5), 212 $[CH_2{=}CHPPh_2]^+$ (5.9), 200 $[C_5H_4CH_2CH_2PPh]^+$ (84.0), 199 $[CH_2PPh_2]^+$ (93.1), 185 $[PPh_2]^+$ (90.8), 121 $[CH{=}PPh]^+$ (100.0), 91 $[C_7H_7]^+$ (92.0).

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