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Synthesis and Molecular Structure of the First Rhodium(I) Complex Containing a Tetra-*tert*-butylcyclopentaphosphanide Ligand

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Na[*cyclo*-($P_5{}^tBu_4$)] (**1**) reacts with [$RhCl(PPh_3)_3$] (1:1) to give the first rhodium(I) complex with a tetra-*tert*-butylcyclopentaphosphanide ligand, [Rh{*cyclo*-($P_5{}^tBu_4$)}($(PPh_3)_2$)] (**2**). **2** was characterized by NMR (^1H, ^{13}C, ^{31}P), MS, IR, and X-ray structure determination.

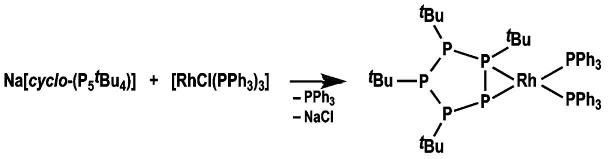
Introduction

Cyclooligophosphanes *cyclo*-$(PR)_n$,[1] which are isolobal to cycloalkanes, have attracted the interest of chemists for a long time. Even though the first example of this class of compounds, *cyclo*-$(PPh)_5$, was synthesized as early as 1877,[2] the first cyclooligophosphanide anions *cyclo*-$(P_nR_{n-1})^-$ were reported only ca. 100 years later,[3,4] and today the number of readily accessible, pure compounds is still small.[5] Most alkali metal compounds, such as K[*cyclo*-($P_3{}^tBu_2$)],[3] K[*cyclo*-(P_5Ph_4)],[5] and Li[*cyclo*-($P_n{}^tBu_{n-1}$)] ($n = 3-5$),[6,7] were only obtained in inseparable mixtures and characterized by ^{31}P NMR spectroscopy. Only recently, we succeeded in synthesizing Na[*cyclo*-($P_5{}^tBu_4$)] (**1**) in high yield and have reported preliminary results on its use in main group[8] and coordination chemistry.[9−12]

Different reactivity patterns are observed in reactions with **1**. While the *cyclo*-($P_5{}^tBu_4$) ligand stays intact in the reaction of **1** with Et_2AlCl[8] or [$PdCl_2(PPh_3)_2$],[11] elimination of ^tBuCl with formation of a nickel(0) cyclopentaphosphene complex is observed in the reaction with [$NiCl_2(PEt_3)_2$].[9] With $SnCl_2$, $PbCl_2$, or $BiCl_3$, a redox reaction occurs with formation of the two structural isomers {*cyclo*-($P_5{}^tBu_4$)}$_2$ and {*cyclo*-($P_4{}^tBu_3$)P^tBu}$_2$ (besides other cyclic phosphines) and elemental metal.[8] In the reaction of **1** with [$AuCl(PPh_3)$] the tetranuclear complex [(Au{*cyclo*-($P_4{}^tBu_3$)P^tBu})$_4$]·4THF is formed, in which a metal−{*cyclo*-($P_4{}^tBu_3$)P^tBu} group is present,[12] which, in case of tin, lead, or bismuth, reductively eliminates {*cyclo*-($P_4{}^tBu_3$)P^tBu}$_2$.[8] We have now observed that **1** reacts with [$RhCl(PPh_3)_3$] to give the first rhodium(I) complex with a tetra-*tert*-butylcyclopentaphosphanide ligand, [Rh{*cyclo*-($P_5{}^tBu_4$)}($(PPh_3)_2$)] (**2**).

Results and Discussion

Synthesis and Spectroscopic Properties. Na[*cyclo*-($P_5{}^tBu_4$)] (**1**) reacts with [$RhCl(PPh_3)_3$] in polar or nonpolar solvents with elimination of NaCl and PPh_3 and formation of [Rh{*cyclo*-($P_5{}^tBu_4$)}($(PPh_3)_2$)] (**2**), which was obtained as red crystals of **2**·THF (eq 1). A $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture showed the formation of **2** (16%) as the only Rh-containing compound, PPh_3 (36.3%), and *cyclo*-($P_4{}^tBu_4$)[13] (5.8%), *cyclo*-($P_3{}^tBu_3$)[14] (9.5%), *cyclo*-($P_5{}^tBu_4H$)[15] (12.2%), and {*cyclo*-($P_5{}^tBu_4$)}$_2$[8] (10.3%), as well as *cyclo*-($P_4{}^tBu_3$)P^tBu}$_2$[8] (6.9%), which were also observed in redox reactions with main group metal halides.[8]



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[†] Crystal structure determination.

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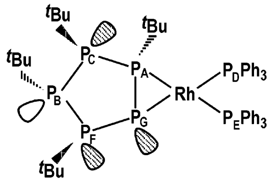
Table 1. $^{31}P\{^1H\}$ NMR Parameters of **2** (Chemical Shifts in ppm, Coupling Constants in Hz)



$\delta_A = +106.54$, m	$^1J_{AC} = -537.5$	$^3J_{CD} = 7.0$
$\delta_B = +88.57$, m	$^1J_{AG} = -447.0$	$^3J_{CE} = 3.5$
$\delta_C = +52.33$, m	$^1J_{BC} = -347.1$	$^3J_{DF} = 1.0$
$\delta_D = +36.17$, m	$^1J_{BF} = -345.3$	$^3J_{EF} = 2.5$
$\delta_E = +38.19$, m	$^1J_{FG} = -396.4$	$^4J_{BD} = 0.0$
$\delta_F = +25.54$, m	$^2J_{AB} = 16.9$	$^4J_{BE} = 0.0$
$\delta_G = -73.83$, m	$^2J_{AD} = 197.8$	
	$^2J_{AE} = 31.3$	
$^1J_{ARh} = -93.9$	$^2J_{AF} = 16.6$	
$^1J_{DRh} = -187.0$	$^2J_{BG} = 4.2$	
$^1J_{ERh} = -179.0$	$^2J_{CF} = 10.5$	
$^1J_{GRh} = -67.0$	$^2J_{CG} = 18.8$	
$^2J_{CRh} = 50.1$	$^2J_{DE} = 35.0$	
$^2J_{FRh} = 7.5$	$^2J_{DG} = 16.0$	
$^3J_{BRh} = 1.9$	$^2J_{EG} = 7.7$	

In the one-dimensional $^{31}P\{^1H\}$ NMR spectrum of **2** (in C_6D_6), six multiplets are observed for the higher order ABCDEFGX spin system at ca. $\delta = 107$, 89, 52, 37, 26, and -74 ppm (ratio 1:1:1:2:1:1). The spectrum appears to be first-order, with the signal at $\delta = 37$ ppm exhibiting an unsymmetrical coupling pattern. The P nuclei D and E fulfill the requirement $|\nu_D - \nu_E|/J_{DE} < 10$, which results in a higher order spectrum. Thus, no coupling constants could be deduced from this multiplet.

The connectivities of the P atoms were obtained from a two-dimensional $^{31}P^{31}P$ COSY45 NMR spectrum, and the chemical shifts and coupling constants were calculated using the simulation program SPINWORKS[16] (Table 1).[17] The observed and calculated coupling patterns are in very good agreement.

The anionic phosphorus atom P_G is the most shielded and thus is observed at high field. The fragment $P_F-P_G-P_A-P_C$ has the largest absolute values for the $^1J_{PP}$ coupling constants (-396.4 to -537.5 Hz), and these are indicative of multiple-bond character between these P atoms, while P_B shows smaller $^1J_{PP}$ coupling constants ($^1J_{BC} = -347.1$ Hz, $^1J_{BF} = -345.3$ Hz), as would be expected for P−P single bonds.[18] This indicates that P_B deviates from the plane formed by the $P_F-P_G-P_A-P_C$ fragment and should therefore form the tip of the envelope conformation (see molecular structure). In the solid state, a short P−P bond is observed only between P_A and P_G.

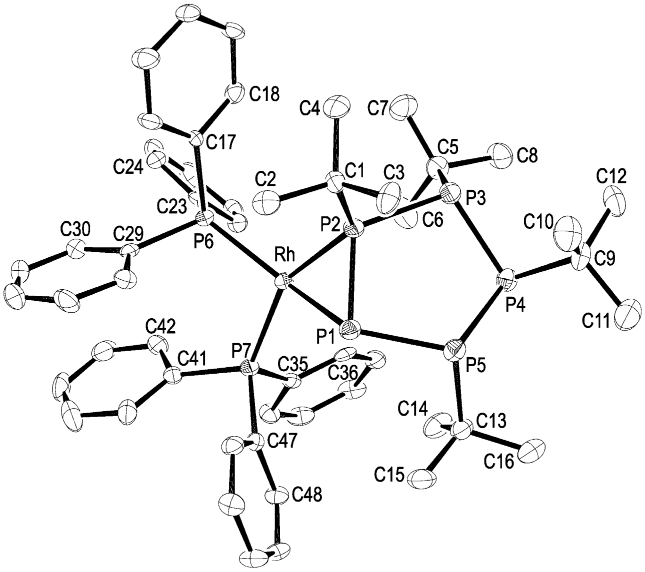


Figure 1. Molecular structure of **2** showing the steric interaction between the PPh_3 ligand (C17−C22) and the *tert*-butyl group at P2 (C1−C4) (ORTEP, 30% probability, SHELXTL PLUS; XP;[24] hydrogen atoms and THF omitted for clarity).

The $^1J_{PRh}$ coupling constants are negative and range from -67 to -187 Hz. The trans effect is also observed here:[19] $^1J_{DRh}$, which is trans to the anionic P atom P_G, is of larger magnitude (-187 Hz) than $^1J_{ERh}$ (-179.0), which is trans to P_A.

The mass spectrum of **2** (FAB MS) shows the molecular ion peak ($m/z = 1010.2$, 4.6%) and characteristic fragments such as $[M^+ - 2PPh_3]$ and $P_5{}^tBu_4{}^+$. Interestingly, observation of the organyl-free fragment $[RhP_5]^+$ indicates that complex **2** could be a suitable precursor for the formation of binary rhodium phosphides.

Molecular Structure of 2. In **2**, the rhodium atom is surrounded in a strongly distorted square-planar fashion by two PPh_3 ligands (P6, P7) and two P atoms (P1, P2) of the chiral nonplanar *cyclo*-$P_5{}^tBu_4$ ligand (Figure 1). The P atom P6 deviates strongly from the best plane formed by P1, P2, P7, and Rh (P6, −118.5(3) pm; deviation from best plane, P1 −3.42(3), P2 +7.78(6), P7 +6.4(5), Rh −10.76(9) pm) (Figure 2). The dihedral angle between the planes P1−P2−Rh and P6−P7−Rh is 28.35(6)°. This deviation from planarity is probably due to the steric demands of the PPh_3 ligands and the *tert*-butyl group of P2 (Figure 1). The differences in the P−Rh−P bond angles are also due to steric effects. Thus, the P6−Rh−P2 bond angle is larger (109.56(6)°) than the P1−Rh−P7 bond angle (99.31(6)°), and the P2···P6 distance (374.3 pm) is longer than the P1···P7 distance (357.2 pm) due to interaction of the phenyl group at P6 with the *tert*-butyl group at P2. The Rh−P(PPh_3) bond lengths are identical (229.4 pm); the Rh−P1 bond is slightly longer (238.5(2) pm; Table 2).

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(16) The signs of the coupling constants $^1J_{PP}$ were generally set to be negative, and the remaining signs and all coupling constants were determined with the program SPINWORKS (Marat, K. *SPINWORKS*, version 05.10.2000; University of Manitoba: Manitoba, Canada, 2000).

(17) No iteration was possible due to the similarity of the coupling constants ^2J and ^3J and broad signals. However, the calculated values are correct as minor alterations in the coupling constants led to completely different coupling patterns.

(18) The dihedral P−P−P−R angles also play a major role in the $^1J_{PP}$ coupling constants. See e.g.: Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 199.

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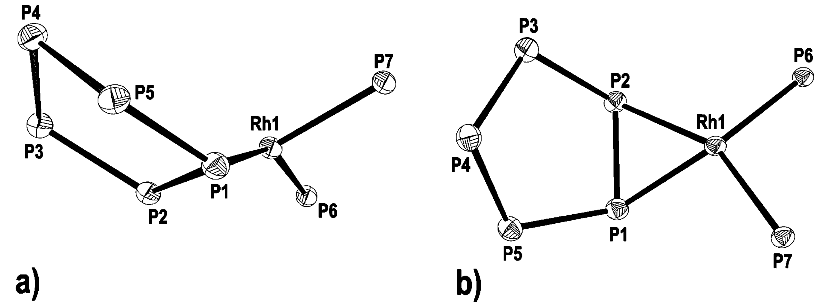

Figure 2. Section of the molecular structure of **2** showing (a) the deviation of P6 from the P1−P2−P7−Rh plane and (b) the distorted square-planar arrangement of the four P atoms P1, P2, P6, and P7 around Rh (ORTEP, 30% probability, SHELXTL PLUS; XP).[24]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

P1−P2	212.9(2)	P2−P1−P5	99.6(1)
P1−P5	220.6(2)	P1−P2−P3	113.3(1)
P2−P3	223.8(2)	P4−P3−P2	104.2(1)
P3−P4	220.8(2)	P3−P4−P5	101.33(9)
P4−P5	224.1(3)	P1−P5−P4	109.34(9)
Rh1−P6	226.9(2)	P6−Rh1−P7	98.05(6)
Rh1−P7	230.1(2)	P6−Rh1−P2	109.56(6)
Rh1−P2	231.3(2)	P2−Rh1−P1	53.87(6)
Rh1−P1	238.5(2)	P7−Rh1−P1	99.31(6)
		P2−P1−Rh1	61.33(6)
		Rh1−P2−P1	64.80(7)

The dihedral angle between the planes P6−Rh−P7 and P1−P2−P3−P5 is 43.89(4)°. The *tert*-butyl groups of the *cyclo*-$P_5{}^tBu_4$ ligand have an all-trans arrangement, and the P_5 ring has an envelope conformation in which P4 deviates from the P1−P2−P3−P5 plane by 69.1(3) pm (deviation from best plane: P1 +13.9(1), P2 −14.5(1), P3 +8.97(7), P5 −8.42(6) pm), and the dihedral angle between the two planes P3−P4−P5 and P1−P2−P3−P5 is 29.4(1)°. As was observed in the starting material **1**, the shorter P1−P2 distance (213.2(1) in **1**, 212.9(2) pm in **2**) indicates multiple-bond character,[20] while the other P−P bonds are in the range of P−P single bonds (220.6(2)−224.1(3) pm).[21] Theoretical studies on the anion [*cyclo*-($P_5{}^tBu_4$)]$^-$ in **1** and [Ni{*cyclo*-($P_5{}^tBu_3$)}(PEt_3)$_2$] confirmed the presence of a shorter P−P bond with multiple-bond character which can be explained by delocalization of the lone pair at P1 into lower unoccupied orbitals (with σ*- and d-orbital contributions) at P2.[9,10]

Experimental Section

General Remarks. All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under nitrogen and kept over a potassium mirror. The NMR spectra were recorded in C_6D_6 with an AVANCE DRX 400 spectrometer (Bruker). ^{1}H (400.13 MHz) and ^{13}C NMR spectra (100.63 MHz) were run with tetramethylsilane as external standard. ^{31}P NMR spectra (161.97 MHz) were run with 85% H_3PO_4 as external standard. The theoretical spectra (coupling constants and signs) were calculated with the program SPINWORKS;[16] the sign of $^1J_{PP}$ was always assumed to be negative. The IR spectrum was recorded with a Perkin-Elmer Spektrum 2000 FT-IR spectrometer between 4000 and 400 cm^{-1} (as KBr disk). The melting point (Gallenkamp) is uncorrected. The mass spectrum was recorded with a VG ZAB-HSQ (FAB, 3-nitrobenzyl alcohol matrix). [RhCl(PPh_3)$_3$][22] and **1**[9] were prepared according to literature procedures.

[Rh{*cyclo*-($P_5{}^tBu_4$)}(PPh_3)$_2$] (2). A solution of **1** (1.46 g, 3.6 mmol) in 20 mL of THF was added slowly to a solution of [RhCl(PPh_3)$_3$] (3.32 g, 3,6 mmol) in 20 mL of THF and stirred at rt (room temperature) for 5 h. A ^{31}P{^{1}H} NMR spectrum of the reaction mixture showed the formation of [Rh{*cyclo*-($P_5{}^tBu_4$)}(PPh_3)$_2$] (16%), *cyclo*-($P_4{}^tBu_4$)[13] (5.8%), *cyclo*-($P_3{}^tBu_3$)[14] (9.5%), *cyclo*-($P_5{}^tBu_4H$)[15] (12.2%), {*cyclo*-($P_5{}^tBu_4$)}$_2$[8] (10.3%), *cyclo*-($P_4{}^tBu_3$)P^tBu}$_2$[8] (6.9%), and PPh_3 (36.3%). The solution was concentrated, and 10 mL of pentane was added. The brown-yellow mixture was filtered and the volume of the filtrate reduced to 8 mL. Cooling to −27 °C gave red rods of **2·**THF. **2** is readily soluble in toluene and THF but only slightly soluble in pentane. Yield: 0.57 g (16%). Mp: 132.7−133.7 °C. ^{1}H NMR (δ/ppm; C_6D_6): 1.32 (d, $^3J_{PH}$ = 15.2 Hz, 9H, ^{t}Bu), 1.36 (d, $^3J_{PH}$ = 13.2 Hz, 9H, ^{t}Bu), 1.41 (d, $^3J_{PH}$ = 11.6 Hz, 9H, ^{t}Bu), 1.44 (d, $^3J_{PH}$ = 12.7 Hz, 9H, ^{t}Bu), 6.90 (m, 6H, *p*-H in Ph), 6.99 (m, 12H, *o*-H in Ph), 7.64 (m, 6H, *m*-H in Ph), 7.72 (m, 6H, *m*-H in Ph). ^{13}C{^{1}H} NMR (δ/ppm): 30.65 (m, CH_3), 31.31 (m, *C*(CH_3)$_3$), 32.07 (m, CH_3), 32.39 (m, *C*(CH_3)$_3$), 32.67 (m, CH_3), 37.07 (m, *C*(CH_3)$_3$), 39.58 (m, *C*(CH_3)$_3$), 132.09 (d, $^4J_{CP}$ = 9.5 Hz, 4-C in Ph), 133.8 (br, 3,5-C in Ph and 4-C in Ph), 134.57 (d, $^2J_{CP}$ = 11.8 Hz, 2,6-C in Ph), 134.95 (d, $^2J_{CP}$ = 13.2 Hz, 2,6-C in Ph), 135.21 (br, 3,5-C in Ph), 138.20 (d, $^1J_{CP}$ = 32.7 Hz, 1-C in Ph), 139.89 (d, $^1J_{CP}$ = 29.9 Hz, 1-C in Ph). ^{31}P{^{1}H} NMR: see Table 1. IR: 3435 w, 3054 w, 2973 s, 2932 s, 2885 s, 2853 s, 2352 w, 2316 w, 1955 w, 1883 w, 1808w, 1651 w, 1584 s, 1571 s, 1504 w, 1467 s, 1434 s, 1383 s, 1371 s, 1356s, 1332 w, 1306 w, 1262 w, 1237 s, 1165 s, 1136 s, 1118 s, 1089 s, 1054 s, 1028w, 1011 w, 999 w, 934 w, 899 w, 844 w, 809 m, 764 m, 750m, 739 m, 618 w, 573 w, 528 s, 518 s, 510 s cm^{-1}. FAB MS: found, *m*/*z* 1011.1 (4.2%, M$^+$ + H), 1010.2 (4.6%, M$^+$), 953.1 (31.7%, M$^+$ − ^{t}Bu), 896.2 (9.1%, M$^+$ − 2^{t}Bu), 857.2 (64.8%, M$^+$ − 2Ph), 839.2 (16.9%, M$^+$ − 3^{t}Bu), 782.7 (9.3%, M$^+$ − 4^{t}Bu), 547.9 (12.2%, M$^+$ − 6Ph = $RhP_7{}^tBu_4$), 519.8 (7.8%, M$^+$ − PPh_3 −4^{t}Bu), 491.0 (2.9%, M$^+$ − 6Ph − ^{t}Bu), 486.0 (9.1%, M$^+$ − 2PPh_3 = $RhP_5{}^tBu_4$), 442.8 (21.4%, M$^+$ − P − 4Ph − 4^{t}Bu), 434.0 (3.9%, M$^+$ − 6Ph − 2^{t}Bu), 383.3 (8.5%, $P_5{}^tBu_4{}^+$)*, 377.0 (5.8%, M$^+$ − 6Ph − 3^{t}Bu), 326.1 (14.3%, $P_5{}^tBu_3{}^+$)*, 319.9 (7.9%, M$^+$ − 6Ph − 4^{t}Bu = RhP_7), 268.9 (9.9%, $P_5{}^tBu_2{}^+$), 257.8 (8.3%, M$^+$ − 2PPh_3 − 4^{t}Bu = RhP_5), and fragmentation products thereof; asterisk indicates the calculated isotopic pattern is in agreement with the observed pattern [$P_5{}^tBu_4$, theor *m*/*z* 383.2; $P_5{}^tBu_3$, theor *m*/*z* 326.1.

Data Collection and Structure Determination of 2·THF. Crystal data: $C_{56}H_{74}OP_7Rh$, M_r = 1082.85; T = 208(2) K; triclinic space group $P\bar{1}$; a = 10.1770(9), b = 14.1912(13), c = 19.3855(17) Å; α = 80.772(2), β = 82.706(2), γ = 88.231(2)°; V = 2.7410(4)

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nm^3; $Z = 2$; $\rho_{calcd} = 1.312$ Mg m^{-3}; $F(000) = 1136$; absorption coefficient = 0.553 mm^{-1}; 20 876 reflections collected, 11 081 independent reflections; $R_{int} = 0.0939$, 586 parameters, R1 ($I > 2\sigma(I)$) = 0.0585, wR2 (all data) = 0.1358; $(\Delta/\rho)_{min} = -0.465$ e Å^{-3}, $(\Delta/\rho)_{max} = 0.795$ e Å^{-3}. Data [λ(Mo Kα) = 0.710 73 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. An empirical absorption correction was performed with SADABS.[23] The structure was solved by direct methods (SHELXTL PLUS[24]). H atoms were located by difference maps and refined isotropically.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC-234500. These data can be obtained from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (internat.) +44-1223/336-033; E-mail deposit@ccdc.cam.ac.uk].

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Supporting Information Available: ^{31}P NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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