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An Unprecedented Dinuclear Alkylrhodium(III) Complex Built up by Two 14-Electron [$RhCl_2$(alkyl)(PR_3)] Units

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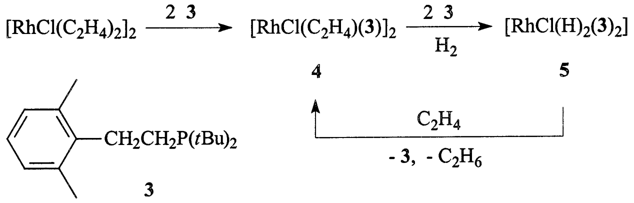
The recent discovery that the functionalized tertiary phosphine ${}^tBu_2PCH_2CH_2C_6H_5$ (**1**), in the presence of olefinrhodium(I) compounds, undergoes C−H activation of the six-membered ring under unusually mild conditions[1] prompted us to prepare some analogues of **1** and study their reactivity toward d^8 metal centers. Since treatment of $[RhCl(C_8H_{14})_2]_2$ or $[RhCl(C_2H_4)_2]_2$ with **1** (pentane, 25 °C) leads exclusively to the insertion of rhodium into the phenyl C−H bond situated in *ortho*-position to the $CH_2CH_2P^tBu_2$ substituent, we were particularly interested to find out what the behavior of a phosphine such as ${}^tBu_2PCH_2CH_2C_6H_3$-2,6-Me_2 (**3**) is which has the two ring carbon atoms next to the β-phosphinoethyl moiety blocked by methyl groups. We were aware of the outstanding work by Milstein et al.[2] illustrating that the pincer-type ligand C_6H-1,3-$(CH_2P^tBu_2)_2$-2,4,6-Me_3 already reacts at room temperature with $[MCl(C_8H_{14})_2]_2$ (M = Rh, Ir) by C−C bond cleavage to give the methylrhodium(III) and -iridium(III) derivatives $[MCl(CH_3)(\kappa^3$-*P*,*C*,*P*-C_6H-2,4-$(CH_2P^tBu_2)_2$-3,5-$Me_2)]$, respectively.

The preparation of the new phosphine **3** occurred in three steps. Dropwise addition of a solution of $ClCH_2CH_2C_6H_3$-2,6-Me_2 (19.7 g, 0.12 mol) in THF (40 mL) to a suspension of finely divided Mg (2.8 g, 0.12 mol) in THF (10 mL), followed by stirring under reflux for 30 min, resulted in the formation of $ClMgCH_2CH_2C_6H_3$-2,6-Me_2. If the solution of this Grignard reagent was added at 0 °C to a solution of ${}^tBuPCl_2$ (18.6 g, 0.12 mol) in THF (60 mL), a white solid ($MgCl_2$) precipitated. Removal of the solvent, repeated extraction of the residue with diethyl ether and fractional distillation (0.002 bar) gave the chlorophosphine $PCl({}^tBu)(CH_2CH_2C_6H_3$-2,6-$Me_2)$ (**2**) as a colorless air- and moisture-sensitive solid. The reaction of **2** (13.0 g, 0.51 mol) in benzene (40 mL) with a 1.6 M solution of ${}^tBuLi$ in pentane (44 mL, 0.74 mol) at 5 °C afforded after hydrolysis with degassed water (20 mL), extraction with diethyl ether (40 mL) and fractional distillation (0.002 bar) the wanted phosphine **3** as an oily liquid (bp 105 °C at 0.002 bar), characterized by NMR and mass spectra as well as by derivatization to the corresponding phosphonium salt $[HP({}^tBu)_2(CH_2CH_2C_6H_3$-2,6-$Me_2)]Cl$ (**3·HCl**).

In contrast to other trialkylphosphines such as $P({}^tBu)_2CH_3$,[3] **3** does not react with $[RhCl(olefin)_2]_2$ (olefin = C_2H_4, C_8H_{14}) to give a mononuclear olefin−rhodium(I) complex *trans*-[RhCl(olefin)(**3**)$_2$]. With $[RhCl(C_2H_4)_2]_2$ as the starting material and a 2-fold excess of **3**, the dinuclear compound **4** (yellow air-stable solid, mp 77 °C dec, yield 93%) is formed instead.[4] The attempted conversion of **4**, *under a hydrogen atmosphere*, with 2 equiv of **3** to [RhCl(**3**)$_2]_n$ (n = 1 or 2) affords the dihydrido complex **5** in almost quantitative yield (Scheme 1). Typical features of **5** (light-yellow solid, mp 104 °C dec) are the high-field resonance at δ −23.0 [dt, ${}^2J$(Rh,H) = 26.2, ${}^3J$(P,H) = 14.5 Hz] in the ${}^1H$ NMR and the Rh−H stretching vibration at 2122 cm^{-1} in the IR spectrum. While **5** is completely inert toward cyclooctene and 3,3-dimethyl-1-butene (pentane, 25 °C), it reacts under the same conditions with ethene to regenerate **4**.

Scheme 1



The reaction of **4** with HCl, undertaken to generate the five-coordinate dichloro(hydrido)rhodium(III) complex $[RhHCl_2(C_2H_4)$-(**3**)] structurally related to **5**, furnished a surprising result. Passing a slow stream of dry HCl gas through a suspension of **4** (123 mg, 0.14 mmol) in CH_2Cl_2 (3 mL) for 10 s at room temperature produces, after removal of the solvent and recrystallization from dichloromethane, an orange solid (mp 102 °C dec, yield 83%), the microanalysis of which is in agreement with the expected composition $[RhHCl_2(C_2H_4)$(**3**)]. However, as shown by the X-ray crystal structure analysis, the isolated product is not a hydrido but the dinuclear ethylrhodium(III) compound **6** which is built up by two 14-electron $[RhCl_2(C_2H_5)$(**3**)] units (Figure 1).[5] These units are linked by two bridging chlorides which are unsymmetrically situated between the two metal centers. The midpoint of the planar Rh_2Cl_2 ring with distances Rh(1)−Cl(2) = 2.3561(6) Å and Rh(1)−Cl(2A) = 2.5257(6) Å constitutes a center of inversion. Since the terminal chlorides Cl(1) and Cl(1A) lie exactly and the phosphorus atoms P(1) and P(1A) nearly in the plane of the Rh_2Cl_2 ring, the coordination geometry around Rh(1) and Rh(1A) can be best described as square-pyramidal. The bond angles Cl(1)−Rh(1)−C(1) and Cl(2)−Rh(1)−C(1) are 87.77(9)° and 94.97(9)°, respectively. We note that the bond length Rh(1)−C(1) of 2.059(3) Å is significantly (ca. 0.11 Å) shorter than in the Milstein complex $[RhCl(CH_3)(\kappa^3$-*P*,*C*,*P*-C_6H-2,4-$(CH_2P^tBu_2)_2$-3,5-$Me_2)]$.[2a]

The reactivity of the ethylrhodium(III) compound **6** is rather unusual. Treatment of **6** with phosphine **3**, undertaken to prepare the mononuclear complex $[RhCl_2(C_2H_5)$(**3**)$_2$] via chloride-bridge cleavage, affords the dichloro(hydrido) derivative **7** (orange solid, mp 103 °C). Therefore, we assume (see Scheme 2) that in solution an equilibrium between a $Rh(C_2H_5)$ and a $RhH(C_2H_4)$ isomer exists and that **7** is formed from the latter by displacement of the olefin.

The same ethene(hydrido)rhodium(III) species is possibly also an intermediate in the reaction of **6** with CO. Stirring a solution of **6** in CH_2Cl_2 under a CO atmosphere for 1 h gives a mixture of products which, according to the ${}^{31}P$ NMR spectrum, consists of dimer **8** and the phosphonium salt **3·HCl**. Alternatively, dimer **8** can be obtained cleanly and without any byproducts if a suspension of **9** (prepared from $[RhCl(C_8H_{14})_2]_2$ and **3** in the molar ratio 1:2) in pentane is stirred under carbon monoxide. In ca. 10 s a yellow solution is formed from which, after partial evaporation of the

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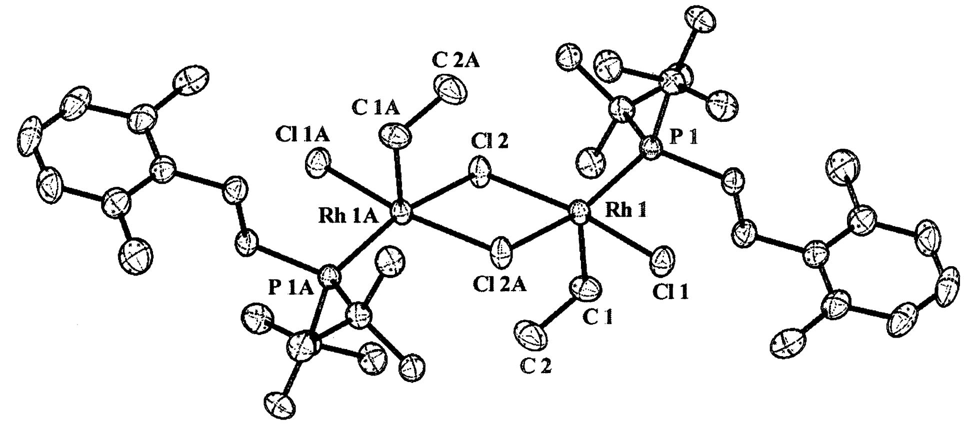
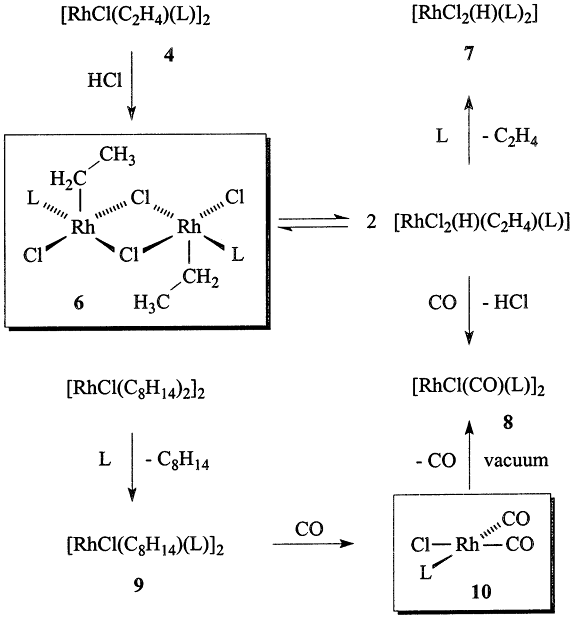


Figure 1.

Scheme 2 [a]



[a] (L = **3**)

solvent in vacuo, a pale yellow solid (mp 195 °C dec, yield 87%) precipitates. Since the IR spectrum of **8** (in KBr) displays only one ν(CO) band at 1962 cm^{-1}, and the ^{31}P NMR spectrum (in CD_2Cl_2), a single resonance at δ 78.6 [d, ^2J(P,Rh) = 174.6 Hz], there is no doubt that the two phosphine ligands are in trans disposition with respect to the central Rh_2Cl_2 fragment. If the time for the reaction of **9** and CO (1 bar) in pentane is extended from 10 s to 1 h and the solvent removed *in the presence of CO*, light-yellow air-stable crystals are isolated which are analyzed as the dicarbonyl complex **10** (mp 94 °C dec, yield 95%). In contrast to **8**, the IR spectrum of **10** (in KBr) shows two CO stretching modes at 2086 and 1999 cm^{-1}. The ^{13}C NMR spectrum of **10** (in CD_2Cl_2) exhibits two doublet of doublet resonances for the CO carbon atoms of which that at δ 181.1 with the larger ^{13}C−^{31}P coupling constant of 112.5 Hz is assigned to the CO group trans to the phosphine and that at δ 184.8 with ^2J(C,P) = 16.2 Hz to the CO group trans to the chloride. The mononuclear complex **10** is probably an intermediate in the formation of **8** from **9** since in vacuo it is easily converted either in solution or in the solid state to **8**.

The results presented here highlight two different aspects. First, the formation and the structure of the dinuclear alkylrhodium(III) compound **6** is without precedent.[6] There are numerous rhodium complexes [Rh(μ-X)(L)(L′)]$_2$ known,[7] which like **6** are also built up by two 14-electron fragments, but in all of these compounds the metal is in the oxidation state +I and not +III. Second, the mononuclear four-coordinate dicarbonyl compound **10** represents, to the best of our knowledge, the first isolated and fully characterized rhodium(I) complex of the general composition *cis*-[RhCl(CO)$_2$(PR$_3$)]. It has been reported by various authors,[8] that those dicarbonylrhodium(I) derivatives are key intermediates in the reactions of [RhCl(CO)$_2$]$_2$ with PR$_3$ and of [RhCl(CO)(PR$_3$)]$_2$ with CO, but due to the preferred dissociation of one Rh−CO bond the attempted isolation of these intermediates failed. We assume that the bulkiness of phosphine **3** somewhat inhibits the conversion of **10** to the more stable dinuclear complex **8**, and experiments to prove this hypothesis are underway.

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Supporting Information Available: Complete list of NMR data for **2**, **3**, **3·HCl**, **4**, **5**, **6**, **7**, **8**, and **10** (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(4) For X-ray crystal structure analysis of **4** see: Brandt, C. D. PhD Dissertation, Universität Würzburg, to be submitted.
(5) Crystal parameters of **6**: $C_{40}H_{72}Cl_4P_2Rh_2$, T = 193 K, $P2_1/c$, Z = 2, a = 10.0093(6) Å, b = 15.4273(9) Å, c = 14.0090(8) Å, β = 92.7580(10)°, V = 2160.7(2) Å^3, d_{calc} = 1.479 g/cm^3, R1 = 0.0311, wR2 = 0.0709. Data were collected on a Bruker Smart Apex diffractometer with D8-Goniometer using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation, and were corrected for Lorentz, polarization, and absorption effects. The structure was solved by direct methods (SHELXS-97) and was refined using the full-matrix least-squares method (SHELXL-97). Full details are described in the Supporting Information.
(6) The nearest relative of **6** we are aware of is the hydrido(silyl)rhodium(III) complex [Rh(μ-Cl)H{Si(CH$_2$Ph)$_3$}(P*i*Pr$_3$)]$_2$, prepared from [RhCl(P^{i}Pr$_3$)$_2$]$_2$ and HSi(CH$_2$Ph)$_3$: Osakada, K.; Koizumi, T.; Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 189−195.
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