## COMMUNICATIONS

### "Grignard-Analogous" Rhodium Phosphane Complexes\*\*

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### Dedicated to Professor J. Halpern

The chemistry of mononuclear rhodium complexes bearing phosphane ligands is dominated by compounds with the transition metal center in the +1 or +11 oxidation state.<sup>[1]</sup> Although  $[(Me_3P)_4Co]^-$  has been well studied,<sup>[2]</sup> corresponding rhodium compounds have so far been restricted to cases where highly  $\pi$ -acidic ligands are present, for example K[(F<sub>3</sub>P)<sub>4</sub>Rh],<sup>[3]</sup> Na[(Ph<sub>3</sub>P)<sub>2</sub>(CO)<sub>2</sub>Rh],<sup>[4]</sup> and Li[(triphos)(CO)Rh] (triphos = {2-[(diphenylphosphano)methyl]-2-methylpropane-1,3-diyl}bis-(diphenylphosphane)).<sup>[5]</sup> In sharp contrast, the reduction of [(Me<sub>3</sub>P)<sub>4</sub>RhCl] with Na/Hg leads to the formation of the heterobimetallic cluster [(Me<sub>3</sub>P)<sub>12</sub>Hg<sub>6</sub>Rh<sub>4</sub>].<sup>[6]</sup>

Here we report the synthesis, spectroscopic properties, and reactivity of bimetallic complexes of the form  $[(P_2)_2Rh][MgCl]$ (1a and 1b,  $P_2$  is the bidentate chelating phosphane ligand  $Ph_2P(CH_2)_nPPh_2$  termed 2a when n = 2 and 2b when n = 3), which contain rhodium in the formal oxidation state -1. They are the first examples of a new class of highly nucleophilic transition metal compounds that can be referred to as "Grignardanalogous" rhodium phosphane complexes.<sup>[7, 8]</sup>

A THF slurry of the yellow chloro complex  $[(2a)_2 RhCl]^{[9]}$ (3a) reacts smoothly with an excess of specially activated magnesium  $(Mg^*)^{[10]}$  at room temperature to give a dark red solution of 1a (Scheme 1). Within 2 h 3a disappears completely, and



Scheme 1. Synthesis of Grignard-analogous rhodium phosphane complexes  $[(P_3)_2Rh][MgCl]$  (1a-b) from the corresponding chloro complexes 3a,b and active magnesium (Mg<sup>\*</sup>). The chelating phosphane ligands are schematically displayed: methylene groups are shown for only one ligand, and the phenyl substituents at the phosphorous atom have been omitted. RT = room temperature.

exactly one equivalent of Mg\* is consumed; no further reaction occurs under these conditions. Monitoring of the reaction by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (81.01 MHz, room temperature)<sup>[11]</sup> indicates the clean formation of **1a**, which is characterized by a doublet of slightly broadened lines centered at  $\delta = 62.0$  (*J*(Rh,P) = 197 Hz).<sup>[12]</sup> Although no directly related data can be found in the literature, identical trends have been observed for [(**2a**)<sub>2</sub>RhX] (X = Cl, H, MgCl) and [(triphos)- Table 1.  ${}^{31}P{}^{1}H$  MMR spectroscopic data for [(2a)<sub>2</sub>RhX] (X = Cl, 3a; X = H, 4a; X = MgCl, 1a) and [(triphos)(CO)RhX] (X = Cl, H, Li) [a].

	X = Cl	X = H	X = M
[( <b>2a</b> ) <sub>2</sub> RhX]	<b>3a</b>	<b>4a</b>	1a, M = MgCl
	$\delta = 58.2, d$	$\delta = 56.7, d$	$\delta$ = 62, d, br
	J = 133 Hz	J = 143 Hz	J = 197 Hz
[(triphos)(CO)RhX]	[b]	[c]	[b], M = Li
	$\delta = 3.0, d$	$\delta = 16$ , d	$\delta$ = 21.4, d
	J = 107 Hz	J = 116 Hz	J = 155 Hz

[a] All values in [D]<sub>8</sub>THF; [b] ref. [5]; [c] ref. [13].

(CO)RhX] (X = Cl, H, Li).<sup>[5, 13]</sup> This strongly supports the assignment as 1a (Table 1).

After filtration, a THF solvate of **1a** can be precipitated from the reaction mixture with pentane. The IR spectrum of this extremely air- and moisture-sensitive, dark red, microcrystalline solid (m.p. =  $110-113 \,^{\circ}C$ )<sup>[14]</sup> reveals the absence of the characteristic bands for the Rh–Cl and Rh–H units in **3a** (353 cm<sup>-1</sup>) and **4a** (1897 cm<sup>-1</sup>) and exhibits a new band for the Mg–Cl vibration at 321 cm<sup>-1</sup>.

The reaction of **3b** with Mg\* proceeds in an identical manner to give **1b**, which exhibits <sup>31</sup>P NMR data similar to that of **1a**  $(\delta \approx 24.8)$ , very broad doublet,  $J \approx 170$  Hz, 121.06 MHz, RT). Preliminary experimental results show that the NMR spectra of **1a** and **1b** are highly dependent on field strength, temperature, and concentration. This suggests an intermolecular dynamic exchange process in solution. The high conductivity of **1a** and **1b** at room temperature<sup>[15]</sup> strongly supports their formulation under these conditions as solvent-separated ion pairs with tetrahedral coordination at the d<sup>10</sup> transition metal center in the  $[(P_2)_2Rh]^-$  core,<sup>[2]</sup> which may be in equilibrium with a pentacoordinated covalent bimetallic species.<sup>[16]</sup> Nevertheless, other possible processes such as Schlenk-type equilibria cannot be ruled out.

The Grignard-analogous reactivity of **1a** (Scheme 2) and **1b** clearly reflects the high nucleophilicity of the rhodium



Scheme 2. Reactivity of the Grignard-analogous rhodium complex 1a towards various electrophiles and carbon dioxide. All reactions were carried out in THF or  $[D]_{8}$ THF at room temperature. P = PPh<sub>2</sub>.

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<sup>[\*\*]</sup> CO<sub>2</sub> Activation, Part 10. This work was supported by the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie. A genereous loan of rhodium(in) chloride hydrate by Degussa AG is gratefully acknowledged. W. L. wishes to thank Prof. K. Jonas for helpful and stimulating discussions, E. Janssen for the conductivity measurements, and Dr. U. Kolb for the EXAFS studies. Part 9: K. Angermund, W. Baumann, E. Dinjus, R. Fornika, H. Görls, M. Kessler, C. Krüger, W. Leitner, F. Lutz, Chem. Eur. J. 1997, 3, issue 5.

centers and gives further unambiguous evidence for their formulation as  $[(P_2)_2Rh][MgCl]$ . Careful protonolysis with stoichiometric amounts of EtOH gives the hydride complexes **4a** and **4b** in quantitative yields. Methylation of **1a** with methyl iodide leads to the rhodium complex **5a**, which can be readily separated from the magnesium salts and isolated in 76% yield.<sup>[17,18]</sup>

In principle, the reaction of Grignard-analogous phosphane complexes with  $R_3SiX$  should offer an interesting approach to bimetallic phosphane complexes with nonbridging Rh-Si units. This class of compounds has attracted considerable interest in recent years.<sup>[19, 20]</sup> However, the reaction of **1a** and Me<sub>3</sub>SiCl at room temperature leads to quantitative formation of the hydride **4a**. GC analysis of the volatile components reveals the presence of the trimethylsilyl ether of 1-butenol. This suggests the intermediate formation of  $[(2a)_2RhSiMe_3]$  (**6a**), which undergoes a ring-opening reaction with solvent THF. The thermal instability of complexes  $[(R_3P)_nRhSiR_3]$  (n = 3,4) is well documented,<sup>[19]</sup> but Aizenberg and Milstein have very recently reported complexes of type  $[(Me_3P)_4RhSiR_3]$ . These species have a limited, but definite lifetime in THF at room temperature.<sup>[20e]</sup>

Complexes 1a and 1b should also be suitable for activation of CO,<sup>[21]</sup> since they contain both a highly electron-rich and an electron-deficient metal center. A similar methodology has been introduced by Floriani and co-workers.<sup>[21, 22]</sup> Replacement of the argon atmosphere over a THF solution of 1a with  $CO_2$ results in the immediate formation of a yellow precipitate, which consists of an approximately 1:1 mixture of 3a and MgCO<sub>3</sub>. The supernatant also contains small amounts of 3a; this is therefore the only phosphorus-containing product. Labeling experiments with <sup>13</sup>CO<sub>2</sub> and GC/MS analysis of the gaseous products revealed the concomitant formation of <sup>13</sup>CO. Thus, the overall process is the conversion of two molecules of CO<sub>2</sub> to CO and  $CO_3^{2-}$ . This reaction has been frequently observed for transition metal complexes that attack carbon dioxide at the Lewis acidic carbon center.<sup>[21a, c]</sup> In the present case, the highly nucleophilic rhodium center provides the two electrons required for this process.

As the starting material (**3a**) for the formation of **1a** is regenerated in this reaction, the possibility of a catalytic cycle based on this process was tested. Unfortunately, conversion of **3a** to **1a** with excess Mg\* under one atmosphere CO<sub>2</sub> was not very effective; only three catalytic turnovers were obtained after 24 h. Nevertheless, this reaction provides the first example of a homogeneously catalyzed reduction of CO<sub>2</sub> to CO at a transition metal center, whereby the two reduction equivalents are provided by a main group metal and not a by photo- or electrochemical process.<sup>[21b]</sup> To the best of our knowledge, this is the first example of a nonelectrochemical catalytic process based on the interconversion of rhodium(- t) and rhodium(t) centers, which are coordinated only to phosphane ligands.

In conclusion, transition metal phosphane complexes such as 3 react with Mg\* to give well-defined molecular compounds 1 with highly nucleophilic, mononuclear rhodium centers in formally negative oxidation states. The phosphorus ligands at the central metal atom provide a straightforward, diagnostic tool for studying the structure and reactivity of these species in solution. Based on their composition and chemical behavior, compounds of type 1 can be referred to as Grignard-analogous transition metal phosphane complexes. Their use as versatile reagents for organometallic transformations, including the synthesis of other heterobimetallic complexes and catalytic processes, offers a broad range of potential applications.

#### Experimental Section

All manipulations were carried out under an argon atmosphere in flame-dried glassware with standard Schlenk techniques. THF and  $[D]_8$ THF were distilled from [Mg·anthracene·3 thf] prior to use. NMR spectra were recorded in sealed tubes or in tubes equipped with J. Young valves.

[(2a)<sub>2</sub>Rh][MgCl] (1a): Mg\* (0.65 g, 24.8 mmol) was added to a slurry of 3a (2.41 g, 2.59 mmol) in THF (80 mL), and the mixture stirred at room temperature. After 2 h the solution was filtered and evaporated to dryness. The residue was then redissolved in THF (10 mL). Subsequent addition of pentane (5/1 v v) yielded 1a·x THF (2.73 g) as a dark red, microcrystalline solid. Analytical data are summarized in Table 1 and in the text. Complex 1b was synthesized by the same procedure on a smaller scale (3b: 0.57 g).

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- The term "inorganic Grignard reagents" is often restricted to bimetallic com-[7] plexes [L<sub>n</sub>MMgCl], for which X-ray diffraction studies suggest a direct M-Mg bond. For example see a) H. Felkin, G. Swierczewski, Tetrahedron 1975, 31, 2735; b) H. Felkin, P. J. Knowles, B. Meunier, J. Organomet. Chem. 1978, 146, 151; c) S. G. Davies, M. L. H. Green, J. Chem. Soc. Dalton Trans. 1978, 1510; d) K. Jonas, G. Koepe, C. Krüger, Angew. Chem. 1986, 98. 901; Angew. Chem. Int. Ed. Engl. 1986, 25, 923. However, many bimetallic transition metal/magnesium complexes containing carbonyl ligands exhibit bridging  $M(\mu$ -CO)Mg units rather than direct M-Mg interactions; examples: e) G. B. Vicker, Inorg. Chem. 1975, 14, 2087; f) S. W. Ulmer, P. M. Skarstad, J. M. Burlitch, R. E. Hughes, J. Am. Chem. Soc. 1973, 95, 4469; g) J. L. Detrich, R. Konečný, W. M. Vetter, D. Doren, A. L. Rheingold, K. H. Theopold, ibid. 1996, 118, 1703. Therefore, we prefer the wider use of inorganic Grignard reagents which implies analogy to organic Grignard reagents in terms of composition, synthesis, and reactivity.
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- [12] The corresponding signal accounts for about 90% of the total intensity in the  ${}^{31}P$  spectrum; the only other detectable product is the hydride **4a** [9]. As THF has been excluded as the hydride source by labeling experiments, this side product is most likely formed by the reaction of **1a** or **3a** with inevitable traces of moisture or MgH<sub>2</sub> (in Mg<sup>\*</sup>), respectively. Furthermore, it has been independently checked that **4a** is inert towards Mg<sup>\*</sup>.
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- [14] The extreme sensitivity of the material has hampered all attempts to detect the anion [(2a)<sub>2</sub>Rh]<sup>-</sup> by ESI-MS. This, together with the tendency of the compounds to retain varying amounts of THF, has also prevented us from obtain ing satisfactory elemental analyses. However, analytically determined elemental ratios of Mg:Rh:Cl:P = 1:1:1:4 are acceptable for both Ia and Ib.
- [15] 1a:  $3.40 \times 10^{-4}$  S (THF,  $c = 0.06 \text{ mol } L^{-1}$ , RT); 1b:  $5.42 \times 10^{-4}$  S (THF,  $c = 0.04 \text{ mol } L^{-1}$ , RT).
- [16] As the quality of the crystals did not allow X-ray diffraction studies, we tried to obtain evidence for a Rh–Mg interaction in the solid state with EXAFS investigations. Unfortunately, due to the small contribution of a Mg back scatterer to the  $\chi(k)k^3$  function, no conclusions about its presence or absence at or below 3.5 Å was possible (FEFF calculations).

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## Supramolecular Complexation of 1,2-Dicarbadodecaborane(12)\*\*

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Although the carboranes o-, m-, and p-C<sub>2</sub>B<sub>10</sub>H<sub>12</sub> [1,2-, 1,7-, and 1,12-dicarbadodecaborane(12)] have been known for over thirty years, their potential for building macromolecules and forming supramolecular assemblies has only recently been explored.<sup>[1-4]</sup> These studies include linkage of the cages through the carbon centers by organic groups<sup>[1, 2]</sup> or metal centers<sup>[3]</sup> and inclusion complexation of  $o-C_2B_{10}H_{12}$  in  $\alpha$ -,  $\beta$ -, or  $\gamma$ -cyclodextrin as 2:1 and 1:1 complexes in aqueous media.<sup>[4]</sup> The formation of the 2:1 complexes possibly involves complete encapsulation of the carborane by two host molecules. In the case of the 1:1 complexes, polymeric structures in which both sides of each cyclodextrin make contact with a carborane may prevail. The different dipole moments of the three carboranes may be a useful property to exploit for purification of the carboranes. Conventional chromatographic techniques make the separation of the *p*- and *m*-isomers difficult.<sup>[5]</sup>

The inclusion chemistry of carboranes has been very limited so far. This is surprising given the nexus between these clusters and the buckminsterfullerene  $C_{60}$ , for which there have been several studies.<sup>[6, 7]</sup> The carboranes and  $C_{60}$  are all remarkably thermally stable, icosahedral clusters with similar diameters of about 8 and 10.0 Å, respectively. However, it is noteworthy that only the *p*-isomer is nonpolarized in the ground state, like  $C_{60}$ .

Here we report complexation of the *ortho*-carboranes by the rigid, bowl-shaped cyclotriveratrylene (CTV)<sup>[8, 9]</sup> and its symmetrically tris(allyl)-substituted analogue (CTV') in non-aqueous media (Scheme 1).<sup>[10]</sup> Both species form complexes

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Scheme 1.

with  $C_{60}$ .<sup>[6]</sup> Despite the use of equimolar amounts of the two starting materials, CTV forms a 2:1 adduct with  $o-C_2B_{10}H_{12}$  in the solid state. While the 2:1 ratio can indicate that two host molecules encapsulate the cluster, the X-ray structure revealed that only one of the ligands binds to the cluster. The other one seems to act as a space filler (see below). The IR spectrum shows a significant shift of  $13.5 \text{ cm}^{-1}$  to lower energy of for the  $v_{C-H}$ band of the carborane and a shift of  $15.3 \text{ cm}^{-1}$  to higher energy for the  $v_{B-H}$  band. This is consistent with the involvement of the C–H bonds in nonclassical hydrogen bonding. Dispersal of the extra charge on the carbon atoms results in a strengthening of the B–H bonds. CTV' also complexes to  $o-C_2B_{10}H_{12}$ , and the product shows similar IR shifts ( $12.5 \text{ cm}^{-1}$ ,  $v_{C-H}$ ;  $3.2 \text{ cm}^{-1}$ ,  $v_{B-H}$ ). However, the crystals obtained were unsuitable for crystallographic studies.

<sup>1</sup>H NMR solution spectra of the 2:1 complex show that a rapid exchange process occurs between complexed and uncomplexed carborane. Single peaks observed for the *o*-carborane C-H groups are significantly shifted upfield. The <sup>1</sup>H NMR spectra of complexed and uncomplexed CTV are essentially the same. Variation of the molar fraction of carborane relative to CTV shows a nonlinear relationship with the chemical shift of the carborane to CTV of 5:1 to 1:5). This implies that the complexation is not a simple 1:1 supramolecule formation. Indeed, the inability to fit the NMR data to this simple model indicates that *o*-carborane can bind in both an *endo* and *exo* fashion to the cavity of the CTV.

In the solid state<sup>[11]</sup> the 2:1 complex consists of  $o-C_2B_{10}H_{12}$ in a host-guest contact with one of the CTV molecules (Figure 1). The other CTV forms a zigzag  $\pi$ -stacked column in which the intermolecular CTV contacts are at the van der Waals limit (Figure 2). The asymmetric unit is made up of one hostguest species and one CTV of the column, which is built up by a screw axis along the *b* axis such that  $\pi$  stacking is only effective for a part of two of the aromatic rings of each CTV. The structure represents the first authentic host-guest complex of a main group cluster other than  $C_{60}$ .<sup>[6]</sup> The lengths of the covalent bonds in the CTV molecules<sup>[9]</sup> and the carborane<sup>[13]</sup> are in the expected range.

The cavity of CTV is shallow relative to the diameter of the carborane, and association of the two units is best described as a perching complex.<sup>[14]</sup> Diffraction data were collected at -100 °C: this facilitated the refinement of the hydrogen

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