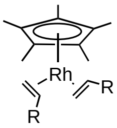
[13] ^{31}P NMR (121.5 MHz, 298 K, 85% phosphoric acid as external standard): $\delta = 117.1$ (d, $^2J(P,P) = 27.6$ Hz, q, $^3J(P,B) = 0.7$ Hz, 3P; uncoordinated phosphorus), 90 (m, broadened through the quadrupole moment of boron, 1P; boron-bearing phosphorus); compare reference [6].
[14] C. Engemann, G. Kohring, A. Pantelouris, J. Hormes, S. Grimme, S. D. Peyerimhoff, J. Clade, F. Frick, M. Jansen, *Chem. Phys.* **1997**, *221*, 189–198; C. Engemann, Dissertation, Universität Bonn, **1997**.
[15] ^{31}P NMR (121.5 MHz, 298 K, 85% phosphoric acid as external standard): $\delta = 94.0-94.6$ (m, 4P; P^{III} corresponding to P2, P3, P6, P7 in **1**), 79.6–80.1 (m, 2P; P^{III} corresponding to P4, P8 in **1**), $-54.3 - -53.6$ (m, 2P; P^{V} corresponding to P1, P5 in **1**).

Dehydrocoupling of Phosphanes Catalyzed by a Rhodium(I) Complex**

Volker P. W. Böhm and Maurice Brookhart*

Although catalytic dehydrocoupling of phosphanes has been reported with Group 4 metallocene catalysts $[K(thf)_2][Cp^*_2ZrH_3]$ and $[Cp_2TiMe_2]$ ($Cp^* = C_5Me_5$, $Cp = C_5H_5$), these reactions are limited to the activation of primary phosphanes RPH_2 in the formation of (cyclic) oligomers and the cross-coupling of primary and secondary phosphanes with primary silanes.[1–3] Late transition metal catalysis of these types of reaction has only been reported for the coupling of phosphanes with borane.[4]

Complexes of the type $[Cp^*Rh(olefin)_2]$ (**1**) are known to activate C–H bonds in arenes,[5] olefins,[6] aldehydes,[7] and alkanes,[6,8] as well as B–H bonds[8] and such activated species have been incorporated into catalytic cycles. The rhodium(v) catalyst **2** which is a precursor to the fragment [Cp*Rh] has been used similarly for the activation of C–H bonds in arenes and alkanes as well as of Si–H bonds.[9] Owing to the lack of reports on the activation of bonds between hydrogen and Group 15 elements, we became interested in the reactivity of secondary phosphanes towards the complex $[Cp^*Rh\{CH_2{=}CH(TMS)\}_2]$ (**1a**).[10]



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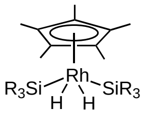
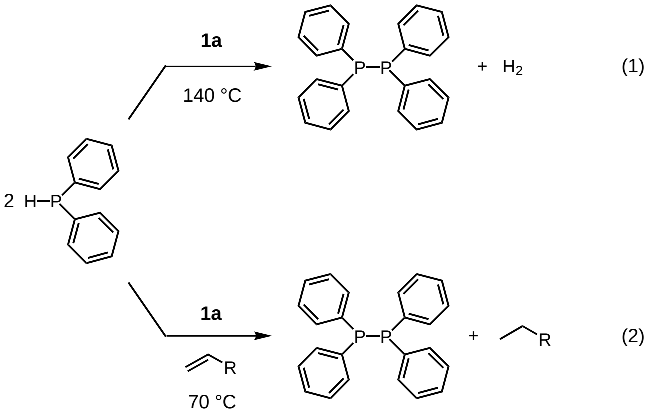


2

Heating diphenylphosphane, $HPPh_2$, in the presence of catalytic amounts of complex **1a** in C_6D_6 at 140 °C results in an immediate color change of the solution from yellow to red accompanied by the formation of a new compound with a ^{31}P NMR signal at $\delta = -13.6$ which does not exhibit $^1J(P,H)$ coupling. At the same time, the ^1H resonance signal for the P-H proton of $HPPh_2$ disappears and a signal for dihydrogen grows in at $\delta = 4.46$ [Eq. (1)]. As a side reaction, vinyltrimethylsilane is partially hydrogenated [Eq. (2)]. The product formed was identified by comparison to an authentic sample as tetraphenyldiphosphane, Ph_4P_2.[11] Repeating the experiment without complex **1a** leads to the recovery of unchanged $HPPh_2$. When an excess of vinyltrimethylsilane is added to the reaction, the coupling occurs at temperatures as low as 70 °C and hydrogenation of the olefin is observed rather than the evolution of dihydrogen [Eq. (2)].



To investigate the scope of this catalytic reaction, various diaryl- and dialkylphosphanes were employed (Table 1). Reactivity is not sensitive to electronic effects but steric demand plays a decisive role. Mesityl (2,4,6-$Me_3C_6H_2$), *tert*-butyl, and cyclohexyl substituents prevent coupling (Table 1, entries 8, 11, and 13) whereas phenyl, *para*-anisyl, ethyl, and isobutyl groups are well-tolerated (Table 1, entries 5, 7, 9, and 10). Turnover numbers (TON) as high as 1300 mol product per mol Rh were achieved with $HPPh_2$ (Table 1, entry 6). An intermediate behavior is exhibited by dicyclopentylphosphane which reacts only very sluggishly (Table 1, entry 12). The rhodium catalyst **1a** also tolerates ether functionalities (Table 1, entries 7 and 17). $HPPh_2$ can be coupled in good yields at 110 °C in the presence of vinyltrimethylsilane or 3,3-dimethyl-1-butene (Table 1, entries 1–4). Lower turnovers in comparison to those achieved in the high-temperature process without added olefin are likely due to increased formation of unreactive 18-electron species bearing olefinic ligands. No hydrophosphination of the olefin is observed in any case.[12] Using phenylphosphane, H_2PPh, and *para*-anisylphosphane in the coupling reaction does not lead to the formation of polymeric or oligomeric polyphosphanes. Instead, the two isomers of diaryldiphosphanes, *rac*- and *meso*-ArHP–PHAr, are formed in equal amounts in low yields (Table 1, entries 14–17). Higher turnovers with primary phosphanes could be achieved only if the reaction was run in neat

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Table 1. Dehydrocoupling of phosphanes catalyzed by **1a**.[a]

$$2\ \text{'RRP—H} \xrightarrow[C_6D_6]{\mathbf{1a}} \text{'RRP—PRR'}$$

Entry	R	R′	[Rh] [mol %]	*t* [h]	*T* [°C]	Olefin[b]	Yield[c] [%]	Conversion[c] [%]
1	C_6H_5	C_6H_5	1.8	17	110	CH_2=CH(TMS)	79	88
2	C_6H_5	C_6H_5	0.3	17	110	CH_2=CH(TMS)	61	63
3	C_6H_5	C_6H_5	7.8	27	70	CH_2=CH*t*Bu	60	63
4	C_6H_5	C_6H_5	0.3	17	110	CH_2=CH*t*Bu	52	57
5	C_6H_5	C_6H_5	2.7	16	140	–	96	99
6	C_6H_5	C_6H_5	0.06	18	140	–	79	80
7	4-$(H_3CO)C_6H_4$	4-$(H_3CO)C_6H_4$	7.8	14	145	–	92	100
8	2,4,6-$(H_3C)_3C_6H_2$	2,4,6-$(H_3C)_3C_6H_2$	1.6	18	140	–	0	1
9	CH_2CH_3	CH_2CH_3	7.1	40	145	–	88	93
10	$CH_2CH(CH_3)_2$	$CH_2CH(CH_3)_2$	2.0	34	140	–	82	84
11	$C(CH_3)_3$	$C(CH_3)_3$	2.0	48	140	–	0	5
12	*cyclo*-C_5H_9	*cyclo*-C_5H_9	5.3	40	145	–	7	14
13	*cyclo*-C_6H_{11}	*cyclo*-C_6H_{11}	4.8	48	140	—	0	6
14	C_6H_5	H	3.1	29	110	CH_2=CH(TMS)	8[d]	10
15	C_6H_5	H	1.1	18	145	–	3[d]	5
16	C_6H_5	H	0.6	26	150	–	30[d,e]	56
17	4-$(H_3CO)C_6H_4$	H	5.8	18	145	–	5[d]	8

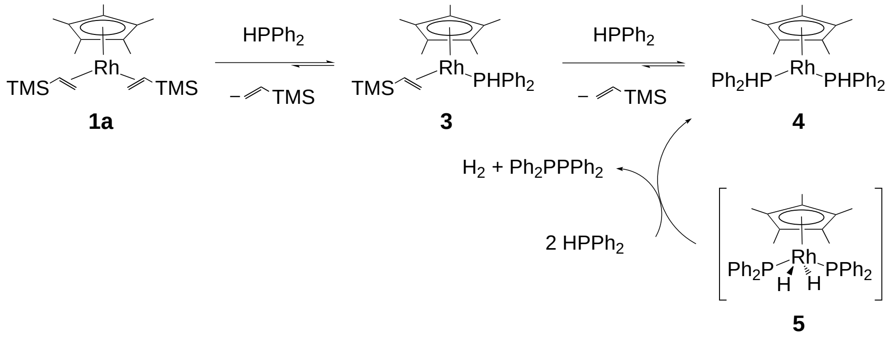
[a] 114 μmol phosphane, 0.7 mL C_6D_6. [b] 1.1 equivalents olefin with respect to phosphane; the olefin serves as the hydrogen acceptor. No olefin added implies release of H_2. [c] Yield and conversion are based on initial phosphane concentration as determined by NMR spectroscopy. [d] Two isomers (*rac* and *meso*) are formed in equal amounts. [e] Reaction in neat phenylphosphane.

phosphane (Table 1, entry 16); however, side reactions giving unassigned products occur under these conditions.

The transformation of $HPPh_2$ was monitored by NMR spectroscopy at 110 °C in [D_8]toluene. At the beginning of the reaction, stepwise exchange of the bound olefins by the phosphane and formation of the complexes **3** and **4** is observed by ^1H and ^{31}P NMR spectroscopy (Scheme 1).[11] The complex [Cp*Rh($PHPh_2$)$_2$] (**4**) is the major resting state of the catalyst during the reaction and accounts for 83 % of the amount of **1a** initially used as determined by integration of ^1H NMR signals. After full conversion of the starting material, three additional unidentified rhodium species build up which are characterized by broad Cp* signals at $\delta = 1.54$, 1.74, and 1.79 in the ^1H NMR spectrum. No doublets in the $^{31}P\{^1H\}$ NMR spectrum could be assigned to phosphorus atoms coordinated to rhodium centers although the product Ph_4P_2 and diphenylphosphide $[Ph_2P]^-$ are known to form complexes with [Cp*Rh] fragments.[13, 14] As the +5 oxidation state for rhodium is well-precedented[15] and as steric demand governs phosphane reactivity, formation of the rhodium(v) intermediate **5** stabilized by phosphide ligands during the catalytic cycle seems plausible (Scheme 1); however, no definitive proof of such a species has been obtained.

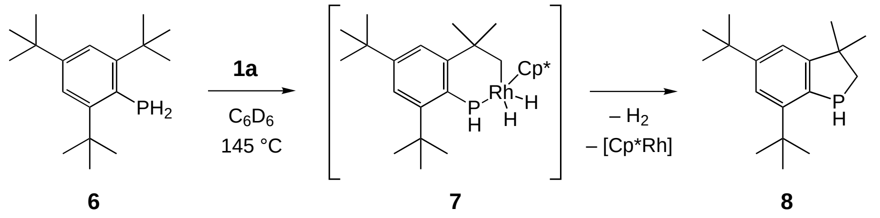
The above-mentioned B–H and Si–H bond activation reactions mediated by catalysts similar to **1a** have been coupled with the activation of C–H bonds, resulting in the catalytic formation of products possessing B–C and Si–C bonds, respectively.[8, 9] However, no cross-coupling with the solvents C_6D_6 or [D_8]toluene is observed during the dehydrocoupling reactions studied here. Additionally, H/D exchange reactions between arenes and olefins usually observed with **1a** in C_6D_6 are also suppressed.[6] However, the formation of $DPPh_2$ in low amounts, as identified in the $^{31}P\{^1H\}$ NMR spectrum, is indicative of the reversible activation of the aromatic solvent and the P–H bond.

While no *intermolecular* P–C bond formation has been seen which might result from dual P–H and C–H bond activation and coupling, we have observed a remarkable catalytic *intramolecular* P–C coupling involving activation of the C–H bond of an unactivated methyl group. Treatment of 2,4,6-tri-*tert*-butylphosphane (supermesitylphosphane; **6**) with **1a** in C_6D_6 at 145 °C results in quantitative formation (93 % yield of isolated product after 4 h) of 3,3-dimethyl-5,7-di-*tert*-butylphosphaindane (**8**; Scheme 2). Such a cyclic phosphane has been observed to form from the phosphinidene 2,4,6-$[(CH_3)_3C]_3C_6H_2P$: by intramolecular C–H insertion;[16] however, this intermediate seems unlikely in the present reaction. Again, a rhodium(v) intermediate **7** is plausible (Scheme 2).



Scheme 1. Proposed mechanism of the dehydrocoupling reaction via rhodium(v) intermediate **5**.

We have shown the late transition metal complex **1a** catalyzes the dehydrocoupling of primary and secondary



Scheme 2. Proposed mechanism for the formation of the cyclic phosphane **8** via rhodium(V) complex **7**.

phosphanes. In particular, the catalytic dehydrocoupling of secondary phosphanes is efficient and has been reported for the first time. Aryl and alkyl substituents are tolerated but reactivity is limited to sterically less demanding substrates. The resting state of the catalyst in the coupling of $HPPh_2$ is the diphosphanerhodium(I) complex **4** that is dominant throughout catalysis. Presumably, the reaction proceeds via a rhodium(V) species such as **5**. This catalytic reaction is advantageous over currently available methods for the synthesis of diphosphanes which produce stoichiometric amounts of salts as by-products.[17]

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The First Dectection of Peroxo and Bis-superoxo Complexes of Aluminum: $FAlO_2$ and $FAlO_4$**

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Peroxo and superoxo complexes are of major importance because of the role they play as oxygen carrier systems in biology[1] and in preparative chemistry.[2–4] For instance, peroxo complexes of vanadium show insulinomimetic properties[2] and complexes of rhenium are applied in olefin epoxidation.[3, 4] Another example from this class of compounds is hemocyanin, which contains a dinuclear copper site capable of binding O_2 in a μ-η^2:η^2 peroxo complex.[1] Finally, peroxo complexes are potential intermediates or products during the oxidation of metals or metal clusters.[5] Consequently, there is substantial interest in the exploration and isolation of new stable peroxo and superoxo complexes. Herein we report on the photolytically induced reaction of AlF with O_2 in solid argon matrices, which leads to the first known peroxo complexes and bis-superoxo complexes of aluminum, namely $FAlO_2$ and $FAlO_4$.[6] All products were identified and characterized on the basis of their IR absorptions (including the effects of isotopic changes ($^{16}O_2$, $^{18}O_2$, $^{16}O_2/^{18}O_2$, $^{16}O^{18}O$) and of quantum-mechanical calculations (ab initio (UHF and, in some cases, MP2) and density functional theory (DFT) calculations). In addition to their relevance for possible applications,[7] the title compounds show interesting electronic properties. While $FAlO_2$ exists in a singlet electronic ground state,[8] the $FAlO_4$ species exhibits a triplet ground state. The complexation of a second dioxygen molecule to $FAlO_4$ thus represents a spin-allowed process, and dioxygen complexes of this kind might well be of significant relevance as intermediates in oxidation processes.

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