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# Transition Metal-Catalyzed Dissociation of Phosphine–Gallane Adducts: Isolation of Mechanistic Model Complexes and Heterogeneous Catalyst Poisoning Studies

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Attempts to induce the catalytic dehydrocoupling of the phosphine–gallane adduct $Cy_2PH\cdot GaH_3$ (Cy = cyclohexyl) (**1**) by treatment with ca. 5 mol % of either the Rh(I) complex $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (cod = cyclooctadiene) or the Rh(0) species $Rh/Al_2O_3$ and $[Oct_4N]Cl$-stabilized colloidal Rh led to catalytic P–Ga bond cleavage to generate the phosphine, $H_2$, and Ga metal. Interestingly, subsequent treatment of the reaction mixtures with $Me_2NH\cdot BH_3$ failed to lead to the formation of $[Me_2N–BH_2]_2$ via Rh-catalyzed dehydrocoupling, which suggested that catalyst deactivation was taking place. Poisoning studies involving the treatment of the active Rh(0) catalyst with $Cy_2PH$, $PMe_3$, or $GaH_3\cdot OEt_2$ showed that deactivation indeed occurred as the dehydrocoupling of $Me_2NH\cdot BH_3$ either dramatically decreased in rate or did not take place at all. The X-ray photoelectron spectroscopy analysis of colloidal Rh(0) that had been treated with $Cy_2PH$ and $PMe_3$ confirmed the presence of phosphorus on the catalyst surface in each case, consistent with catalyst poisoning via phosphine ligation. A mechanism for the Rh-catalyzed P–Ga bond cleavage reaction of **1** and $Me_3P\cdot GaH_3$ (**2**) is proposed and involves the initial reaction of Ga–H bonds with the Rh colloid surface, which weakens and ultimately breaks the P–Ga bond. The reasonable nature of this mechanism is supported by a model reaction between the zerovalent group 9 complex $Co_2(CO)_8$ and **2** which afforded $Me_3P\cdot Ga[Co(CO)_4]_3$ (**3**). Consistent with the elongated and thus weakened P–Ga bond in **3**, solutions of this species in $Et_2O$ subsequently form the known complex $[(Me_3P)Co(CO)_3]_2$ (**4**) and Ga metal after 4 h at 25 °C.

## Introduction

Although metal-catalyzed bond formation and cleavage reactions have played a critical and widespread role in modern synthetic organic chemistry, the use of transition metal catalysts to form or cleave hetero- and homonuclear bonds between main-group elements is still in its relative infancy. Traditionally, synthetic methods in main-group chemistry often utilize metathesis reactions such as salt elimination to generate new bonds. However, the discoveries in the early 1980s that $PtBr_2$ acts as a general dehydrodimerization catalyst for boron hydrides and carboranes by Sneddon and co-workers[1] and of Ti-catalyzed dehydropolymerization of primary silanes by Harrod and co-workers[2] launched the development of catalytic routes to rings, chains, and polymers based on p-block elements.[3]

Our research group has reported late transition metal-catalyzed dehydrocoupling reactions as an alternative route

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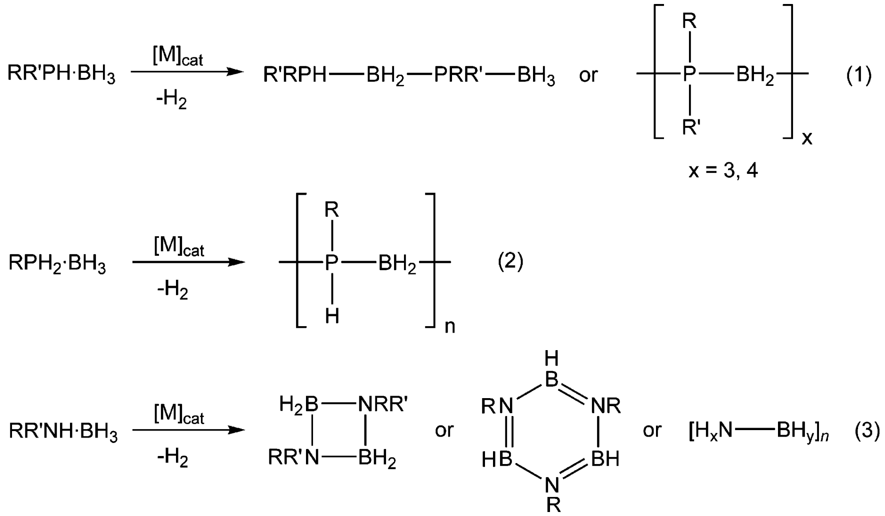
**Scheme 1**



to generating P−B[4] bonds from phosphine−borane adducts, which has allowed routes to novel rings, chains, and polymers $[RR'P-BH_2]_n$ (eqs 1 and 2 in Scheme 1).[5] Such reactions proceed at particularly mild temperatures for fluoroaryl phosphine−borane derivatives, and preliminary investigations have shown that the resultant polyphosphinoboranes function as a negative-tone resist in electron-beam lithography.[6] In addition, we have reported that the dehydrocoupling of primary and secondary amine−borane adducts and $H_3N{\cdot}BH_3$ is promoted by Rh (pre)catalysts affording oligomers and/or insoluble, presumably cross-linked materials $[H_xN-BH_y]_n$ (eq 3 in Scheme 1).[7] Transition metal-catalyzed dehydrocoupling also has potential utility in hydrogen storage applications, which are desirable, as hydrogen is a clean energy source that can potentially replace the petroleum-derived products that currently fuel vehicles.[8] For example, there is considerable current interest in amine−borane adducts such as $H_3N{\cdot}BH_3$, which possesses one of the highest densities of hydrogen available (19.6 wt % $H_2$), and there have been numerous recent reports related to the thermal or catalytic dehydrogenation of $H_3N{\cdot}BH_3$ or other high $H_2$ content amine−borane adducts.[9,10] In addition, the catalytic dehydrocoupling of $Me_2NH{\cdot}BH_3$ to afford the cyclic dimer $[Me_2N-BH_2]_2$ has been employed as a means of transfer hydrogenation when carried out in a closed system in the presence of unsaturated organic species.[11]

Interestingly, catalytic dehydrocoupling reactions of phosphine− and amine−borane adducts using the (pre)catalyst $[\{Rh(1,5\text{-cod})(\mu\text{-Cl})\}_2]$ (cod = cyclooctadiene) were found to operate under different mechanisms where the former is a homogeneous process and the latter is a heterogeneous process involving colloidal Rh metal.[12,13] We have also detailed that heterogeneous Rh(0) catalysts, when treated with a variety of group 13 hydrides, generate $H_2$ gas and a passivating layer incorporating the group 13 element on the surface of the metal, thereby deactivating the catalyst toward the dehydrocoupling of amine−borane adducts.[14] Recently, we have demonstrated the use of the early transition-metal complex $[Cp_2Ti]$ for amine−borane adduct dehydrocoupling and found that it exhibits increased catalytic activity relative to Rh catalysts.[15] Notably, this catalyst appears to operate in a homogeneous fashion in contrast to the heterogeneous Rh-based system. Goldberg, Heinekey, and co-workers have described a highly active, homogeneous Ir catalyst that dehydrocouples $H_3N{\cdot}BH_3$ at room temperature to afford the

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[10] It has proven challenging to regenerate $H_3N{\cdot}BH_3$ from the aminoborane-based products, rendering the system reversible. In this context, Stephan and co-workers have recently reported a remarkable phosphonium−borate species that demonstrates reversible $H_2$ activation in the absence of a metal, see: Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. *Science*, **2006**, *314*, 1124.

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[13] Autrey and co-workers have studied the dehydrocoupling of $Me_2NH{\cdot}BH_3$ using Rh catalysts and reaction conditions that differ from those used in our group. On the basis of their observations, they propose that the process may be homogeneous: Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254.

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cyclic pentamer $[H_2N{-}BH_2]_5$, as characterized by powder X-ray diffraction and IR spectroscopy.[9d] Similarly, Baker and co-workers have also shown that a Ni-based catalyst promotes the dehydrocoupling of $H_3N{\cdot}BH_3$, yielding a soluble, cross-linked borazine structure in 4 h at 60 °C.[9i]

As part of our continuing research program to develop novel extended structures based on main-group elements, we have investigated the reactivity of other Lewis acid−base adducts toward the dehydrocoupling process. In this paper, we report on our attempts to extend this new synthetic method to some analogous adducts containing heavier group 13 elements, namely, phosphine−gallanes.[16]

## Experimental Section

**General Methods and Materials**. All reactions and product manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a Mbraun glovebox filled with dry nitrogen. Tetrahydrofuran (THF) and diethyl ether were dried over Na/benzophenone and distilled prior to use. Toluene and hexanes were purified using the Grubbs method.[17] Ga metal (99.9995%), $PMe_3$, $Rh/Al_2O_3$ (5 wt. % Rh), and HCl (2.0 M solution in $Et_2O$) were purchased from Aldrich and used as received. $Cy_2PH$ was acquired through a generous donation from Cytec. $Me_2NH{\cdot}BH_3$ and $[Co_2(CO)_8]$ were purchased from Strem. $Me_2NH{\cdot}BH_3$ was further purified by sublimation at 25 °C whereas $[Co_2(CO)_8]$ was sublimed immediately before use. $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$,[18] $Rh_{colloid}/[Oct_4N]Cl$,[19] $Me_3P{\cdot}GaH_3$ (**2**),[20] and $Li[GaH_4]$[21] were synthesized by literature procedures.

**Equipment**. NMR spectra were recorded on either Varian Gemini 300 MHz or Varian VRX-S (Unity) 400 MHz spectrometers. Chemical shifts are reported relative to residual solvent peaks ($^1H$, $^{13}C$) or external $H_3PO_4$ ($^{31}P$) or $BF_3{\cdot}OEt_2$ ($^{11}B$) references. The NMR spectra were obtained at 300 MHz ($^1H$), 100 MHz ($^{13}C$), 121 MHz ($^{31}P$), and 96 MHz ($^{11}B$). The mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Elemental analyses were obtained on a Perkin-Elmer Series 2400 CHNS analyzer maintained by the Analest facility at the University of Toronto. Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer using KBr windows. The silicon (100) substrates were purchased from Wafer World, Inc., and cleaned by successive sonication treatments in $CH_2Cl_2$, isopropanol, piranha solution ($H_2O_2/H_2SO_4$, 1:3 vol %; ***Caution**: piranha solution is extremely corrosive!)*, and deionized water followed by drying in air. X-ray photoelectron spectroscopy (XPS) samples were solution deposited onto a clean silicon substrate and analyzed on a PHI 500 ESCA system. A monochromated Al Kα source with a photon energy of 1486.6 eV was used and recorded at a photoelectron takeoff angle of 45°. The peak positions were aligned and corrected for charge effects based on an adventitious C(1s) peak position at 284.8 eV. For the depth-profiling analysis, an $Ar^+$ ion beam of 3 keV was used for 15 min and the spectra were reacquired.

**Table 1.** Crystallographic Data and Summary of Data Collection and Refinement for Structure **3**

| | | | |
|---|---|---|---|
| emp formula | $C_{15}H_9Co_3GaO_{12}P$ | $Z$ | 2 |
| fw | 658.70 | $D_C$ (g/cm$^3$) | 1.928 |
| $T$ (K) | 150(2) | $\mu$ (mm$^{-1}$) | 3.456 |
| $\lambda$ (Å) | 0.71073 | $F$(000) | 644 |
| cryst syst | triclinic | $q$ range (deg) | 2.71−27.58 |
| space group | $P\bar{1}$ | index ranges | $-11 \le h \le 11$ |
| cryst size (mm) | 0.60 × 0.10 × 0.04 | | $-13 \le k \le 13$ |
| $a$ (Å) | 8.7826(4) | | $-17 \le l \le 17$ |
| $b$ (Å) | 10.0257(4) | reflns collected | 14 601 |
| $c$ (Å) | 13.4787(5) | ind reflns | 5181 |
| α (deg) | 84.370(3) | $R_{int}$ | 0.0886 |
| $\beta$ (deg) | 85.783(3) | GOF on $F^2$ | 1.040 |
| $\gamma$ (deg) | 74.101(2) | R1$^a$ ($I > 2\sigma(I)$) | 0.0458 |
| $V$ (Å$^3$) | 1134.57(8) | wR2$^b$ (all data) | 0.1266 |
| | | peak/hole (e·Å$^3$) | 0.673/ −1.247 |

$^a$ $R1 = S||F_o| - |F_c||/S|F_o|$. $^b$ $wR2 = \{S[w(F_o^2 - F_c^2)^2]/S[w(F_o^2)^2]\}^{1/2}$.

**X-Ray Structural Determination.** Diffraction data were collected on a Nonius Kappa-CCD with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were integrated and scaled with the *Denzo-SMN* package.[22] The structures were solved and refined with the *SHELXTL-PC* version 5.1 software package.[23] Refinement was by full-matrix least squares on $F^2$ of all data (negative intensities included). All molecular structures are presented with thermal ellipsoids at a 30% probability level. In all structures, hydrogens bonded to carbon atoms were included in calculated positions and treated as riding atoms. Crystallographic data and the summary of data collection and refinement for structure **3** are presented in Table 1. CCDC-249316 (**3**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Synthesis of $Cy_2PH{\cdot}GaH_3$ (1).** $[Cy_2PH_2]Cl$ was prepared by adding HCl (4.03 mL of a 2.0 M solution in diethyl ether, 8.06 mmol) to a solution of $Cy_2PH$ (1.63 mL, 8.06 mmol) in 5 mL $Et_2O$ at 25 °C causing a white solid to precipitate immediately. A solution of $Li[GaH_4]$ in $Et_2O$ (0.65 g, 8.05 mmol) was added to $[Cy_2PH_2]Cl$ at −78 °C and stirred for 3 h at 20 °C. The solution was filtered to separate LiCl, and the solvent was removed in vacuo affording **1** as a white solid in 79% yield (1.72 g, 6.35 mmol). In some cases, a white viscous residue was obtained upon solvent removal. Subsequent recrystallization of this oil from hexane at −35 °C also afforded **1** as a white solid. $^1H$ NMR ($C_6D_6$): $\delta$ 4.36 (s, $GaH_3$), 3.37 (d, PH, $^1J_{P-H} = 125.8$ Hz), 1.70 (m, *i*-CH), 1.47 (m, $\beta$-$CH_2$), 1.21 (m, $\gamma$-$CH_2$), 0.95 (m, $\delta$-$CH_2$). $^{13}C\{^1H\}$ NMR ($C_6D_6$): $\delta$ 31.2 (s), 30.1 (d, $J_{CP} = 6.8$ Hz), 29.1 (d, $J_{CP} = 22$ Hz), 27.1 (d, $J_{CP} = 27.3$ Hz), 26.3 (s). $^{31}P$ NMR ($C_6D_6$): $\delta$ −15.7 (d, PH, $^1J_{P-H} = 308.5$ Hz). EI-MS (70 eV): *m/z* 198 ($M^+ - GaH_3$). Elemental Anal. Calcd for $C_{12}H_{26}PGa$ (271.04): C, 53.18; H, 9.67. Found: C, 53.40; H, 9.45.

**Reaction of 1 with $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$.** A catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (ca. 5 mol % Rh) was added to a solution of **1** (ca. 0.125 g) in toluene (ca. 2 mL), causing the reaction mixture to immediately turn black with vigorous gas evolution. After 16 h of stirring at 25 °C, an aliquot of the reaction mixture was removed and the $^{31}P$ NMR spectrum showed a single resonance at $\delta$ −28.1 ppm corresponding to free $Cy_2PH$.

**Reaction of 1 with $Rh/Al_2O_3$ or $Rh_{colloid}/[Oct_4N]Cl$.** In a typical experiment, a catalytic amount of $Rh/Al_2O_3$ (ca. 5 mol % Rh) was added to a solution of **1** (ca. 0.125 g) in toluene (ca. 2 mL), resulting

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in vigorous gas evolution. After 16 h of stirring at 25 °C, an aliquot of the reaction mixture was removed and the $^{31}$P NMR spectrum showed a single resonance at $\delta$ −28.1 corresponding to free $Cy_2PH$. Similar results were obtained with $Rh_{colloid}$/[$Oct_4N$]Cl.

**Treatment of 1 with Ga Metal.** To a solution of **1** (0.150 g, 0.55 mmol) in toluene (ca. 1 mL) a catalytic amount of Ga metal (ca. 5 mol % Ga) was added, giving a slightly gray solution, which was stirred at 25 °C. After 9 h, an aliquot of the reaction mixture was removed and the $^{31}$P NMR spectrum showed only unreacted **1**.

**Attempted Catalytic Dehydrocoupling of $Me_2NH{\cdot}BH_3$ in the Presence of 1.** A solution of **1** (0.217 g, 0.801 mmol) and $Me_2NH{\cdot}BH_3$ (0.047 g, 0.798 mmol) in toluene (ca. 1 mL) was stirred with no color change or gas evolution observed for 3 h at 25 °C. An aliquot of the reaction mixture was removed, and both $^{31}$P and $^{11}$B NMR spectra indicated no dehydrocoupling activity, as only the starting materials were observed. To the above solution a catalytic amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 5 mol %) was added, causing the reaction mixture to immediately turn black with vigorous gas evolution. After 5 h of stirring at 25 °C, an aliquot of the reaction mixture was removed and the $^{31}$P NMR spectrum showed a single resonance at $\delta$ −28.1 corresponding to free $Cy_2PH$ whereas the $^{11}$B NMR spectrum showed a single resonance at $\delta$ −13.9 corresponding to unreacted $Me_2NH{\cdot}BH_3$.

**Treatment of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] with 1 equiv of $Cy_2PH$ and Testing for Catalytic Activity.** To a solution of $Me_2NH{\cdot}BH_3$ (0.240 g, 4.07 mmol) in toluene (ca. 1 mL) a catalytic amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 2 mol %) and $Cy_2PH$ (ca. 2 mol %) was added and stirred at 25 °C, giving a red-brown solution over time. After 16 h, an aliquot of the reaction mixture was removed and the $^{11}$B NMR spectra were obtained. The % conversion was calculated from the integration of the product ($^{B}\delta$ 5 ppm) and reactant ($^{B}\delta$ −13 ppm) resonances.

**Treatment of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] with an Excess of $Cy_2PH$ and Testing for Catalytic Activity.** To a solution of $Me_2NH{\cdot}BH_3$ (0.100 g, 1.69 mmol) in toluene (ca. 1 mL) a catalytic amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 3 mol %) and $Cy_2PH$ (ca. 10 mol %) was added and stirred at 25 °C, giving an orange solution over time. After 16 h, an aliquot of the reaction mixture was removed and the $^{11}$B and $^{31}$P NMR spectra obtained. The % conversion was calculated from the integration of the product ($^{B}\delta$ 5 ppm) and reactant ($^{B}\delta$ −13 ppm) resonances whereas the $^{31}$P NMR spectrum revealed a resonance at $\delta$ −28.1 corresponding to free $Cy_2PH$ in addition to two multiplets at $^{P}\delta$ 33 (dd; $^{1}J_{P-Rh} = 131$ Hz, $^{2}J_{P-P} = 40$ Hz) and 50 (dt; $^{1}J_{P-Rh} = 174$ Hz, $^{2}J_{P-P} = 40$ Hz).

**Treatment of $Rh_{colloid}$/[$Oct_4N$]Cl with $Cy_2PH$ and Subsequent Testing for Catalytic Activity.** $Cy_2PH$ (0.013 g, 0.066 mmol) was added to a solution of $Rh_{colloid}$/[$Oct_4N$]Cl (0.042 g, 0.135 mmol) in THF (ca. 1 mL) and stirred at 25 °C. After 16 h, all volatiles were removed and the crude reaction mixture was washed with 2−3 mL portions of hexanes. The treated Rh(0) colloids were then dried overnight. To a solution of $Me_2NH{\cdot}BH_3$ (0.200 g, 3.39 mmol) in toluene (ca. 1 mL) a catalytic amount of the treated $Rh_{colloid}$/[$Oct_4N$]Cl (0.006 g, 5 mol % Rh) was added at 25 °C. After 16 h of stirring, an aliquot of the reaction mixture was removed and the $^{11}$B NMR spectrum was obtained. The % conversion was calculated from the integration of the product ($^{B}\delta$ 5 ppm) and reactant ($^{B}\delta$ −13 ppm) resonances.

**Testing for Lewis Acid Exchange between 1 and $BH_3{\cdot}THF$.** To a solution of **1** (0.100 g, 0.369 mmol) in toluene (ca. 2 mL) $BH_3{\cdot}THF$ (0.74 mL, 0.740 mmol) was added and stirred at 25 °C. After 75 min, an aliquot of the reaction mixture was removed and the $^{11}$B and $^{31}$P NMR spectra were obtained, showing complete consumption of **1** and new resonances at $^{P}\delta$ 19 and $^{B}\delta$ −45 corresponding to $Cy_2PH{\cdot}BH_3$.[24]

**Testing for Lewis Acid Exchange between 2 and $BH_3{\cdot}THF$.** To a solution of **2** (0.080 g, 0.538 mmol) in toluene (ca. 2 mL) $BH_3{\bullet}THF$ (1.10 mL, 1.10 mmol) was added and stirred at 25 °C. After 75 min, an aliquot of the reaction mixture was removed and the $^{11}$B and $^{31}$P NMR spectra were obtained, showing complete consumption of **2** and new resonances at $^{P}\delta$ −1 and $^{B}\delta$ −37 corresponding to $Me_3P{\cdot}BH_3$.[25]

**Treatment of 2 with [{Rh($\mu$-Cl)(1,5-cod)}$_2$].** To a solution of **2** (0.088 g, 0.591 mmol) in toluene (ca. 2 mL) a catalytic amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 2 mol %) was added, giving a red solution which was stirred at 25 °C. After 16 h, the $^{31}$P NMR spectrum showed a single resonance at $\delta$ −39.1 corresponding to unreacted **2**.

**Treatment of 2 with a Stoichiometric Amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$].** To a solution of **2** (0.100 g, 0.672 mmol) in toluene (2 mL) 1 equiv of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (0.166 g, 0.337 mmol) was added, resulting in vigorous gas evolution and the formation of an amber solution and black precipitate. After 16 h, the $^{31}$P and $^{1}$H NMR spectra were obtained, showing complete consumption of **2** and resonances corresponding to [($Me_3P$)RhCl(1,5-cod)].[26]

**Treatment of 2 with Substoichiometric Amounts of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] and Subsequent Testing of Catalytic Dehydrocoupling Activity Toward $Me_2NH{\bullet}BH_3$.** To a solution of **2** (0.100 g, 0.672 mmol) and $Me_2NH{\cdot}BH_3$ (0.040 g, 0.679 mmol) in toluene (ca. 2 mL) a substoichiometric amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 50 mol %) was added, resulting in vigorous gas evolution and the formation of a dark brown solution and black precipitate. After 16 h, an aliquot of the reaction mixture was removed and the $^{11}$B and $^{31}$P NMR spectra were obtained. The % conversion was calculated from the integration of the product ($^{B}\delta$ 5 ppm) and reactant ($^{B}\delta$ −13 ppm) resonances whereas the $^{31}$P NMR spectrum revealed several resonances at $\delta$ −8 ([($Me_3P$)RhCl(1,5-cod)]),[26] −18 (d; $J = 28$ Hz), −22 (d; $J = 97$ Hz), and −29 (d; $J = 176$ Hz) (unidentified).

Similar results were obtained for the reaction employing 10 mol % [{Rh($\mu$-Cl)(1,5-cod)}$_2$].

**Treatment of 2 with [{Rh($\mu$-Cl)(1,5-cod)}$_2$] and Subsequent Testing of Catalytic Dehydrocoupling Activity.** To a solution of **2** (0.088 g, 0.591 mmol) in toluene (ca. 1 mL) a catalytic amount of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] (ca. 2 mol %) was added, giving a red solution which was stirred at 25 °C. After 5 h, the $^{31}$P NMR spectrum showed a single resonance at $\delta$ −39.1 corresponding to unreacted **2**. To this solution, $Me_2NH{\cdot}BH_3$ (0.035 g, 0.594 mmol) was added and stirred at 25 °C. After 16 h, an aliquot of the reaction mixture was removed and the $^{31}$P NMR spectrum showed unreacted **2** whereas the $^{11}$B NMR spectrum showed a single resonance at $\delta$ −13.9 corresponding to unreacted $Me_2NH{\cdot}BH_3$.

**Reaction of 2 with $Rh/Al_2O_3$ or $Rh_{colloid}$/[$Oct_4N$]Cl.** To a solution of **2** (0.088 g, 0.591 mmol) in toluene (ca. 2 mL) a catalytic amount of $Rh/Al_2O_3$ (ca. 2 mol %) was added, resulting in vigorous gas evolution and giving a black solution, which was stirred at

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[24] The $^{31}$P NMR spectroscopic characterization of $Cy_2PH{\cdot}BH_3$ in $CDCl_3$ ($^{P}\delta$ 19 ppm) has been previously reported, see: Stankevic, M.; Pietrusiewicz, K. M.; *Synthesis* **2005**, *8*, 1279. We independently carried out the synthesis of the compound by treatment of $Cy_2PH$ with $BH_3{\cdot}THF$ in THF and observed, in situ, a multiplet centered at $\delta$ −45 in the $^{11}$B NMR spectrum (d of q; $^{1}J_{B-P} = 47$ Hz, $^{1}J_{B-H} = 97$ Hz).

[25] Schmidbaur, H.; Weiss, E.; Müller, G. *Synth. React. Inorg. Met-Org. Chem.* **1985**, *15*, 401.

[26] Kulzick, M. A.; Price, R. T.; Andersen, R. A.; Muetterties, E. L. *J. Organomet. Chem.* **1987**, *333*, 105.

25 °C. After 5 h, the $^{31}P$ NMR spectrum showed a single resonance at $\delta$ −60.9 corresponding to free $PMe_3$. Similar results were obtained with $Rh_{colloid}/[Oct_4N]Cl$.

**Treatment of 2 with $Rh/Al_2O_3$ and Subsequent Testing of Catalytic Dehydrocoupling Activity.** To a solution of **2** (0.088 g, 0.591 mmol) and $Me_2NH{\cdot}BH_3$ (0.035 g, 0.594 mmol) in toluene (ca. 2 mL) a catalytic amount of $Rh/Al_2O_3$ (ca. 2 mol %) was added, resulting in vigorous bubbling and giving a black solution, which was stirred at 25 °C. After 16 h, the $^{31}P$ NMR spectrum showed a single resonance at $\delta$ −60.9 corresponding to free $PMe_3$ whereas the $^{11}B$ NMR spectrum showed a single resonance at $\delta$ −13.9 corresponding to unreacted $Me_2NH{\cdot}BH_3$.

**Synthesis of $Me_3P{\cdot}Ga[Co(CO)_4]_3$ (3).** A solution of **2** in $Et_2O$ (0.100 g, 0.672 mmol) was added to a solution of $[Co_2(CO)_8]$ in $Et_2O$ (0.115 g, 0.336 mmol) at 25 °C. This led to vigorous bubbling due to the release of a gas that was identified as $H_2$ by $^1H$ NMR when the reaction was performed in $C_6D_6$ ($\delta$ 4.46). After 1 min, the solvent was removed in vacuo and the residue dissolved in toluene, giving a maroon solution that was recrystallized at −30 °C affording orange-red crystals of **3** in 78% yield (0.115 g, 0.175 mmol). $^1H$ NMR ($C_6D_6$): $\delta$ 0.92 (d, $PMe_3$, $^2J_{PH} = 10.5$ Hz). $^{13}C$ NMR ($C_6D_6$): $\delta$ 198.9 (s, CO), 10.5 (d, $PMe_3$, $^1J_{CP} = 31.1$ Hz). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ −32 (s, $PMe_3$). IR (toluene solution): $\nu_{CO} = 1966, 1982, 2000, 2025, 2072, 2088$ cm$^{-1}$. EI-MS characterization was attempted numerous times but did not yield useful data presumably due to the exceptional reactivity and sensitivity of the compound.

**Synthesis of $[(Me_3P)Co(CO)_3]_2$ (4).**[27] A solution of **2** in $Et_2O$ (0.100 g, 0.672 mmol) was added to a solution of $[Co_2(CO)_8]$ in $Et_2O$ (0.115 g, 0.336 mmol) at 25 °C. This led to vigorous bubbling due to the release of a gas that was identified as $H_2$ by $^1H$ NMR when the reaction was performed in $C_6D_6$ ($\delta$ 4.46). After 16 h, the solvent was removed in vacuo and the residue dissolved in hexane, giving a maroon solution that was recrystallized at −30 °C affording dark red-brown crystals of **4** in 78% yield (0.038 g, 0.087 mmol). $^1H$ NMR ($C_6D_6$): $\delta$ 0.65 (d, $PMe_3$, $^2J_{PH} = 10.8$ Hz). $^{13}C$ NMR ($C_6D_6$): $\delta$ 203.1 (s, CO), 18.8 (d, $PMe_3$, $^1J_{CP} = 31.9$ Hz). $^{31}P\{^1H\}$ NMR ($C_6D_6$): $\delta$ 26 (s, $PMe_3$). EI-MS (70 eV) *m/z*: 409 ($M^+ - CO$). IR (hexadecane solution): $\nu_{CO} = 1950, 1972$ cm$^{-1}$.[27a]

## Results and Discussion

**Catalytic Dissociation and Poisoning Behavior of $Cy_2PH{\cdot}GaH_3$ (1).** Lewis acid−base adducts of group 13/15 compounds such as phosphine−gallanes have been the subject of considerable interest as single-source metal-organic chemical vapor deposition (MOCVD) precursors in thin-film deposition for microelectronic device fabrication.[28] Generally, compounds of this type are synthesized by salt elimination reactions. The secondary phosphine−gallane $Cy_2PH{\cdot}GaH_3$ (**1**) (Cy = cyclohexyl) was prepared in 79% yield from the dehydrogenative metathesis reaction of $Li[GaH_4]$ and $[Cy_2PH_2]Cl$. Compound **1** is stable in solution at room temperature for several hours before decomposition to $Cy_2PH$ and Ga metal is detected. However, treatment of **1** with 5 mol % of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ in toluene led to a rapid color change from orange to black, and gas evolution was also observed. The volatile product was assumed to be $H_2$ based on the detection of this dissolved gas in the reaction solution by $^1H$ NMR ($^H\delta$ 4.46; lit. $^H\delta$ 4.46).[29] The color change observed was similar to that detected during the catalytic dehydrocoupling of amine−borane adducts, in which the reduction of the Rh(I) (pre)catalyst occurs over a period of 45−200 min to give catalytically active Rh(0) colloids.[7,12] In addition, complete adduct dissociation rather than dehydrocoupling was observed based on the quantitative formation of free $Cy_2PH$ detected by $^{31}P$ NMR ($^P\delta$ −28.1) and the apparent generation of Ga metal as a precipitate (eq 4).

$$\underset{\mathbf{1}}{Cy_2PH{\cdot}GaH_3} \xrightarrow[\text{toluene, 25 °C}\ -H_2]{\text{ca. 5 mol \% [Rh]}} Cy_2PH + Ga \qquad (4)$$

It has been previously reported that Ga metal autocatalytically promotes the decomposition of $Li[GaH_4]$.[30] To test for similar chemistry, we treated **1** with a catalytic amount of Ga metal but did not observe any reaction, which suggests that Rh(0) is the sole contributor to the metal-assisted dissociation process. Further evidence for the reduction of the Rh(I) (pre)catalyst to catalytically active Rh(0) metal particles was provided by the observation that treatment of **1** with 5 mol % of $Rh/Al_2O_3$ or $[Oct_4N]Cl$-stabilized Rh colloids (hereafter referred to as $Rh_{colloid}/[Oct_4N]Cl$) similarly resulted in $H_2$ evolution and the quantitative formation of $Cy_2PH$. Thus, the gallane moiety in **1** presumably behaves as a "borohydride-type" reducing agent to afford Rh(0) metal.

Previously, our group has reported that $Me_2NH{\cdot}BH_3$ undergoes Rh-catalyzed dehydrocoupling at 25 °C to afford the cyclic dimer $[Me_2N\text{–}BH_2]_2$ (eq 3).[7] A mixture of **1** and $Me_2NH{\cdot}BH_3$ was stirred for several hours with no change detected in the $^{31}P$ and $^{11}B$ NMR spectra. However, upon the addition of a catalytic amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ to this mixture, the solution again immediately turned black and $H_2$ evolution was observed. The $^{31}P$ and $^{11}B$ NMR spectra were recorded and showed the presence of free $Cy_2PH$ and, surprisingly, unreacted $Me_2NH{\cdot}BH_3$, respectively. The absence of dehydrocoupling of the latter was intriguing and implied that deactivation of the Rh(0) catalyst was taking place. There is well-established precedent for the poisoning of transition metal catalysts by strongly coordinating ligands such as $PPh_3$[31] or $CS_2$[32], which block access of the substrate to the active site. Indeed, the stoichiometry of the donor ligand per metal atom required for effective catalyst poisoning acts as an aid in determining whether a process proceeds by a heterogeneous or homogeneous mechanism. Thus, Finke et al. have demonstrated that if substantially less than 1 equiv of the added ligand (per metal atom) poisons the catalyst completely, then it is highly suggestive of a heterogeneous

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(27) (a) Samir Arabi, M.; Maisonnat, A.; Attali, S.; Poilblanc, R. *J. Organomet. Chem.* **1974**, *67*, 109. (b) Jones, R. A.; Seeberger, M. H.; Stuart, A. L.; Whittlesey, B. R.; Wright, T. C. *Acta Crystallogr.* **1986**, *C42*, 399.

(28) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed.* **1989**, *28*, 1208.

(29) Böhm, V. P. W.; Brookhart, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 4694.

(30) Greenwood, N. N. *New Pathways in Inorganic Chemistry*; Ebsworth, E. A. V., Maddock, A. G., Sharpe, A. G., Eds.; Cambridge University Press: Cambridge, U.K., 1968; p 37.

catalyst.[31] The presence of $Cy_2PH$ along with unreacted $Me_2NH{\cdot}BH_3$ suggested that the decomposition of $Cy_2PH{\cdot}GaH_3$ occurred with subsequent binding of the phosphine to the active Rh catalyst, poisoning it toward the dehydrocoupling of $Me_2NH{\cdot}BH_3$.

To investigate the poisoning of the Rh catalyst toward the dehydrocoupling of $Me_2NH{\cdot}BH_3$ in the presence of substoichiometric amounts of $Cy_2PH$, $Rh_{colloid}$/[$Oct_4N$]Cl was treated with 0.5 equiv of $Cy_2PH$ and allowed to react for 1 day. Following the evacuation of volatiles, washing with hexanes, and drying overnight to remove excess phosphine, a portion of the $Rh_{colloid}$/[$Oct_4N$]Cl was removed and used in an attempt to catalyze the dehydrocoupling of $Me_2NH{\cdot}BH_3$.[33] It was found that there was greatly reduced catalytic activity, as only 2.5% conversion to $[Me_2N{-}BH_2]_2$ was observed by $^{11}B$ NMR spectroscopy after 16 h. This suggested that $Cy_2PH$ does indeed bind to most of the active sites on the Rh(0) catalyst surface. Furthermore, the strength of binding is significant, as the phosphine ligands were not readily eliminated under reduced pressure or solvent washing.[34] The colloidal Rh catalyst was also examined by XPS before and after treatment with $Cy_2PH$. As expected, the XPS spectrum of the colloids before treatment showed essentially no phosphorus content, as indicated by the lack of a P(2p) peak. However, the colloids after treatment with $Cy_2PH$ showed a P(2p) peak at 132.6 eV, which falls into the typical range for phosphine oxides (ca. 132.0−134.0 eV).[35] In addition, the expected $Rh(3d_{5/2})$ peak at 308.0 eV was observed, which is characteristic of an oxide species, as it falls into the typical range for $Rh_2O_3$ (ca. 308.2−308.8 eV).[35] In the case of both Rh and P, it is likely that an oxide species forms when the colloids are exposed to the atmosphere during preparation of the sample for XPS analysis. Neglecting the other elements present (e.g., C, O, Si), the relative atomic concentrations of Rh and P in the colloids exposed to $Cy_2PH$ were found to be approximately 1:2. After sputtering the surface with $Ar^+$ ions, it was found that the relative atomic concentration of Rh increased while that of P decreased (3:1 ratio). This is indicative of a higher concentration of phosphorus on the surface of the colloids. Upon sputtering, the $Rh(3d_{5/2})$ peak remained unchanged but the P(2p) peak was observed at a lower binding energy of 130.2 eV which is characteristic of elemental phosphorus (ca. 129.7−130.3 eV), although the presence of free $Cy_2PH$ cannot be ruled out, as the binding energy values for phosphines span the range of 130.9−132.5 eV.[35] It is possible that the phosphine may undergo degradation upon treatment with the $Ar^+$ ion beam resulting in decomposition to elemental phosphorus. Nevertheless, the key result is that the studies of colloidal Rh treated with $Cy_2PH$ employing XPS verified the presence of phosphorus on the surface of the catalyst particles.

We were also interested in investigating the fate of the $GaH_3$ moiety in the catalytic P−Ga bond cleavage reactions and the possibility that this may also act as a potential source of catalyst deactivation. As noted above, we have previously reported the poisoning of heterogeneous Rh(0) dehydrocoupling catalysts by group 13 hydride species including Ga−H bonds such as those present in $GaH_3{\cdot}OEt_2$.[14] In light of these observations, the potential role of the $GaH_3$ moiety in **1** as an additional contributor to the deactivation of the Rh(0) catalyst cannot be ruled out. Unfortunately, accurate XPS studies of $Rh_{colloid}$/[$Oct_4N$]Cl samples treated with $GaH_3{\cdot}OEt_2$ or **1** could not be carried out, as Ga metal, a byproduct of both reactions, and colloidal Rh(0) could not be separated.

**Catalytic Dissociation and Poisoning Behavior of $Me_3P{-}GaH_3$ (2).** Next, we turned our attention toward the tertiary phosphine−gallane $Me_3{\cdot}GaH_3$ **2**.[36] Compound **2** was prepared, as previously reported, from the dehydrogenative metathesis reaction of Li[$GaH_4$] and [$Me_3PH$]Cl as a white crystalline solid which is stable in solution under $N_2$ at room temperature for over 24 h.[20]

In contrast to that of **1**, treatment of **2** with a catalytic quantity (ca. 2 mol %) of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ did not result in gas evolution or a color change to black, characteristic of substantial Rh(I) reduction to Rh(0) colloidal metal. Furthermore, a $^{31}P$ NMR spectrum of the mixture showed no evidence of reaction after 16 h. This suggested that, in contrast to **1**, adduct **2** is not sufficiently hydridic to reduce the Rh(I) (pre)catalyst to Rh(0) metal, although a reaction that prevents Rh(I) reduction may occur below the spectroscopic detection limit and therefore could not be ruled out. With this in mind, we explored the reaction of **2** with a stoichiometric amount of $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ (e.g., P/Rh = 1:1). Significantly, this solely afforded the known compound $[(Me_3P)RhCl(1,5\text{-}cod)]$ as determined by $^{31}P$ and $^1H$ NMR spectroscopy.[26] The reactivity of **2** with 50 and 10 mol % $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ was also investigated, and in both cases, $^{31}P$ NMR spectra revealed a complex mixture of products, including $[(Me_3P)RhCl(1,5\text{-}cod)]$, with several unassigned doublets observed consistent with the presence of P−Rh coupling. As a result of these observations, it appears that although the reduction of the Rh(I) species by **2** does not take place, an alternative reaction indeed occurs. Consistent with this behavior, the addition of 2 mol % $[\{Rh(\mu\text{-}Cl)(1,5\text{-}cod)\}_2]$ to an equimolar mixture of **2** and $Me_2NH{\cdot}BH_3$ resulted in no reaction after 16 h, as detected by $^{31}P$ and $^{11}B$ NMR spectroscopy.[37] This and the previous

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(31) Widegren, J. A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.

(32) Hornstein, B. J.; Aiken, J. D., III.; Finke, R. G. *Inorg. Chem.* **2002**, *41*, 1625.

(33) In stoichiometric reactions no evidence for ligand exchange between $Cy_2PH$ and $Me_2NH{\cdot}BH_3$, to yield $Cy_2PH{\cdot}BH_3$, was observed by either $^{31}P$ or $^{11}B$ NMR spectroscopy. See ref 24 for spectroscopic details for $Cy_2PH{\cdot}BH_3$.

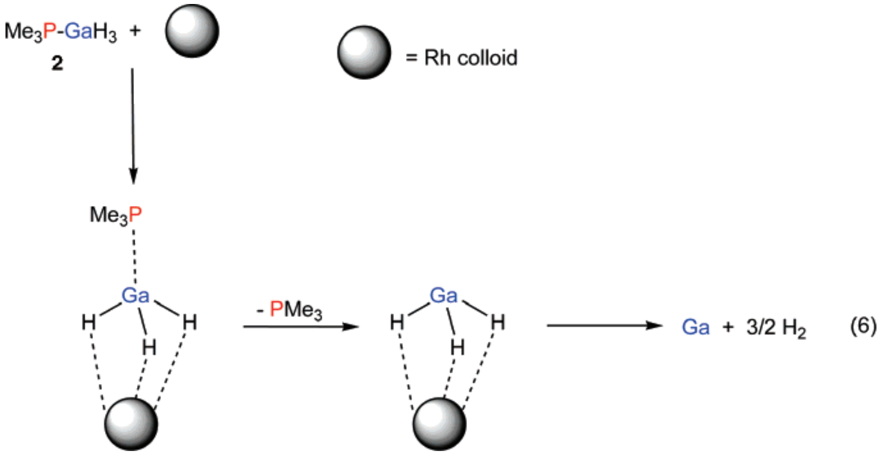
(34) Analysis of these Rh(0) colloids treated with $Cy_2PH$ by $^{31}P$ NMR spectroscopy has been unsuccessful despite numerous attempts.

(35) Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Chastain, J., Ed.; Perkin-Elmer: Eden Prairie, MN, 1992.

(36) We probed the existence of exchange reactions between $BH_3{\cdot}THF$ and both **1** and **2**. In both cases, complete P−Ga bond cleavage was observed with concomitant formation of $Cy_2PH{\cdot}BH_3$ and $Me_3P{\cdot}BH_3$, respectively. This indicates that for both adducts, the P−Ga bond is thermodynamically labile. See the Experimental Section for details.

(37) Similar to the case of **1**, no exchange reaction between **2** and $Me_2NH{\cdot}BH_3$ was detected by $^{31}P$ and $^{11}B$ NMR spectra.

**Scheme 2.** Postulated Mechanism of Rh(0)-catalyzed P−Ga Bond Dissociation in **2**



observations strongly suggest that the treatment of **2** with a catalytic quantity of [{Rh($\mu$-Cl)(1,5-cod)}$_2$] leads to PMe$_3$ binding to the Rh(I) center (which is below the spectroscopic detection limit). This prevents reduction to catalytically active Rh(0) metal and consequently hinders the dehydrocoupling of $Me_2NH{\cdot}BH_3$. Indeed, even when 10 or 50 mol % [{Rh($\mu$-Cl)(1,5-cod)}$_2$] was added, only 2% and 6% conversion to $[Me_2N{-}BH_2]_2$ was observed, respectively, by $^{11}$B NMR spectroscopy.

In contrast to the results with Rh(I) precatalysts, treatment of **2**, which is stable in solution at room temperature for up to 24 h, with 2 mol % Rh/Al$_2$O$_3$ in toluene or Rh$_{colloid}$/[Oct$_4$N]Cl in THF, resulted in immediate gas evolution (H$_2$ by $^1$H NMR) and complete adduct dissociation to afford free PMe$_3$, which was detected by $^{31}$P NMR spectroscopy ($^P\delta$ −60.9) as the only product after 16 h (eq 5). Similar to the reaction with [{Rh($\mu$-Cl)(1,5-cod)}$_2$] noted above, a mixture of **2** and $Me_2NH{\cdot}BH_3$ was also treated with a catalytic amount of the Rh(0) source Rh/Al$_2$O$_3$. After 16 h, $^{31}$P and $^{11}$B NMR characterization of the black suspension showed free PMe$_3$ and unreacted $Me_2NH{\cdot}BH_3$, respectively. This observation, similar to the case with **1**, supports the hypothesis that PMe$_3$ binds to the Rh(0) surface (below the spectroscopic detection limit), poisoning the active sites on the heterogeneous catalyst and consequently preventing the dehydrocoupling of $Me_2NH{\cdot}BH_3$.

$$\underset{\mathbf{2}}{Me_3P{\cdot}GaH_3} \xrightarrow[-H_2]{[Rh^0]} PMe_3 + Ga \qquad (5)$$

In an analogous manner to the case of **1**, the colloidal catalyst was examined by XPS before and after treatment with PMe$_3$. The XPS spectrum of the colloids before treatment showed essentially no phosphorus present, as indicated by the lack of a P(2p) peak. However, similar to **1**, the colloids after treatment showed a P(2p) peak at 131.9 eV, falling close to the typical range for phosphine oxides (ca. 132.0−134.0 eV).[35] Here, neglecting the other elements present (e.g., C, O, Si), the relative atomic concentrations of Rh and P were found to be approximately 2:1. This can be compared to the 1:2 ratio found in the case of Rh colloids that had been treated with Cy$_2$PH, which indicated that there is more phosphorus on the surface of the colloidal Rh with the secondary phosphine than the tertiary phosphine. Similar to the case for Cy$_2$PH, a higher concentration of phosphorus on the surface of the colloids was indicated as the atomic concentration of Rh to P increased to 3.5:1 after sputtering with Ar$^+$ ions. Upon sputtering, the Rh(3d$_{5/2}$) peak remained unchanged but the P(2p) peak was again observed at a lower binding energy of 130.0 eV, which is characteristic of elemental phosphorus, possibly due to ion beam-induced degradation effects (129.7−130.3 eV).[35] In summary, studies of colloidal Rh treated with PMe$_3$ employing XPS again verified the presence of phosphorus on the surface of the catalyst particles. As was the case with **1**, despite previous evidence for $GaH_3{\cdot}OEt_2$ acting as a dehydrocoupling catalyst poison,[14] accurate XPS studies of Rh$_{colloid}$/[Oct$_4$N]Cl samples treated with $GaH_3{\cdot}OEt_2$ or **2** could not be carried out.

**Synthesis, Characterization, and Reactivity of Model Compounds $Me_3P{\cdot}Ga(Co(CO)_4)_3$ (3) and $[(Me_3P)Co(CO)_3]_2$ (4).** The Rh(0)-catalyzed P−Ga bond dissociation to afford the free phosphine and Ga metal that is observed when **1** and **2** are treated with Rh(0) suggests that cleavage of the P−Ga bond occurs through an interaction with the metal surface. A possible initial step involves the interaction of the hydridic hydrogen substituents in the GaH$_3$ group of **1** and **2** with the Rh(0) surface. This might weaken the P−Ga bond in the adduct, resulting in dissociation. Subsequently, this would be accompanied by decomposition of the GaH$_3$ moiety, as Ga metal and H$_2$ gas were both observed (Scheme 2).

To gain further insight into this interesting reactivity, we attempted to model the process by studying the reaction of **2** with a convenient, zerovalent group 9 metal complex. A reaction between **2** and [Co$_2$(CO)$_8$] in Et$_2$O at 25 °C caused immediate gas evolution (H$_2$ by $^1$H NMR) after only 1 min along with a small change in the $^{31}$P NMR chemical shift to −32 ppm (cf. $^P\delta$ −39 for $Me_3P{\cdot}GaH_3$), affording the cobalt carbonyl-substituted phosphine−gallane complex **3** in 78% yield (eq 7).

$$\underset{\mathbf{2}}{Me_3P{\cdot}GaH_3} + Co_2(CO)_8 \xrightarrow[-H_2]{\substack{Et_2O,\ 25\ °C \\ 1\ min}} \underset{\mathbf{3}}{Me_3P{\cdot}Ga[Co(CO)_4]_3} \qquad (7)$$

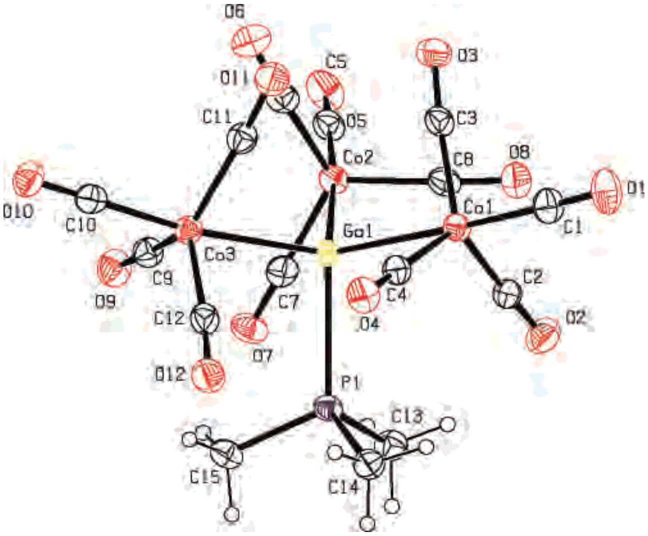


**Figure 1.** Molecular structure of **3**. Selected bond lengths (Å) and angles (deg): Ga(1)−P(1) 2.5108(12), Ga(1)−Co(1) 2.5557(7), Ga(1)−Co(2) 2.5552(7), Ga(1)−Co(3) 2.5686(7), Co−C 1.790(5) av.; P(1)−Ga(1)−Co(1) 103.91(3), P(1)−Ga(1)−Co(2) 109.10(3), P(1)−Ga(1)−Co(3) 102.23(3), Co−Ga(1)−Co 113.49(3) av., C−P(1)−C 104.0(2) av., C−P(1)−Ga(1) 114.50(16) av.

Orange-red crystals were obtained from toluene at −30 °C, and analysis by X-ray crystallography confirmed the structure of **3** (Figure 1). The P−Ga bond length in **3** was found to be 2.5108(12) Å, significantly longer than that found in **2** (2.3857(6) Å).[38] Notably, the P−Ga bond length in the bulky adduct $Cy_3P{\cdot}GaH_3$ is also considerably longer than that in **2** (2.460(2) Å).[39] Therefore, the lengthened P−Ga bond length in **3** may be a consequence of the increased steric bulk of the three $Co(CO)_4$ ligands around the Ga center relative to the smaller hydrogen atoms. However, an electronic effect probably also plays a role as the electron-rich $Co(CO)_4$ substituents will tend to relieve the electron deficiency at Ga, thereby decreasing the strength of the P−Ga bond. Both the P and Ga centers adopt a distorted tetrahedral geometry with angles ranging from 102° to 115° whereas the Me and $Co(CO)_4$ substituents around those centers are staggered relative to each other. The average Co−Ga bond length in **3** is 2.5598(7) Å, which falls into the range of 2.38−2.58 Å for typical Co−Ga single bonds.[40]

Transition metal complexes containing bonds with group 13 elements are an intriguing class of compounds that have received attention due to their use as potential precursors for MOCVD.[41] Fischer and co-workers have reported the preparation of transition metal substituted gallanes by salt elimination reactions of transition carbonyl metallates with various chlorogallium species.[42] Cowley and co-workers have described the unique cobalt−gallium complex $[\{2,6\text{-}Me_2{-}NCH_2)_2C_6H_3\}Ga\{Co(CO)_4\}_2]$, which features intramolecular base stabilization by one of the dimethylamine groups.[43] More recently, the first gallane-coordinated metal complex, $(OC)_5W(\eta^1\text{-}GaH_3{\cdot}(\text{quinuclidine}))$, was synthesized from $W(CO)_6$ and $H_3Ga{\cdot}(\text{quinuclidine})$ via a photolysis method.[44] Structural characterization of the product revealed that the gallane is bound to the tungsten fragment via a W−H−Ga three-center two-electron bond. Shimoi and co-workers have reported the reaction of $[Co_2(CO)_8]$ with the diadduct $B_2H_4{\cdot}2PMe_3$ that yielded $[\{Co(CO)_3\}_2(\mu\text{-}CO)(\mu\text{-}BH{-}PMe_3)]$, which contains a bridging borylene−Lewis base unit.[45] In the case of **3**, the binding of three $Co(CO)_4$ fragments to a single Ga center is a unique entry in bonding for these types of systems. The IR spectrum of **3** in toluene was recorded and showed six bands corresponding to CO stretches ranging from 1966 to 2088 $cm^{-1}$, values which fall in the accepted approximate values of 1850−2125 $cm^{-1}$ for a terminal carbonyl moiety. Interestingly, the IR spectrum for the previously mentioned cobalt−gallium complex reported by Cowley and co-workers also showed six bands attributed to the CO ligands on the $Co(CO)_4$ fragments in the region between 1878 and 2080 $cm^{-1}$.[43]

Consistent with the weakened P−Ga bond, solutions of **3** in $Et_2O$ form the known complex **4** over several hours at 25 °C (eq 8). To the best of our knowledge, **4** has only been characterized by IR spectroscopy[27a] and X-ray crystallography.[27b] We confirmed the identity of **4** by these methods as well as multinuclear NMR spectroscopy and mass spectrometry. For instance, the $^{31}P$ NMR spectrum revealed a single resonance at 26 ppm whereas two resonances were observed in the $^{13}C$ NMR spectrum, a singlet at 203 ppm and a doublet at 18 ppm ($^1J_{CP} = 31.9$ Hz), corresponding to CO and Me carbon atoms, respectively. The IR spectrum of **4** contains two bands corresponding to CO stretches at 1950 and 1972 $cm^{-1}$, which, on average, appear at lower wavenumber values than those observed for **3**. This can be attributed to the presence of the strong $\sigma$-donor $PMe_3$ molecules capping both ends of the $Co_2(CO)_6$ chain in **4**, placing more electron density on the metal centers and, thus, increased back donation into the CO $\pi^*$ orbitals. In contrast, the Lewis acidic gallium center in **3** does not donate significant electron density onto the Co centers, as reflected in the relatively high CO stretching frequencies.

The conversion of **3** to **4** intriguingly mimics the proposed mechanism in Scheme 2 for the reaction involving colloidal Rh with **1** and **2**. Weakening of the P−Ga bond is clearly observed in **3** and subsequently results in P−Ga bond cleavage; in this case, free $PMe_3$ is not generated, as this

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coordinates to reactive Co carbonyl fragments to form **4**.[46]

$$\underset{\mathbf{3}}{Me_3P{\cdot}Ga[Co(CO)_4]_3} \xrightarrow[-H_2,\ -Ga]{Et_2O,\ 25\ ^\circ C,\ 4\ h} \underset{\mathbf{4}}{[(Me_3P)Co(CO)_3]_2} \quad (8)$$

## Conclusions

The successful formation of P−B and N−B bonds by the transition metal-catalyzed dehydrocoupling of phosphine− and amine−borane adducts, respectively, prompted our investigations into the potential extension of this synthetic approach to P−Ga systems. Consequently, the secondary phosphine−gallane **1** was treated with Rh(I) or Rh(0) catalysts in toluene at 25 °C. However, instead of dehydrocoupling, this resulted in the formation of Ga metal, release of $H_2$ gas, and catalytic P−Ga bond cleavage generating the phosphine quantitatively. Similarly, the tertiary phosphine−gallane **2** also dissociated when treated with a catalytic amount of Rh(0). Interestingly, when $Me_2NH{\cdot}BH_3$ was subsequently added to the reaction mixture, no dehydrocoupling to afford the cyclic dimer $[Me_2N{-}BH_2]_2$ was detected, indicating that catalyst deactivation is taking place. Studies involving the treatment of the Rh(0) colloidal catalyst with $Cy_2PH$, $PMe_3$, and $GaH_3{\cdot}OEt_2$ revealed that both phosphines and the gallane poison the catalyst to varying degrees. XPS studies verified the presence of phosphorus on the surface of the Rh(0) colloids. A model reaction with a zerovalent group 9 metal complex was performed in an effort to probe the mechanism behind the metal-assisted dissociation process. Specifically, the reaction between $[Co_2(CO)_8]$ and **2** first afforded **3**, which possesses a P−Ga bond, and subsequently afforded **4**, with concomitant Ga metal precipitation. This suggests that a reasonable mechanism involves the reaction of the Ga−H bonds on the Rh colloid surface and the weakening of the P−Ga bond leading to adduct dissociation. Future work is directed at studying the catalytic P−Ga bond cleavage process in more detail and extending our studies to adducts containing other heavier group 13 and 15 elements.

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(46) There is also a possibility that the reactions with $[Co_2(CO)_8]$ may proceed via routes involving radicals, and this cannot be ruled out at this time.