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Molecular Models of Titania – Silica Systems and a Late Transition Metal Complex Grafted Thereon**

Rosa Fandos,* Antonio Otero,* Ana Rodríguez,
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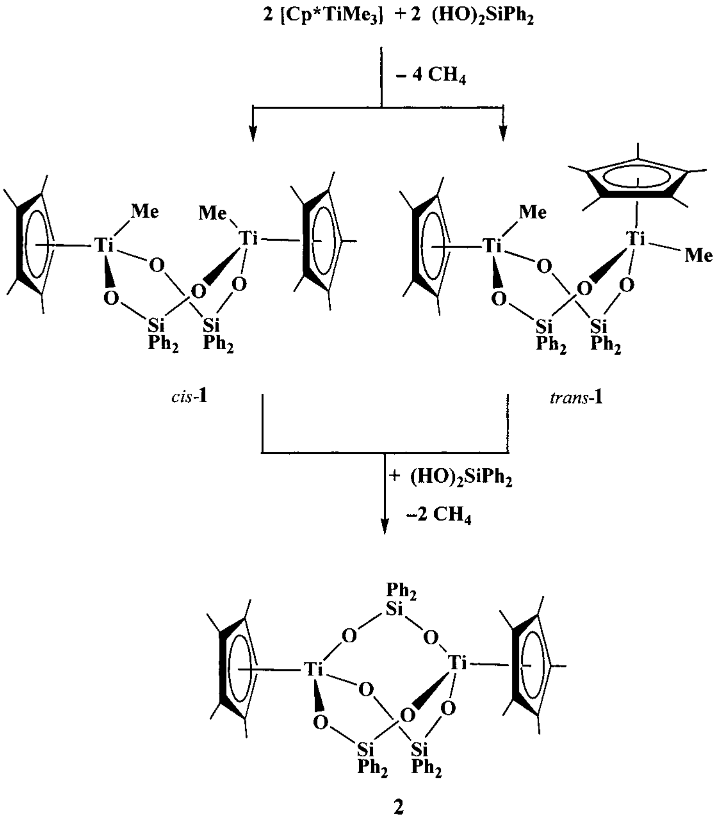
Titania – silica materials are the focus of much attention on account of their unique properties:[1, 2] 1) they can act as catalysts for a wide variety of processes; 2) they are suitable supports for late transition metal catalysts because they improve the mechanical strength, thermal stability, and surface area relative to TiO_2 supports.[3] Although titania – silica materials have been extensively used as catalysts and supports for a great variety of reactions, and several well-defined soluble metallasiloxanes[4, 5] have been used to mimic and facilitate the understanding of the situation in solid materials, until now no molecular models have been reported for late transition metal catalysts supported on titania – silica. We previously reported[6] the synthesis of the complex $[Cp^*Ti(\mu_3\text{-}O)_3\{Rh(cod)\}_3]$ (cod = 1,5-cyclooctadiene, Cp* = η^5-C_5Me_5), which can be regarded as a model of rhodium supported on titania. We have now extended our studies to modeling a rhodium complex supported on titania – silica. Here we report on the synthesis of the dimetallic titanium alkyl siloxide complexes $[\{Cp^*TiMe(O_2SiPh_2)\}_2]$ (**1**) and $[Cp^*Ti(O_2SiPh_2)_3TiCp^*]$ (**2**), which can be regarded as models for the above-mentioned titania – silica systems. The reaction of **1** with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ leads to the formation of $[\{Cp^*Ti(O_2SiPh_2)(\mu_3\text{-}O)Rh(cod)\}_2]$ (**3**), which can be regarded as an unprecedented molecular model of a late transition metal supported on titania – silica.

The titanium complex $[Cp^*TiMe_3]$ reacts with diphenylsilanediol to afford the yellow solid **1** (Scheme 1), which was isolated in good yield (76 %) as a mixture of two isomers. By comparison with the previously reported analogous titanium complexes,[7] we propose that **1** is a dimer in which the siloxide ligands act as bridges between two titanium atoms, and the two isomers are the *cis* and *trans* forms.[8] According to variable-temperature (VT) NMR experiments in $[D_8]$toluene, the ratio of the two isomers does not change up to 353 K. It is also independent of the concentration of the sample and the solvent ($[D_8]$toluene, C_6D_6, $CDCl_3$, $[D_8]$THF). According to



Scheme 1. Synthesis of **1** and **2**.

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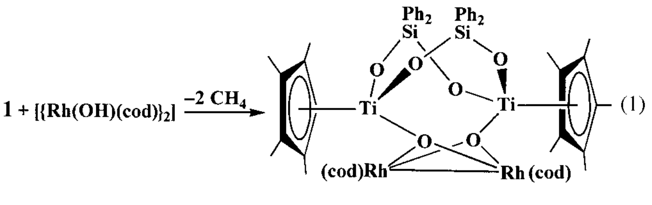
the ^{13}C NMR spectrum, the phenyl groups in the *trans* isomer are in the same chemical environment, while those in the *cis* isomer are not; this was to be expected in the case of conformationally flexible molecules. Reaction of *cis*-/*trans*-**1** with one equivalent of diphenylsilanediol in chloroform at 60 °C affords exclusively **2**, which was isolated as a yellow solid in 69 % yield (Scheme 1). Reaction of **1** with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$[9] gave the heterometallic complex $[\{Cp^*Ti(O_2SiPh_2)(\mu_3\text{-}O)Rh(cod)\}_2]$ (**3**) [Eq. (1)]. It was isolated as a crystalline orange solid. The molecular structure of **3** was determined by an X-ray diffraction study[10] and shows an eight-membered titanium-containing siloxane ring to which the two rhodium atoms are anchored by μ_3-oxo ligands (Figure 1). The geometry around the titanium atom is that of a distorted tetrahedron, and the rhodium atoms are in approximately square-planar environments. Distances from the titanium atom to the oxygen atoms bonded to the silicon are somewhat longer than those in $[\{Cp^*TiCl(O_2SiPh_2)\}_2]$,[7] while angles around the oxygen atoms are smaller, probably due to the more constrained geometry. The Rh1–Rh2 distance (2.746(1) Å) is short enough to propose a metal–metal bonding interaction,[11] while the Ti–Rh distances, which range between 3.491(2) and 3.608(3) Å, are so large that metal–metal interactions can be ruled out.[6]



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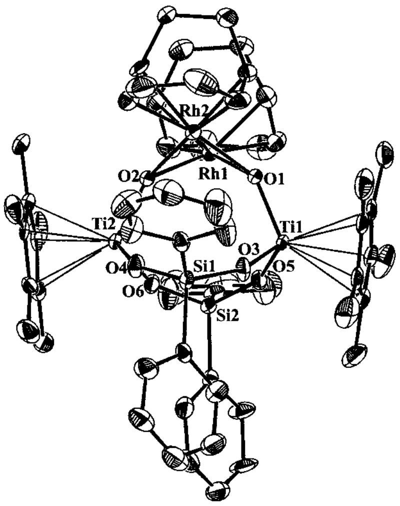
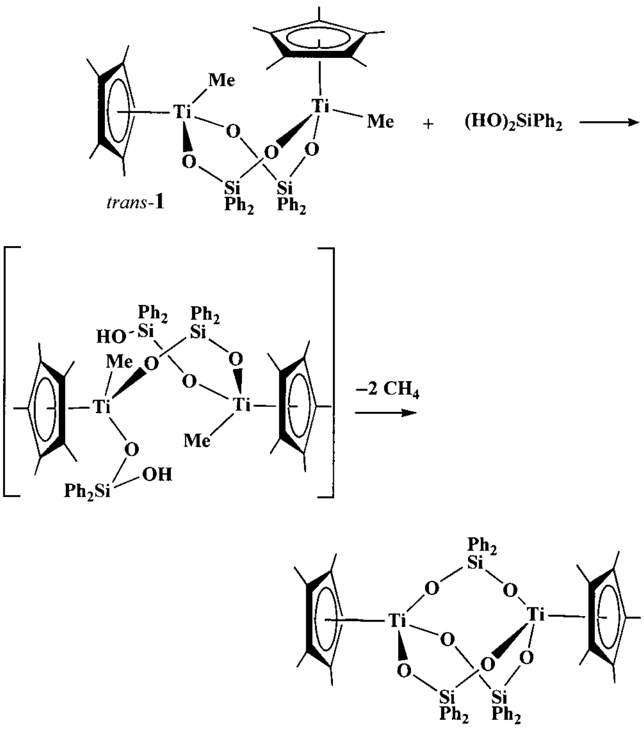


Figure 1. Structure of complex **2**. Selected bond lengths [Å] and angles [°]: Ti1-O1 1.796(6), Ti1-O3 1.847(6), Ti1-O5 1.860(6), Ti2-O2 1.784(6), Ti2-O4 1.846(6), Ti2-O6 1.863(6), Rh1-O1 2.135(6), Rh1-O2 2.145(6), Rh1-Rh2 2.746(1), Si1-O3 1.612(6), Si1-O4 1.625(6); O1-Rh1-O2 78.8(2), O1-Ti1-O3 104.5(3), Ti1-O1-Rh2 134.0(3), Ti1-O1-Rh1 125.1(3), Ti2-O2-Rh2 131.9(3), Ti2-O2-Rh1 130.7(3), Rh2-O1-Rh1 80.3(2).

The room-temperature ^{13}C and ^{1}H NMR spectra of complex **3** show that the two siloxane groups are in the same chemical environment, while the phenyl groups bonded to each silicon atom are different, in agreement with the structural data. On the other hand, both cod ligands are also equivalent. A ^{1}H VT-NMR experiment showed that these ligands are fluxional. At 291 K the spectrum contains two broad signals corresponding to the two different chemical environments for the olefinic protons of the cod ligand. At 297 K they coalesce, and the broad signal at higher temperatures points to rapid interchange. According to the spectra, no other ligand is involved in the interchange process. In agreement with these ^{1}H NMR data, both *cis*- and *trans*-**1** react with $Ph_2Si(OH)_2$ and $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ at approximately the same rate to yield **2** and **3**, respectively. Hence, under the reaction conditions the *trans* isomer must undergo rearrangement to form these complexes. To explain this process we propose that the first step in the reaction of *trans*-**1** with diphenylsilanediol (Scheme 2) could be the protonolysis of a Ti–O bond to yield a $Ti(OSiPh_2OH)$ moiety that subsequently induces protonolysis of the Ti–Me bonds to give **2**. This implies the unusual preferential breaking of a Ti–O bond rather than a Ti–Me bond. However, it agrees with the proposal that the reactivity of Ti–O–Ti bonds toward H_2O or MeOH (or protonolysis in general) is responsible for the deactivation of titania–silica catalysts in oxidation reactions[12] and for the formation of inhomogeneous materials in sol–gel processes.[13] The formation of **3** by reaction of **1** with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ could be explained by the same reaction path. To prove that protonolysis of the



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Scheme 2. Proposed steps in the synthesis of **2** from *trans*-**1**.

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Ti–O bond is a feasible step in the mechanism of formation of **2** and **3** from **1**, we treated **2** with an excess of [{Rh(μ-OH)(cod)}$_2$] in a NMR tube in C_6D_6 at 70 °C, and **3** was formed as the main product.

The FT-IR spectra show strong absorptions at 979 and 941 cm^{-1} for **1**, 994 and 935 cm^{-1} for **2**, and 974, 967, 941, and 923 cm^{-1} for **3**, which can be tentatively assigned to the Si-O-Ti stretching/bending modes. The features of the Ti-O-Si ring-breathing mode cannot be assigned unambiguously, because they overlap with characteristic absorptions of the phenyl groups between 750 and 700 cm^{-1}.[14] In **3**, the bands at 675 and 614 cm^{-1} can be ascribed to Ti-O-Rh. The Raman spectra show very weak bands for the Si-O-Ti groups in **1** and **2**, while in the spectrum of **3** this vibration mode is located at 953 cm^{-1}. The binding energy of the Ti 2p$_{3/2}$ core level for **3** is 458.0 eV, which is 1.1 eV higher than that of [Cp*Ti(μ_3-O)$_3${Rh(cod)}$_3$]. This is consistent with the presence of Si-O-Ti moieties in which Si can withdraw electron density from Ti^{IV}.[1] The Rh 3d$_{5/2}$ binding energy is 308.9 eV, in agreement with expected values for Rh^{I} complexes.[15]

In conclusion, we have described new dimetallic titanium alkyl siloxide complexes which can be considered as molecular models for titania–silica species, and a novel molecular model for a late transition metal supported on titania–silica. We are extending our work to prepare other late transition metal molecular models and to study their potential catalytic activity in epoxidation and oxidation processes.

Experimental Section

1: Diphenylsilanediol (0.257 g, 1.19 mmol) was added to a solution of [Cp*TiMe$_3$] (0.273 g, 1.19 mmol) in toluene (5 mL). After 1 h, the solvent was removed under vacuum and the residue extracted with pentane. The solvent was partially evaporated, and the solution was cooled to −30 °C overnight to yield **1** as a crystalline yellow solid. Yield: 0.373 g (76 %); IR (KBr): $\tilde{\nu} = 1428$ (m), 1377 (w), 1120 (s), 1110 (s) 1030 (s), 998 (s), 979 (vs), 941 (vs), 887 (w), 740 (m), 713 (s), 700 (s), 516 cm^{-1} (s); ^{1}H NMR (200 MHz, $CDCl_3$): mixture of isomers (42 % *cis*, 58 % *trans*): $\delta = 0.48$ (s, TiMe, *cis* isomer), 0.53 (s, TiMe, *trans* isomer), 1.70 (s, Cp*, *cis* isomer), 1.73 (s, Cp*, *trans* isomer), 7.29 (m, Ph, *cis* and *trans*), 7.49 (m, Ph, *cis* and *trans*); ^{13}C{^{1}H} NMR: *trans* isomer: $\delta = 12.2$ (s, Cp*), 49.4 (s, TiMe), 123.4 (Cp*), 127.5 (s, Ph), 129.5 (s, Ph), 134.9 (s, Ph), 138.1 (s, *ipso*-C of Ph); *cis* isomer:$\delta = 12.2$ (s, Cp*), 49.6 (s, TiMe), 123.2 (Cp*), 128.0 (s, Ph), 128.1 (s, Ph), 129.9 (s, Ph), 130.0 (s, Ph), 135.1 (s, Ph), 135.4 (s, Ph), 136.7 (s, *ipso*-C of Ph), 139.7 (s, *ipso*-C of Ph); elemental analysis (%) calcd for $C_{46}H_{56}O_4Si_2Ti_2$: C 66.98, H 6.84; found: C 66.34, H 6.80.

2: Diphenylsilanediol (0.084 g, 0.39 mmol) was added to a solution of **1** (0.320 g, 0.39 mmol) in chloroform (5 mL), and the solution was heated to 60 °C for 6 h. Then the solvent was removed under vacuum and the residue washed twice with pentane (3 mL) to yield **2** as a yellow solid. Yield: 0.273 g (69 %); IR (KBr): $\tilde{\nu} = 1428$ (m), 1377 (w), 1123 (s), 1113 (s) 1027 (s), 1015 (s), 999 (s), 994 (vs), 935 (s), 907 (vs), 876 (s), 860 (m), 740 (m), 713 (m), 799 (s), 507 cm^{-1} (s); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.93$ (s, 30 H, Cp*), 7.08 (m, 12 H, Ph), 7.25 (m, 6 H, Ph), 7.42 (m, 12 H, Ph); ^{13}C{^{1}H} NMR: $\delta = 12.5$ (s, Cp*), 126.6 (Cp*), 127.8 (s, Ph), 129.6 (s, Ph), 135.5 (s, Ph), 137.9 (s, *ipso*-C of Ph); elemental analysis (%) calcd for $C_{56}H_{60}O_6Si_3Ti_2$: C 66.65, H 5.99; found: C 66.42, H 6.15.

3$\cdot 0.5\,C_7H_8 \cdot 0.25\,C_5H_{12}$: [{Rh(OH)(cod)}$_2$] (0.081 g, 0.18 mmol) was added to a solution of **1** (0.143 g, 0.18 mmol) in THF. The suspension was allowed to stand at room temperature for 24 h. The solvent was removed under vacuum and the residue extracted with toluene. Slow diffusion of pentane into the toluene solution yielded **3** as yellow crystals. Yield: 0.130 g (54 %); IR (KBr): $\tilde{\nu} = 1475$ (w), 1448 (w), 1428 (w), 1374 (w), 1110 (s), 1030 (w), 998 (sh), 994 (s), 974 (vs), 967 (s), 957 (vs), 941 (s), 923 (vs), 891 (w), 868 (m), 775 (w), 744 (s), 737 (s), 700 (s), 682 (m), 675 (m), 614 (w), 515 (s), 504 cm^{-1} (m); ^{1}H NMR (200 MHz, C_6D_6): $\delta = 1.20$ (br, 4 H, cod), 1.42 (br, 8 H, cod), 2.06 (s, 30 H, Cp*), 2.38 (br, 4 H, cod), 4.10 (br, 4 H, cod), 4.19 (br, 4 H, cod), 6.82 (m, 3 H, Ph), 7.43 (m, 5 H, Ph), 8.38 (m, 2 H, Ph); ^{13}C{^{1}H} NMR: $\delta =$ 12.51 (Cp*), 30.1 (br, cod) 31.2 (br, cod), 72, 3 (br, cod), 75.5 (br, cod), 122.1 (s, Cp*), 126.7 (s, Ph), 128.2 (s, Ph), 128.9 (s, Ph), 129.2 (s, Ph), 135.5 (s, Ph), 135.7 (s, Ph), 139.8 (s, Ph), 142. 21 (s, Ph); elemental analysis (%) calcd for $C_{64.75}H_{81}O_6Rh_2Si_2Ti_2$: C 59.24, H 6.21; found C 59.16, H 6.39.

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[10] X-ray crystal structure determination of **3**: Suitable crystals of **3**$\cdot 0.5\,C_7H_8 \cdot 0.25\,C_5H_{12}$ were grown from toluene/pentane. A orange crystal of approximate dimensions 0.5 × 0.3 × 0.2 mm was mounted in a glass capillary. Intensity data were collected at 298 K on a NONIUS-MACH3 diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) by using $\omega/2\theta$ scans up to a maximum value of 56°. The intensities of two representative reflections measured every hour did not change significantly during the course of data collection. The asymmetric unit contains one molecule of **3**$\cdot 0.5\,C_7H_8 \cdot 0.25\,C_5H_{12}$. Data were corrected for Lorentzian and polarization effects, and empirical absorption correction was not necessary ($\mu = 8.68$ cm^{-1}). The structure was solved by direct methods (SIR92).[16] Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL97).[17] All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in calculated position and were refined isotropically. Crystal data: $C_{60}H_{78}O_6Rh_2Si_2Ti_2 \cdot 0.5\,C_7H_8 \cdot 0.25\,C_5H_{12}$, $M_r = 1313.10$; monoclinic, space group $C2$, $a = 22.054(5)$, $b = 11.954(7)$, $c = 23.265(4)$ Å, $\beta = 91.67(2)°$, $V = 6131(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.423$ g cm^{-3}; data/restraints/parameters: 14784/5/678, final R indices: $R_1 = 0.0557$, $wR_2 = 0.1648$ for reflections with $I > 2\sigma(I)$, GOF: 1.183; max./min. residual electron density: 1.354/−1.120 e Å^{-3}. Crystallographic data (excluding structure factors) for the structure reported in this paper have been

deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156951. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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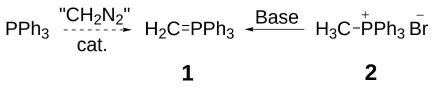
Methylenation of Aldehydes: Transition Metal Catalyzed Formation of Salt-Free Phosphorus Ylides**

Hélène Lebel,* Valérie Paquet, and Caroline Proulx

Among the olefination processes,[1] the methylenation of carbonyl derivatives is a very important transformation in synthesis.[2] Recently even more attention has been devoted to this reaction since terminal alkenes are ideal precursors for ring-closing metathesis reactions.[3] Although the Wittig reaction has been quite reliable for performing this transformation, several drawbacks are still associated with it. The most important problems include the low reactivity of the reagent with sterically hindered carbonyl derivatives as well as the possible epimerization of base-sensitive substrates.[4] Several systems employing stoichiometric amounts of organometallic reagents have been developed to overcome these problems. For example, organometallic compounds based on titanium (Tebbe/Petasis) and zinc (Oshima/Lombardo) provide efficient methylenation of numerous carbonyl substrates.[5] However, the use of stoichiometric amounts of expensive and in some cases pyrophoric compounds, as well as the competitive reductive coupling of aldehydes observed with these reagents,[6] are undesired factors and indicate that there is still a significant need to develop new reagents to carry out this transformation. Few approaches to transition metal catalyzed olefinations have been disclosed, but they are all limited to the synthesis of α,β-unsaturated esters.[7, 8]

Numerous methods for the preparation of phosphorus ylides by deprotonation of phosphonium salts with a base have been reported.[9] Conversely, sulfur, oxonium, nitrogen, carbonyl, and thiocarbonyl ylides have been successfully prepared from diazo compounds with the use of transition metal catalysts.[10] However, with the exception of one report by Fujimura and Honma on the use of diazoacetate precursors,[11] such a strategy has never been applied to the preparation of phosphorus ylides. Here we disclose the first transition metal catalyzed methylenation of aldehydes, based on the synthesis of salt-free phosphorus ylides from diazo reagents.

In principle, the generation of $Ph_3P{=}CH_2$ (**1**) requires the use of CH_2N_2 as the diazo precursor (Scheme 1). Our first attempts at the methylenation of cinnamaldehyde (**3**) with CH_2N_2 using $[RuCl(NO)(PPh_3)_2]$ as the catalyst were very disappointing (Table 1, entries 1, 2). No alkene product was observed, although $[RuCl(NO)(PPh_3)_2]$ is known to produce stable carbene species in the presence of CH_2N_2.[12] We also investigated $TMSCHN_2$ (TMS = trimethylsilyl) as a safer alternative to CH_2N_2, since $Ph_3P{=}CHTMS$ can be rapidly desilylated in the presence of an alcohol to generate the corresponding salt-free phosphorus methylide.[13, 14] The methylenation of **3** proceeded smoothly with $TMSCHN_2$ in the presence of PPh_3 and $[RuCl(NO)(PPh_3)_2]$. In the absence of an alcohol, diene **4** was produced quantitatively in 16 h (entry 3). In contrast, conversion was quantitative after 2 h when one equivalent of 2-propanol was added (entry 4). For comparison, only 45 % conversion was observed for the formation of α,β-unsaturated ester **5** under similar conditions with ethyl diazoacetate (EDA, entry 5). We then surveyed various catalysts for the methylenation of **3** with $TMSCHN_2$, PPh_3, and 2-propanol. Many ruthenium and rhodium complexes effectively catalyzed the methylenation with $TMSCHN_2$ and 2-propanol, whereas low activity was often observed with EDA. The best catalytic activity was observed with Wilkinson's catalyst, $[RhCl(PPh_3)_3]$, which allowed the quantitative conversion of **3** into diene **4** within 30 min at 25 °C with $TMSCHN_2$ (entry 14). Again, the combination of $TMSCHN_2$ and 2-propanol proved to be superior to CH_2N_2 and EDA (entries 12, 13). Under similar conditions, $[\{Rh(OAc)_2\}_2]$ was inefficient at catalyzing the olefination of **3** (entries 23, 24).



$$PPh_3 \xrightarrow[\text{cat.}]{\text{"}CH_2N_2\text{"}} H_2C{=}PPh_3 \xleftarrow{\text{Base}} H_3C{-}\overset{+}{P}Ph_3\ \overset{-}{Br}$$

1 **2**

Scheme 1. Generation of **1**.

The catalyst loading could be lowered to 2.5 mol % with no detrimental effect on the activity when $[RhCl(PPh_3)_3]$ was

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