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# Multifaceted Chemistry of $[(Cymene)RuCl_2]_2$ and $PCy_3$

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The reaction of $[(cymene)RuCl_2]_2$ (**1**) with $PCy_3$ was investigated using different stoichiometries and reaction conditions. Whereas a mixture of complex **1** and 2 equiv of $PCy_3$ in methanol gave the known adduct $[(cymene)RuCl_2(PCy_3)]$ (**2**), the utilization of 4 equiv gave the hydrido complex $[(cymene)RuHCl(PCy_3)]$ (**3**) along with the phosphonium salt $[PCy_3(CH_2OH)]Cl$ (**4**). Prolonged heating of **1** and 4 equiv of $PCy_3$ in methanol under argon resulted in the formation of complex $[RuHCl(CO)(PCy_3)_2]$ (**5**). Dinuclear, chloro-bridged complexes were generated when **1** was reacted with only 1 equiv of $PCy_3$. In a mixture of THF and allyl alcohol, the carbonyl complex $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(CO)(PCy_3)]$ (**6**) was formed. In dioxane, however, intramolecular C−H activation of the $PCy_3$ ligand was observed, resulting in the formation of $[(cymene)Ru(\mu\text{-}Cl)_3RuCl\{PCy_2(C_6H_9)\}]$ (**7**). When the reaction was performed under an atmosphere of $H_2$, the dihydrogen complex $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(H_2)(PCy_3)]$ (**8**) could be isolated. An inert trinuclear cluster of the formula $[RuCl_2(PCy_3)]_3$ (**10**) was formed when **1** was heated with 2 equiv of $PCy_3$ in THF. The complexes **3**, **6**, **7**, **8**, and **10** as well as the phosphonium salt **4** were characterized by single-crystal X-ray analysis.

## Introduction

The chloro-bridged complex $[(cymene)RuCl_2]_2$ (**1**) was first described in 1972.[1] It is easily accessible from α-phellandrene and $RuCl_3(H_2O)_n$[2] and has become a frequently used starting material in organometallic,[3] medicinal inorganic,[4] and supramolecular[5] chemistry. Complex **1** reacts with monodentate $PR_3$ ligands to give adducts of the general formula $[(cymene)RuCl_2(PR_3)]$.[1,6] When sterically demanding phosphine ligands such as $PCy_3$ are employed, the cymene π-ligand can be cleaved off by photochemical or thermal activation (Scheme 1). The resulting ruthenium complexes have been employed as catalysts for ring-closing metathesis (RCM)[7] and for ring-opening metathesis polymerization (ROMP) reactions[8,9] as well as for atom transfer radical addition (ATRA) and polymerization (ATRP) reactions (Scheme 1).[10]

So far, there is very limited knowledge about what type of complexes are formed upon liberation of the π-ligand. In the context of studies about Ru-catalyzed radical reactions we have recently observed that a partial displacement of the arene ligand with $PCy_3$ may lead to the formation of

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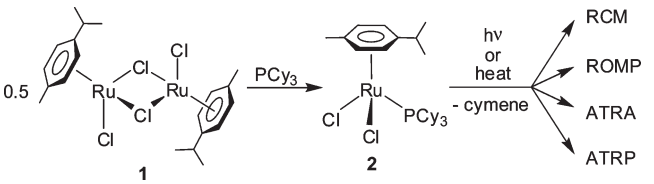
**Scheme 1**




halogeno-bridged complexes of the formula [(arene)-$Ru(\mu\text{-}Cl)_3RuCl(L)(PCy_3)$] (L = $\mu$-$N_2$ or $\eta^2$-$C_2H_4$).[11,12] In the following we describe more detailed investigations about the reaction of complex **1** with $PCy_3$. It is shown that mononuclear hydrido complexes are formed in alcoholic solvents. Partial arene displacement in nonprotic organic solvents results in the generation of highly reactive dinuclear complexes, which may even promote C−H activation. The complete displacement of the cymene ligand, on the other hand, gives a trinuclear cluster of low reactivity.

## Results and Discussion

In a first set of experiments, we have investigated the reaction of the dimer **1** with $PCy_3$ in methanol. When **1** was reacted with 2 equiv of $PCy_3$, the known mononuclear complex [(cymene)$RuCl_2(PCy_3)$] (**2**) was obtained in 80% yield in the form of a microcrystalline material (Scheme 2). When 4 equiv with respect to the dimer **1** were used, an orange powder precipitated. This complex turned out to be the hydrido complex [(cymene)$RuHCl(PCy_3)$] (**3**) (Scheme 2), as evidenced by NMR spectroscopy and a single-crystal X-ray analysis (Figure 1). An alternative synthesis for complex **3** was recently described by Demerseman et al.[13,14] They have obtained **3** in a multistep synthesis with a final ligand exchange reaction between [(cymene)-$RuCl_2(PCy_3)$] and the dihydrido complex [(cymene)-$RuH_2(PCy_3)$] (yield: 39%). The much simpler preparation of complex **3** from [(cymene)$RuCl_2]_2$ and $PCy_3$ should thus be of interest.

To elucidate the fate of the excess $PCy_3$ in our reaction, we have investigated the filtrate. Evaporation of the methanol followed by recrystallization from hot toluene gave the phosphonium salt **4**, which was characterized by NMR spectroscopy and a crystallographic analysis (picture not shown). It is known that hydroxymethylphosphonium salts are easily formed from tertiary phosphines, formaldehyde, and HCl.[15] The formation of **4** can thus be rationalized by assuming a Ru-induced oxidation of methanol to formaldehyde via a $\beta$-hydride elimination of a methoxy complex with concomitant reaction of $CH_2O$ and HCl with $PCy_3$.

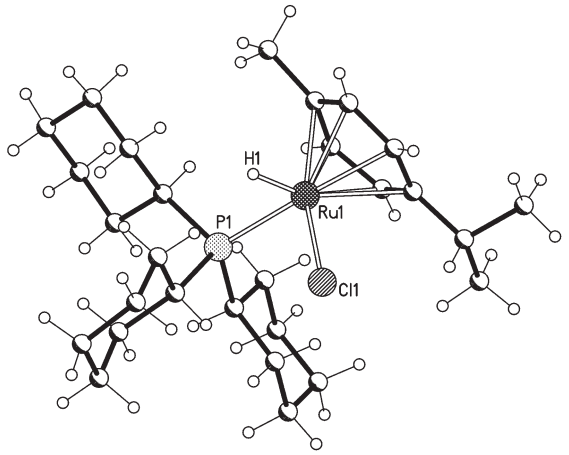
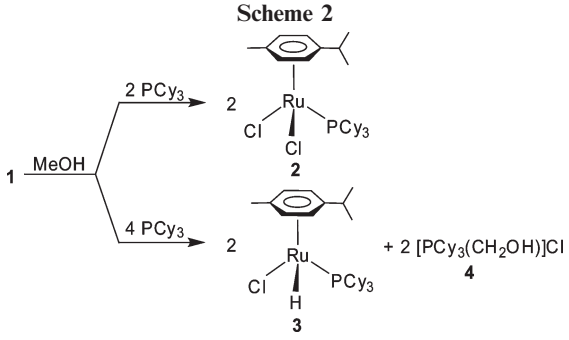
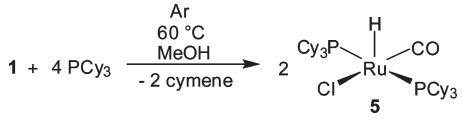



**Figure 1.** Graphic representation of the molecular structure of complex **3** in the crystal. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.4393(12), Ru1−H1 1.48(5), Ru1−P1 2.3222 (12); P1−Ru1−Cl1 89.64(4), P1−Ru1−H1 75.8(18), Cl1−Ru1−H1 88.9(17).

**Scheme 2**




**Scheme 3**




The molecular structure of complex **3** in the crystal is shown in Figure 1. It displays the expected "piano stool" geometry with a facial orientation of the hydrido, the chloro, and the $PCy_3$ ligand. The hydrido ligand was located crystallographically, and the Ru−H bond distance was found to be 1.48(5) Å. The lengths of the Ru−P bond (2.3222(12) Å) and of the Ru−Cl bond (2.4393(12) Å) are within the expected range.[14a]

When the reaction of **1** with 4 equiv of $PCy_3$ was performed under more forcing conditions (60 °C, 48 h), the cymene $\pi$-ligand was cleaved off and the hydrido complex [RuHCl-$(CO)(PCy_3)_2$] (**5**) was obtained in 70% yield (Scheme 3). Several synthetic routes for complex **5** have already been described. Moers and co-workers reported that **5** can be obtained along with the dichloro complex [$RuCl_2(CO)$-$(PCy_3)_2$] by reacting $RuCl_3(H_2O)_n$ with $PCy_3$ in 2-methoxyethanol.[16] In 1999, Yi et al. described a high-yield synthesis of **5** starting from $[RuCl_2(cod)]_2$.[17] However, the group of

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Fogg has recently reported that the synthesis via $[RuCl_2(cod)]_2$ tends to give small amounts of impurities, which are difficult to remove.[18] As a result, they have devised an improved route, which starts with hydride complex $[RuHCl(CO)(PPh_3)]$.[18] It is interesting to note that complex **5** can also be formed by decomposition of the metathesis catalysts $[RuCl_2(=CHR)(PCy_3)_2]$ (R = Ph, OEt).[19] The special attention that complex **5** has received over the last years is mainly due to the fact that it can be used as a potent catalyst for numerous organic transformations. For example, complex **5** has been used as a catalyst for the hydrogenation of alkenes,[20] for the hydrovinylation of vinylarenes,[21] for the silylation of terminal alkenes[22] and alkynes,[23] for the synthesis of alkynylgermanes,[24] for the isomerization of double bonds,[19a] and for the coupling of cyclic amines and alkenes.[25] Our new synthesis of complex **5** should be of interest because it is a simple one-step procedure staring from commercially available **1**.

We have also investigated the reaction of **1** with $PCy_3$ in various nonprotic solvents. Heating complex **1** with 1 equiv of $PCy_3$ in dibutyl ether at 110 °C for 4 h resulted in the formation of an orange precipitate (**6**). IR spectroscopic investigation of this precipitate showed a strong peak at $\nu$=1951 $cm^{-1}$, indicating the presence of a complex with a CO ligand. This was supported by the $^{13}C$ NMR spectrum, which showed a peak at $\delta = 205.2$ ppm. The peak appeared as a doublet ($J$=18 Hz), suggesting that the CO ligand is situated next to a $PCy_3$ ligand. This was confirmed by a crystallographic analysis, which established that **6** is a dinuclear complex of the formula $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(CO)(PCy_3)]$ (Figure 2).[26]

The source of the CO ligand in complex **6** was puzzling. We therefore repeated the reaction with freshly distilled dibutyl ether, and we were unable to reproduce the formation of complex **6**. Analysis of the original dibutyl ether by GC-MS revealed the presence of small amounts of butyl peroxide and 1-butanol. Attempts to prepare **6** by a reaction in a mixture of freshly distilled dibutyl ether and 1-butanol (9:1) failed, however. Searching for a reproducible synthetic pathway we finally found that heating **1** and 2 equiv of $PCy_3$ in a mixture of THF and allyl alcohol formed complex **6** in good yield (Scheme 4). The mechanism of this carbonylation reaction may involve the metal-catalyzed isomerization of allyl alcohol into propanal, but more detailed mechanistic studies would be needed to clarify this point. It is noteworthy, however, that when the reaction was performed in a mixture of THF and 1-butanol instead of allyl alcohol, the desired CO complex **6** was not obtained.

When complex **1** was heated with 1 equiv of $PCy_3$ in dioxane at 70 °C for three days, a new compound was formed (**7**) (Scheme 5). The NMR data of this compound were rather complex: the $^{31}P$ NMR spectrum showed two singlets at 73.9 and 73.2 ppm with the relative intensity of 5:3. A double set of signals with a major and a minor component was also observed for the $^1H$ and the $^{13}C$ NMR spectra. The presence of 2 × 4 signals for the aromatic CH protons of the cymene $\pi$-ligand indicated that complex **7** was chiral. A striking feature was the presence of $^1H$ NMR signals in the range

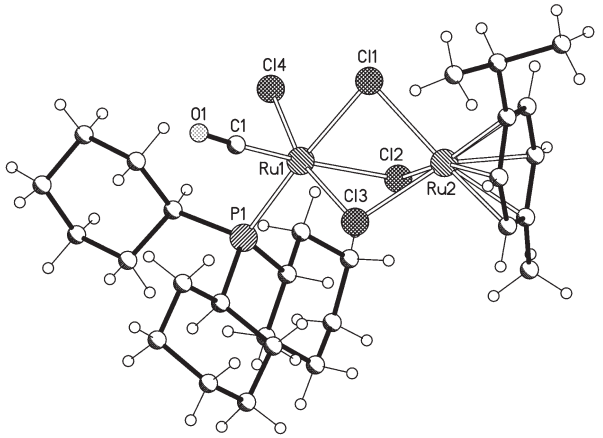
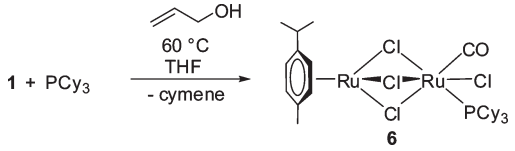
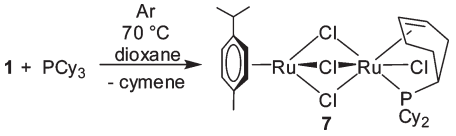



**Figure 2.** Graphic representation of the molecular structure of complex **6** in the crystal. The solvent molecule ($CH_2Cl_2$) is not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.552(4), Ru1−Cl2 2.514(5), Ru1−Cl3 2.424(5), Ru1−Cl4 2.381(5), Ru1−P1 2.327(4), Ru1−C1 1.848(15), C1−01 1.107(16), Ru1···Ru2 3.301(6); P1−Ru1−C1 89.7(4), P1−Ru1−Cl4 91.85(16), P1−Ru1−Cl1 176.20(13), Ru1−C1−O1 177.1(13).

**Scheme 4**




**Scheme 5**

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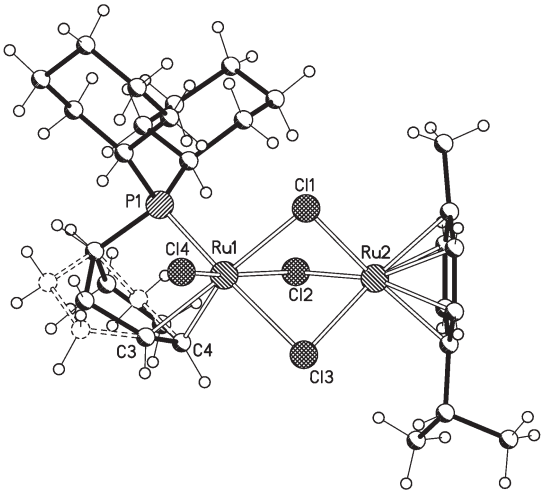


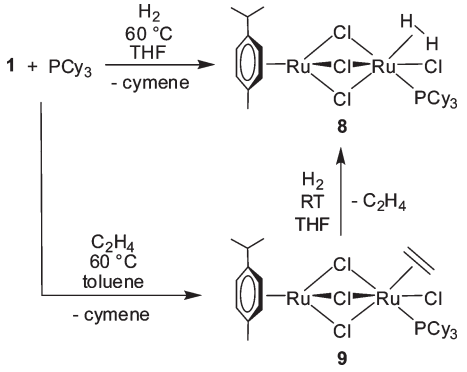

**Figure 3.** Graphic representation of the molecular structure of complex **7** in the crystal. The disorder of the cyclohexene ring is indicated by dotted lines. The solvent molecule (dioxane) is not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.4902(13), Ru1−Cl2 2.4253(12), Ru1−Cl3 2.5561 (14), Ru1−Cl4 2.3942(12), Ru1−P1 2.2402(14), Ru1−C4 2.179 (6), Ru1−C3 2.185(5), C3−C4 1.361(8), Ru1···Ru2 3.2926(6); P1−Ru1−Cl4 94.32(5), P1−Ru1−Cl1 100.78(5), P1−Ru1−Cl3 174.06(5).

4.40−4.69 ppm, which pointed to the presence of metal-bound olefinic protons.

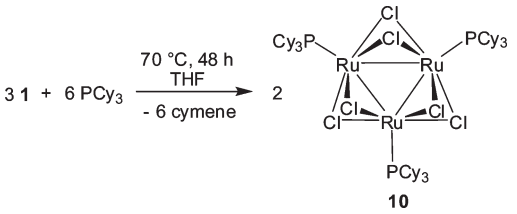
An explanation for the NMR data was provided by the result of a crystallographic analysis. Complex **7** shows a dinuclear, chloro-bridged structure, which is similar to that of **6** (Figure 3). Instead of the CO ligand, a $\eta^2$-bound cyclohexene group completes the coordination sphere of the Ru center. The latter is derived from the $PCy_3$ ligand, which has undergone a partial dehydrogenation reaction. The acceptorless dehydrogenation of phosphine ligands has been observed occasionally for tricyclopentylphosphine complexes.[27] The analogous reaction with $PCy_3$ is known to be much more difficult and generally requires the addition of hydrogen acceptors such as $CH_2{=}CH^tBu$.[27c,27f,28]

The crystallographic analysis revealed some disorder of the $\eta^2$-bound cyclohexene group. The dehydrogenated $PCy_2(C_6H_9)$ ligand is chiral, and the Ru1 center represents a stereogenic center. Consequently, two diastereoisomers are possible. In the main isomer in the crystal (90%), the Ru-bound C3 atom is two carbon atoms apart from the P atom, whereas in the minor isomer (10%), the C3 atom is three carbon atoms apart from the P atom (Figure 3). It seems likely that these diastereoisomers are responsible for the double set of signals that was observed by NMR spectroscopy. The bond lengths observed for the $\eta^2$-bound olefin in complex **7** (Ru1−C4 2.179(6), Ru1−C3 2.185(5), C3−C4 1.361(8)) are similar to what was observed for a previously characterized $Ru\{PCy_2(\eta^2\text{-}C_6H_9)\}$ complex.[28b]

**Scheme 6**




**Scheme 7**




The clean formation of complex **7** via C−H activation of the cyclohexane group is evidence that the putative intermediate $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(PCy_3)]$, which is formed by displacement of one cymene ligand of complex **1** by one $PCy_3$ ligand, is highly reactive. Attempts to isolate this intermediate were so far not successful. However, it was possible to capture this intermediate by addition of dihydrogen. Thus, when a solution of complex **1** was heated with 1 equiv of $PCy_3$ in THF at 60 °C under an atmosphere of dihydrogen, the dihydrogen complex $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(H_2)(PCy_3)]$ (**8**) could be isolated in 50% yield (Scheme 6). An alternative, much cleaner formation of complex **8** was achieved by treating the ethylene complex **9**[11c] with dihydrogen. In this case, the isolated yield of complex **8** was 90%.

The $^1H$ NMR spectrum of complex **8** in $CD_2Cl_2$ shows a doublet at −11.83 ppm, which can be attributed to the dihydrogen ligand. The $H_2$ ligand is not bound very strongly: when solutions of complex **8** were stored under reduced pressure, the NMR signals of **8** gradually disappeared with the concomitant appearance of signals for several unidentified complexes. We have also attempted to convert the olefin complex **7** into the dihydrogen complex **8** by treatment with $H_2$, but complex **7** did not react with $H_2$, even at elevated temperatures.

The molecular structure of complex **8** in the crystal resembles that of the CO complex **6**. As expected, the Ru−Cl bond trans to the dihydrogen ligand is slightly shorter than what was observed for the Ru−Cl bond trans to the CO ligand of complex **6** (2.4532(16) vs 2.514(5) Å).

Next, we have examined whether it is possible to completely remove the cymene $\pi$-ligands of complex **1** in a nonprotic

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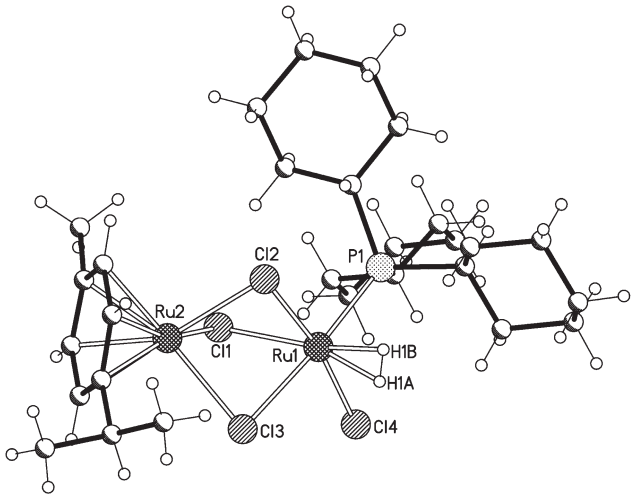


**Figure 4.** Graphic representation of the molecular structure of complex **8** in the crystal. The solvent molecules (1.5 toluene) are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.4532(16), Ru1−Cl2 2.4194(19), Ru1−Cl3 2.5468(18), Ru1−Cl4 2.3902(19), Ru1−P1 2.2871(19), Ru1−H1A 1.67(7), Ru1−H1B 1.79(7), Ru1···Ru2 3.2747(9); P1−Ru1−C1 98.84(6), P1−Ru1−Cl4 91.68(7), P1−Ru1−Cl2 96.55 (6), Cl4−Ru1−C2 170.66(6).

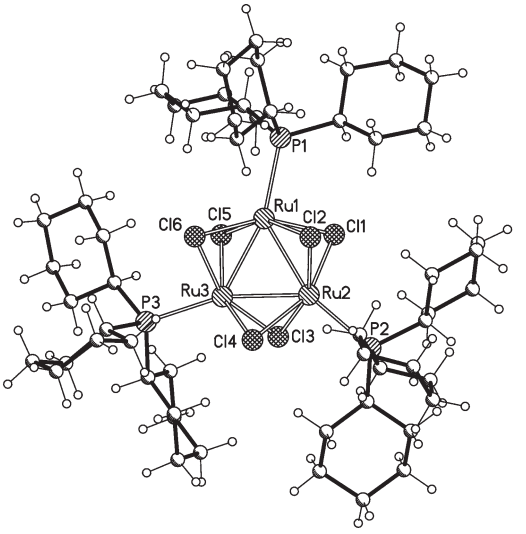


**Figure 5.** Graphic representation of the molecular structure of complex **10** in the crystal. The solvent molecules (6 THF) are not shown for clarity. Selected bond lengths (Å) and angles (deg): Ru1−Cl1 2.3908(14), Ru1−Cl2 2.4150(14), Ru1−Cl5 2.3712 (14), Ru1−Cl6 2.3649(15), Ru1−P1 2.4075(15), Ru1−Ru2 2.5885(6), Ru2−Ru3 2.5947(6), Ru1−Ru3 2.5944(6); Cl1−Ru1−Cl2 82.03(5), Cl5−Ru1−Cl2 155.23(5), Cl2−Ru1−P1 92.69(5).

solvent. This was achieved by heating a solution of complex **1** with 2 equiv of $PCy_3$ in THF for two days (Scheme 7). The product mixture was purified by column chromatography ($CHCl_3$, silica) to give complex **10** in 65% yield.

The complete loss of the cymene ligand was confirmed by NMR spectroscopy: the spectra showed only the signals for the $PCy_3$ ligand. A crystallographic analysis revealed that complex **10** possesses a trinuclear structure, in which the three $RuCl_2(PCy_3)$ fragments are connected by Ru−Ru bonds and by bridging chloro ligands (Figure 5). The Ru−Ru distances (2.5885(6), 2.5947(6), and 2.5944(6) Å) point to very strong metal−metal interactions. For comparison, the Ru−Ru bonds in trinuclear hydrido complexes of the general formula $[Ru_3H_3(O)(arene)_3]^+$ are approximately 0.2 Å longer (Ru−Ru=2.74−2.81 Å).[29] The compact $Ru_3$ core also shows rather short Ru−Cl bonds (Ru−Cl = 2.36−2.42 Å). The dinuclear complexes **6**, **7**, and **8**, for example, have Ru-($\mu$-Cl) distances between 2.42 and 2.56 Å. At 2.4075(15), 2.4014(15), and 2.4007(15) Å, the Ru−P bonds of **10** are within the expected range.[30]

Structurally related trimers with the sterically very demanding phosphine ligands $PAd_2Bu$ and $P^tBu_2Cy$ have recently been described.[31] These trimers were found to be very inert toward addition or substitution reactions. Similarly, complex **10** did not react with monodentate or bidentate phosphine ligands such as $PPh_3$, diphenylphosphinobutane, or 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP), even at elevated temperatures (70 °C, toluene, 3 h).

## Conclusion

In order to better understand the chemistry of the common catalyst precursor $\{\mathbf{1} + n\ PCy_3\}$, we have investigated the reaction of complex **1** with $PCy_3$ using different stoichiometries and reaction conditions. When methanol was used as the solvent, the hydrido complexes [(cymene)RuHCl($PCy_3$)] (**3**) and [RuHCl(CO)($PCy_3$)$_2$] (**5**) were obtained. Different synthetic routes have been described for both compounds, but our facile one-step procedures are attractive alternatives. This is particularly relevant for the 16 $e^-$ complex **5**, which is a potent catalyst for different organic transformations.

In nonprotic solvents, completely different reaction products were isolated. When **1** was reacted with 1 equiv of $PCy_3$, dinuclear complexes were formed. Of special interest is the olefin complex **7**, which contains a partially dehydrogenated $PCy_3$ ligand. This complex is indirect evidence that the intermediate species formed after $PCy_3$-induced release of one cymene $\pi$-ligand is highly reactive. The reactivity of the dinuclear complexes is in contrast to the inert cluster $[RuCl_2(PCy_3)]_3$ (**10**), which was obtained by complete removal of the cymene ligands. The fact that such an inert cluster can form by reacting **1** with $PCy_3$ should be considered for catalytic applications, as the formation of **10** might represent a possible deactivation pathway for the catalyst.

## Experimental Section

**General Procedures.** The synthesis of all complexes was performed under an atmosphere of dry dinitrogen or argon, using standard Schlenk techniques or a glovebox. The solvents were either dried using a solvent purification system from

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Innovative Technologies, Inc., or distilled from appropriate drying agents. The complexes $[(cymene)RuCl_2]_2$ (**1**)[1,2] and $[(cymene)Ru(\mu\text{-}Cl)_3RuCl(C_2H_4)(PCy_3)]$ (**9**)[11c] were prepared according to a literature procedure. $PCy_3$ (97%) was purchased from Strem Chemicals. The $^1H$ and $^{13}C$ spectra were recorded on a Bruker Advance DPX 400 or a Bruker Advance 200 spectrometer using the residual protonated solvents as internal standards. All spectra were recorded at room temperature.

**[(Cymene)RuCl$_2$(PCy$_3$)] (2).** A mixture of complex **1** (50 mg, 82 $\mu$mol) and $PCy_3$ (46 mg, 164 $\mu$mol) in MeOH (5 mL) was heated under dinitrogen for a few minutes until a clear solution was obtained. On cooling to room temperature, the product precipitated in the form of red microcrystals. They were collected, washed with pentane, and dried under vacuum (yield: 96 mg, 80%). Anal. Calcd (%) for $C_{28}H_{47}Cl_2PRu$: C 57.33, H 8.07. Found: C 57.15, H 8.05. The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra correspond to what has been described previously.[8d]

**[(Cymene)RuHCl(PCy$_3$)] (3).** A solution of complex **1** (100 mg, 163 $\mu$mol) in MeOH (10 mL) was added to a solution of $PCy_3$ (183 mg, 650 $\mu$mol) in MeOH (10 mL) under dinitrogen, and the mixture was stirred for 12 h at room temperature. The product precipitated in the form of an orange powder, which was isolated by filtration, washed with pentane, and dried under vacuum (yield: 117 mg, 65%). Anal. Calcd (%) for $C_{28}H_{48}ClPRu$: C 60.90, H 8.76. Found: C 60.69, H 8.86. The $^1H$, $^{13}C$, and $^{31}P$ NMR spectra correspond to what has been described previously.[13]

**[P(CH$_2$OH)Cy$_3$]Cl (4).** After separation of complex **3**, the solvent of the filtrate was evaporated and the resulting solid was dissolved in toluene (10 mL) with heating. On cooling to room temperature, a white microcrystalline solid precipitated, which was isolated by filtration, washed with pentane, and dried under vacuum (yield: 100 mg, 70%). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.34−2.48 (m, 33 H, $PCy_3$), 4.54 (s, 2 H, $CH_2OH$), 7.58 (s, 1 H, $CH_2OH$). $^{31}P$ NMR (162 MHz, $CD_2Cl_2$): $\delta$ (ppm) 26.94. Anal. Calcd (%) for $C_{19}H_{36}ClOP \times C_7H_8$: C 71.13, H 10.10. Found: C 70.74, H 10.46.

**[RuHCl(CO)(PCy$_3$)$_2$] (5).** A solution of complex **1** (50 mg, 82 $\mu$mol) in MeOH (25 mL) was added to a solution of $PCy_3$ (92 mg, 327 $\mu$mol) in MeOH (25 mL) under argon, and the mixture was stirred for 48 at 60 °C. After cooling to room temperature, the solution was concentrated to ∼10 mL. The product precipitated in the form of a yellow-brown powder, which was isolated by filtration, washed with hexane, and dried under vacuum (yield: 83 mg, 70%). Anal. Calcd (%) for $C_{37}H_{67}ClOP_2Ru$: C 61.18, H 9.30. Found: C 61.59, H 9.21. The $^1H$ and $^{31}P$ NMR spectra correspond to what has been described previously.[17,18]

**[(Cymene)Ru($\mu$-Cl)$_3$RuCl(CO)(PCy$_3$)] (6).** A solution of complex **1** (100 mg, 163 $\mu$mol) and $PCy_3$ (46 mg, 164 $\mu$mol) in a mixture of THF (10 mL) and allyl alcohol (1 mL) was heated to 60 °C under argon. After 48 h, the mixture was cooled to room temperature and concentrated to 2 mL. The addition of hexane (5 mL) resulted in the formation of an orange precipitate, which was filtered, washed with hexane, and dried under vacuum (yield: 90 mg, 70%). IR: $\nu$ (cm$^{-1}$) 1957 (CO). $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.23−1.33 (m, 9 H, $PCy_3$), 1.37 (d, $^3J$=7 Hz, 3 H, $CH(CH_3)_2$), 1.36 (d, $^3J$=7 Hz, 3 H, $CH(CH_3)_2$), 1.57 − 2.17 (m, 24 H, $PCy_3$), 2.31 (s, 3 H, $CH_3$), 2.95 (sept, $^3J$ = 7 Hz, 1 H, $CH(CH_3)_2$), 5.47 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.49 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.62 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.69 (d, $^3J$=6 Hz, 1 H, CH, cymene). $^{13}C$ NMR (101 MHz, $CD_2Cl_2$): $\delta$ (ppm) 18.73 ($CH_3$), 22.11, 22.22 ($CH(CH_3)_2$), 26.57−29.04 ($PCy_3$), 31.45 ($CH(CH_3)_2$), 35.72 (d, $J_{P,C}$=24 Hz, $PCy_3$), 78.52, 78.62, 79.20, 79.70 (CH, cymene), 96.95, 101.49 (C, cymene), 203.93 (d, $J_{P,C}$=18 Hz, CO). $^{31}P$ NMR (162 MHz, $CD_2Cl_2$): $\delta$ (ppm) 61.12 (s). Anal. Calcd (%) for $C_{29}H_{47}Cl_4OPRu_2$: C 44.28, H 6.02. Found: C 44.51, H 6.06. Single crystals were obtained by slow diffusion of pentane into a solution of complex **6** in $CH_2Cl_2$.

**[(Cymene)Ru($\mu$-Cl)$_3$RuCl{PCy$_2$(C$_6$H$_9$)}] (7).** A suspension of complex **1** (1.00 g, 1.63 mmol) and $PCy_3$ (457 mg, 1.63 mmol) in dioxane (50 mL) was heated to 70 °C under argon. After 3 days, the mixture was cooled to room temperature and concentrated to 30 mL. The addition of hexane (100 mL) resulted in the formation of an orange-brown precipitate, which was filtered, washed with hexane, and dried under vacuum (yield: 865 mg, 70%). The complex exists in the form of two isomers; the major isomer is labeled with an A, the minor isomer with a B. $^1H$ NMR (400 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.10−2.51 (m, $PCy_3$, A + B), 1.34 (d, $^3J$=7 Hz, $CH(CH_3)_2$, B), 1.36 (d, $^3J$=7 Hz, $CH(CH_3)_2$, A), 2.26 (s, $CH_3$, B), 2.28 (s, $CH_3$, A), 2.89−3.00 (m, $CH(CH_3)_2$, A + B), 4.40−4.69 (m, $CH_{olefin}$, A + B), 5.37 (d, $^3J$ = 6 Hz, CH, cymene, B), 5.41 (d, $^3J$=6 Hz, CH, cymene, A), 5.42 (d, $^3J$=6 Hz, CH, cymene, B), 5.47 (d, $^3J$=6 Hz, CH, cymene, A), 5.55 (d, $^3J$ = 6 Hz, CH, cymene, B), 5.61 (d, $^3J$=6 Hz, CH, cymene, A), 5.63 (d, $^3J$=6 Hz, CH, cymene, B), 5.66 (d, $^3J$=6 Hz, CH, cymene, A). $^{13}C$ NMR (101 MHz, $CD_2Cl_2$): $\delta$ (ppm) 18.69−38.50 (m, $CH_3$, $CH(CH_3)_2$, $PCy_3$, $CH(CH_3)_2$, A + B), 71.16 (d, $J_{P,C}$ = 2 Hz, $C_{olefin}$, B), 73.76 (d, $J_{P,C}$=2 Hz, $C_{olefin}$, A), 77.39 (d, $J_{P,C}$=2 Hz, $C_{olefin}$, B), 78.31, 78.69, 79.06, 79.74 (CH, cymene, A), 78.27, 78.49, 78.79, 79.57 (CH, cymene, B), 80.74 (d, $J_{P,C}$=2 Hz, $C_{olefin}$, A), 96.54, 96.70, 100.71, 100.82 (C, cymene, A + B). $^{31}P$ NMR (162 MHz, $CD_2Cl_2$): $\delta$ (ppm) 73.87 (A), 73.20 (B). Anal. Calcd (%) for $C_{28}H_{45}Cl_4PRu_2$: C 44.45, H 6.00. Found: C 44.43, H 5.97. Single crystals were obtained from a saturated dioxane solution.

**[(Cymene)Ru($\mu$-Cl)$_3$RuCl(H$_2$)(PCy$_3$)] (8).** Method A: A solution of complex **1** (500 mg, 816 $\mu$mol) and $PCy_3$ (229 mg, 816 $\mu$mol) in THF (70 mL) was heated at 60 °C under an atmosphere of dihydrogen. After 48 h, the mixture was cooled to room temperature. The product precipitated in the form of an orange powder, which was filtered and washed with hexane (yield: 310 mg, 50%). Method B: A suspension of complex

**Table 1. Crystallographic Data for Complexes 3 and 4**

| | **3** | **4**·0.5 $C_7H_8$ |
|---|---|---|
| empirical formula | $C_{28}H_{48}ClPRu$ | $C_{22.5}H_{40}ClOP$ |
| molecular weight [g mol$^{-1}$] | 552.15 | 392.97 |
| cryst size | 0.26 × 0.11 × 0.10 | 0.20 × 0.15 × 0.15 |
| cryst syst | monoclinic | tetragonal |
| space group | $P2_1/c$ | $P\bar{4}2_1/c$ |
| $a$ [Å] | 9.8265(5) | 15.0494(7) |
| $b$ [Å] | 10.6166(6) | 15.0494(7) |
| $c$ [Å] | 25.9342(14) | 20.1228(15) |
| α [deg] | 90 | 90 |
| $\beta$ [deg] | 91.287(4) | 90 |
| $\gamma$ [deg] | 90 | 90 |
| volume [Å$^3$] | 2704.9(3) | 4557.5(5) |
| $Z$ | 4 | 8 |
| density [g cm$^{-3}$] | 1.356 | 1.145 |
| temp [K] | 140(2) | 140(2) |
| absorp coeff [mm$^{-1}$] | 0.751 | 0.246 |
| $\theta$ range [deg] | 3.10 to 25.03 | 2.89 to 25.03 |
| index ranges | −11 → 11, −12 → 12, −30 → 30 | −17 → 17, −15 → 16, −23 → 23 |
| reflns collected | 15 813 | 26 991 |
| indep reflns | 4558 ($R_{int}$ = 0.0494) | 4012 ($R_{int}$ = 0.1284) |
| absorp corr | semiempirical | none |
| max. and min transmn | 0.9330 and 0.8201 | |
| data/restraints/params | 4558/0/284 | 4012/42/250 |
| goodness-of-fit on $F^2$ | 1.122 | 0.883 |
| final $R$ indices [$I > 2\sigma(I)$] | R1=0.0485, wR2=0.1012 | R1=0.0598, wR2=0.0477 |
| $R$ indices (all data) | R1=0.0626, wR2=0.1068 | R1=0.1385, wR2=0.0634 |
| largest diff peak/hole [e Å$^{-3}$] | 1.905/−0.535 | 0.390/−0.257 |

**Table 2. Crystallographic Data for Complexes 6 and 7**

| | **6**·$CH_2Cl_2$ | **7**·$C_2H_8O_2$ |
|---|---|---|
| empirical formula | $C_{30}H_{49}Cl_6OPRu_2$ | $C_{32}H_{53}Cl_4O_2PRu_2$ |
| molecular weight [g mol$^{-1}$] | 871.50 | 844.65 |
| cryst size | 0.20 × 0.18 × 0.10 | 0.29 × 0.25 × 0.19 |
| cryst syst | monoclinic | triclinic |
| space group | $P2_1/c$ | $P\bar{1}$ |
| $a$ [Å] | 10.117(15) | 9.4728(5) |
| $b$ [Å] | 18.24(3) | 14.6608(9) |
| $c$ [Å] | 20.20(2) | 14.6925(9) |
| α [deg] | 90 | 63.632(6) |
| $\beta$ [deg] | 100.04(10) | 76.162(5) |
| $\gamma$ [deg] | 90 | 81.792(5) |
| volume [Å$^3$] | 3672(10) | 1773.55(18) |
| $Z$ | 4 | 2 |
| density [g cm$^{-3}$] | 1.576 | 1.582 |
| temp [K] | 100(2) | 140(2) |
| absorp coeff [mm$^{-1}$] | 1.325 | 1.226 |
| $\theta$ range [deg] | 3.03 to 25.02 | 2.64 to 26.02 |
| index ranges | −12 → 12, −21 → 21, −24 → 23 | −11 → 11, −18 → 17, −17 → 18 |
| reflns collected | 52 633 | 15 703 |
| indep reflns | 6448 ($R_{int}$=0.2160) | 6928 ($R_{int}$=0.0431) |
| absorp corr | semiempirical | semiempirical |
| max. and min transmn | 1.0000 and 0.8846 | 0.792 and 0.588 |
| data/restraints/params | 6448/162/349 | 6928/331/453 |
| goodness-of-fit on $F^2$ | 1.159 | 0.962 |
| final $R$ indices [$I > 2\sigma(I)$] | R1=0.0923, wR2=0.1936 | R1=0.0494, wR2=0.1194 |
| $R$ indices (all data) | R1=0.1735, wR2=0.2398 | R1=0.0735, wR2=0.1265 |
| largest diff peak/hole [e Å$^{-3}$] | 2.160/−1.739 | 2.723/−0.977 |

**Table 3. Crystallographic Data for Complexes 8 and 10**

| | **8**·1.5$C_7H_8$ | **10**·6THF |
|---|---|---|
| empirical formula | $C_{38.5}H_{61}Cl_4PRu_2$ | $C_{78}H_{147}Cl_6P_3Ru_3$ |
| molecular weight [g mol$^{-1}$] | 898.78 | 1789.78 |
| cryst size | 0.19 × 0.12 × 0.10 | 0.30 × 0.22 × 0.21 |
| cryst syst | triclinic | monoclinic |
| space group | $P\bar{1}$ | $P2_1/n$ |
| $a$ [Å] | 9.6821(7) | 18.1411(7) |
| $b$ [Å] | 11.6760(10) | 26.1711(13) |
| $c$ [Å] | 19.3627(18) | 18.2851(10) |
| α [deg] | 73.612(8) | 90 |
| $\beta$ [deg] | 83.743(7) | 102.078(4) |
| $\gamma$ [deg] | 81.386(7) | 90 |
| volume [Å$^3$] | 2071.2(3) | 8493.7(7) |
| $Z$ | 2 | 4 |
| density [g cm$^{-3}$] | 1.441 | 1.400 |
| temp [K] | 140(2) | 140(2) |
| absorp coeff [mm$^{-1}$] | 1.051 | 0.820 |
| $\theta$ range [deg] | 2.98 to 25.03 | 2.98 to 25.03 |
| index ranges | −11 → 11, −13 → 13, −22 → 23 | −20 → 20, −31 → 31, −21 → 21 |
| reflns collected | 12 265 | 50 232 |
| indep reflns | 6405 ($R_{int}$=0.0667) | 13 584 ($R_{int}$=0.0548) |
| absorp corr | none | semiempirical |
| max. and min transmn | | 0.9456 and 0.8904 |
| data/restraints/params | 6405/85/461 | 13 584/40/840 |
| goodness-of-fit on $F^2$ | 0.914 | 0.876 |
| final $R$ indices [$I > 2\sigma(I)$] | R1=0.0550, wR2=0.1259 | R1=0.0413, wR2=0.0853 |
| $R$ indices (all data) | R1=0.0858, wR2=0.1364 | R1=0.0862, wR2=0.0946 |
| largest diff peak/hole [e Å$^{-3}$] | 1.486/−1.416 | 1.144/−0.837 |

[(cymene)Ru($\mu$-Cl)$_3$RuCl($C_2H_4$)($PCy_3$)] (**9**) (1.00 g, 1.30 mmol) in THF (100 mL) was stirred for 3 days under an atmosphere of dihydrogen. During this time, the dihydrogen atmosphere was refreshed several times by briefly applying vacuum followed by addition of dihydrogen. The product precipitated in the form of an orange powder, which was filtered and washed with hexane (yield: 870 mg, 90%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ (ppm) −11.83 (d, $J_{P,H}$=12 Hz, 2 H, Ru($H_2$)), 1.12−2.08 (m, 33 H, $PCy_3$), 1.35 (d, $^3J$=7 Hz, 6 H, CH($CH_3$)$_2$), 2.95 (sept, $^3J$=7 Hz, 1 H, C*H*($CH_3$)$_2$), 5.40 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.44 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.56 (d, $^3J$=6 Hz, 1 H, CH, cymene), 5.62 (d, $^3J$=6 Hz, 1 H, CH, cymene). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ (ppm) 18.74 ($CH_3$), 22.12, 22.27 (CH(*C*$H_3$)$_2$), 26.83 − 29.25 (m, $PCy_3$), 31.37 (*C*H($CH_3$)$_2$), 35.42 (d, $J_{P,C}$=24 Hz, $PCy_3$), 78.51 (br, CH, cymene), 78.89 (CH, cymene), 96.11, 101.45 (C, cymene). $^{31}$P NMR (162 MHz, $CD_2Cl_2$): $\delta$ (ppm) 67.40 (s). Anal. Calcd (%) for $C_{28}H_{49}Cl_4PRu_2$: C 44.21, H 6.49. Found: C 44.25, H 6.41. Single crystals were obtained from a saturated toluene solution upon cooling.

**[$RuCl_2(PCy_3)$]$_3$ (10).** A solution of complex **1** (100 mg, 163 $\mu$mol) and $PCy_3$ (92 mg, 326 $\mu$mol) in THF (5 mL) was heated to 70 °C. After 48 h, the solvent was evaporated under reduced pressure and the product was extracted with warm pentane. After elimination of the solvent under reduced pressure, the product was dissolved in chloroform and purified by column chromatography ($CHCl_3$, silica). The resulting powder was finally washed with a small amount of cold pentane (yield: 106 mg, 65%). $^1$H NMR (400 MHz, $CD_2Cl_2$): $\delta$ (ppm) 1.64−2.40 (m, 99 H, $PCy_3$). $^{13}$C NMR (101 MHz, $CD_2Cl_2$): $\delta$ (ppm) 27.91 (s, $PCy_3$), 29.17−29.27 (m, $PCy_3$), 31.62 (s, $PCy_3$), 36.72−38.86 (m, $PCy_3$). $^{31}$P NMR (162 MHz, $CD_2Cl_2$): $\delta$ (ppm) 62.97 (s). Anal. Calcd (%) for $C_{54}H_{99}Cl_6Ru_3P_3$: C 47.79, H 7.35. Found: C 47.84, H 7.55. Single crystals were obtained from a saturated THF solution upon cooling.

**Crystallographic Investigations.** The relevant details of the crystals, data collection, and structure refinement can be found in Tables 1−3. The diffraction data for **3**, **4**, **7**, **8**, and **10** were collected using Mo Kα radiation on a 4-circle kappa goniometer equipped with an Oxford Diffraction Sapphire/KM4 CCD at 140(2) K, and all data were reduced by Crysalis PRO.[32] The data for complex **6** were collected with a Bruker APEX II CCD at 100(2) K, and the data were reduced by EvalCCD.[33] Absorption correction was applied to all data sets using a semiempirical method.[34] All structures were refined using full-matrix least-squares on $F^2$ with all non-H atoms anisotropically defined. The hydrogen atoms were placed in calculated positions using the "riding model" with $U_{iso} = aU_{eq}$ (where $a$ is 1.5 for methyl hydrogen atoms and 1.2 for others). Structure refinement and geometrical calculations were carried out on all structures with SHELXTL.[35] Some disorder problems have been found for every structure having solvent molecules within the asymmetric unit. Restraints have been applied to obtain acceptable displacement parameters and/or atomic distances. A particular disorder has been found in the last stages of refinement of compound **7**; it deals with the bonded cyclohexene moiety and, in particular, with the $CH_2$ carbons of the cycle. It was possible to determine the two different orientations (named A and B) and to treat them anisotropically by applying some restraints (SADI and SIMU) to the final split

(32) *CrysAlis Software* system, Version 1.171.32; Oxford Diffraction Ltd., 2007.
(33) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220–229.
(34) Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33–38.
(35) Sheldrick, G. M. *SHELXTL*; University of Göttingen: Göttingen, Germany, 1997; Bruker AXS, Inc.: Madison, WI, 1997.

model of the cycle. For the complexes **3** and **8**, the hydrogen atoms directly bonded to the metal centers were located from the difference Fourier map and were treated as isotropic with $U_{iso} = 1.2U_{eq}$(Ru); the H−H distance of complex **8** was restrained to 0.76 Å by means of the DFIX card.

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**Supporting Information Available:** X-ray crystallographic file in CIF format is available free of charge via the Internet at http://pubs.acs.org.