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Copper(I) Halide Catalyzed Trans−Cis Isomerization of $RuCl_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$)

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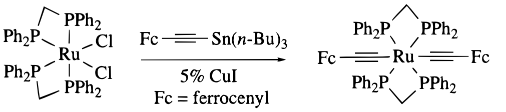
The complex *trans*-$RuCl_2(dppm)_2$ (*trans*-**1**) (dppm = $Ph_2PCH_2PPh_2$) has been converted to the corresponding cis isomer (*cis*-**1**) at room temperature in the presence of catalytic CuCl or CuI. The halide-bridged heterotrimetallic [{*cis*-$RuCl_2(dppm)_2$}$_2$Cu][$CuCl_2$] (**2**) was isolated when *trans*-**1** or *cis*-**1** was reacted with excess CuCl. Complex **2** was crystallized and characterized by single-crystal X-ray diffraction. Cell parameters for **2**·solvent: $a = 11.6059(4)$ Å, $b = 13.8415(5)$ Å, $c = 36.163(1)$ Å, $\beta = 95.03(1)°$ with $Z = 2$ in space group *P*2/*c*. The ^{31}P NMR spectrum of **2** indicates that several complexes are present in solution. Adding a small amount of **2** to a solution of *trans*-**1** results in isomerization to *cis*-**1**. Complex **2** was converted quantitatively to *cis*-**1** by reaction with excess [*n*-Bu_4N]Cl or HCl(aq). A mechanism for the catalytic isomerization of *trans*-**1** to *cis*-**1** and the formation of **2** is proposed.

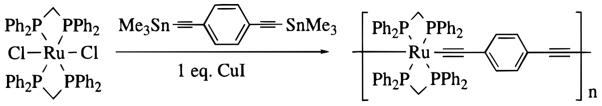
Introduction

Coupling reactions of ruthenium halide complexes with organostannane derivatives in the presence of copper(I) halides were recently reported (for example eqs 1 and 2).[1−4] These reactions are important in the synthesis of metal-containing conjugated polymers which are of significant current interest as organometallic "molecular wires".[2,5−10]



cis-**1**

(1)



trans-**1**

(2)

The function of the copper(I) halide in these reactions is not well understood, although it is likely that transmetalation of the acetylide group from RC≡CSnR'_3 (R′ = Bu, Me) to CuI is involved in the catalysis. This is very similar to the use of copper(I) compounds as cocatalysts in Stille reactions, in which organic electrophiles are coupled with organostannanes using Pd(0) catalysts.[11,12] In the Stille reaction, the Cu(I) has been shown to function by transmetalation with the organostannane as well as by scavenging phosphine from the Pd catalyst.[13]

The dual roles of Cu(I) in the Stille reaction suggested to us that the copper(I) halide catalysts in eqs 1 and 2 may play a more significant role than purely to increase the reactivity of the stannane by transmetalation. In order to investigate this question, we chose to examine the reactivity of CuCl or CuI with *trans*-$RuCl_2(dppm)_2$ (*trans*-**1**) or *cis*-$RuCl_2(dppm)_2$ (*cis*-**1**). Meyer has previously reported that the isomerization of *cis*-**1** to *trans*-**1** occurs by photochemical means or by oxidation and subsequent reduction and that the reverse process (*trans*-**1** → *cis*-**1**) occurs thermally in 1,2-dichloroethane at reflux (83 °C) in 10 h.[14] We report herein that CuCl or CuI may be used as a catalyst for the isomerization of *trans*-**1** to *cis*-**1**. In addition, we report the isolation and structural characterization of a halide-bridged heterotrimetallic complex that forms when *trans*-**1** or *cis*-**1** reacts with excess CuCl.

Experimental Section

General Details. All reactions were carried out under N_2 using Schlenk techniques. Bis(diphenylphosphino)methane (dppm),[15] *trans*-$RuCl_2(dppm)_2$,[16] *cis*-$RuCl_2(dppm)_2$,[14] and CuCl[17] were all prepared using literature procedures. Ruthenium(III) chloride hydrate (40−43% ruthenium) was purchased from Strem Chemicals. Electronic absorp-

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tion spectra were obtained in quartz cells on a UNICAM UV–vis spectrometer. The ^1H and $^{31}P\{^1H\}$ NMR experiments were performed on a Bruker CPX-200, Varian XL-300, or Bruker WH-400 spectrometer. Spectra were referenced to residual solvent (^1H) or external 85% H_3PO_4 (^{31}P).

Copper(I) Halide Catalyzed Conversion of *trans*-1 to *cis*-1. CuCl (0.7 mg, 0.007 mmol, 8 mol %) was added to a solution of *trans*-**1** (87 mg, 0.093 mmol) dissolved in methylene chloride (20 mL). The solution was stirred for 24 h at room temperature in the dark, during which the solution turned bright greenish yellow. Residual copper salts were removed by washing the solution with 2 M HCl (aq) and distilled water and drying over $MgSO_4$. The solution was reduced to approximately 2 mL and poured into hexanes (50 mL) to afford 74 mg of a yellow powder, which was 95% *cis*-**1** and 5% *trans*-**1**. Pure *cis*-**1** was obtained when the reaction was allowed to proceed for 6 days. When CuI was used as the catalyst under identical conditions, the same results were obtained.

[{*cis*-RuCl$_2$(dppm)$_2$}$_2$Cu][CuCl$_2$] (2). CuCl (17 mg, 0.17 mmol) was added to a solution of *trans*-**1** (96 mg, 0.10 mmol) dissolved in methylene chloride (20 mL). The suspension was stirred at room temperature for 2 h, during which it turned from orange-yellow to green-yellow. The solution was filtered through Celite 545, and the filtrate was reduced to approximately 2 mL. The solution was poured into hexanes (100 mL), yielding a yellow powder. The solid was recrystallized from layered methylene chloride/hexanes to give yellow needles, which were dried at 90 °C under vacuum for 2 days. Yield = 94 mg (89%). Anal. Calcd for $C_{100}H_{88}Cl_6P_8Cu_2Ru_2$: C, 57.70; H, 4.26. Found: C, 57.79; H, 4.13.

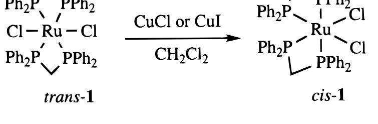
Crystallographic Structural Determination. A suitable single crystal, grown by slow diffusion of hexanes into a 1,2-dichloroethane solution of **2**, was selected and mounted inside a thin-walled glass capillary which contained mother liquor. Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. The systematic absences in the diffraction data and the determined unit-cell parameters were consistent for space groups *P*2/*c* and *Pc*. The *E* statistics strongly suggested the centric option, which yielded chemically reasonable and computationally stable results. A trial application of a semiempirical absorption correction based on redundant data at varying effective azimuthal angles yielded T_{max}/T_{min} at unity and was ignored.

The [{*cis*-RuCl$_2$(dppm)$_2$}$_2$Cu] cation is located at a 2-fold axis. A [CuCl$_2$] anion is located at an inversion center. Attempts to model several peaks of significant electron density, located away from the compound molecules, as a chemically recognizable, cocrystallized solvent molecule were not successful. These peaks were assigned arbitrary carbon atom identities with refined partial site occupancies. All non-hydrogen atoms were refined with anisotropic displacement coefficients except those on the apparent solvent molecules, which were refined isotropically. Phenyl groups were refined as idealized, flat, rigid bodies. All hydrogen atoms were treated as idealized contributions except those on the apparent solvent molecules, which were ignored.

The structure was solved by direct methods, completed by subsequent Fourier syntheses, and refined with full-matrix least-squares methods. All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library (G. M. Sheldrick, Siemens, Madison, WI). (See Table 1 for details.)

Results

Catalytic Isomerization of *trans*-1. When a CH_2Cl_2 solution of *trans*-**1** was stirred in the presence of CuCl or CuI (5–10 mol %) at room temperature for 24 h, *cis*-**1** was formed in high yield (90–95%) (eq 3). If the reaction was allowed to proceed for 6 days at room temperature in the absence of light, *trans*-**1** was quantitatively converted to *cis*-**1**. No *cis*-**1** was formed from *trans*-**1** at room temperature in the absence of catalyst.



(3)

Table 1. Crystallographic Data for **2**·solvent

formula	$C_{107.13}H_{88}Cl_6Cu_2P_8Ru_2$
fw	2165.02
crystal system	monoclinic
space group	*P*2/*c*
a, Å	11.6059(4)
b, Å	13.8415(5)
c, Å	36.163(1)
β, deg	95.03(1)
V, Å^3	5787.0(3)
Z	2
R(F),[a] %	5.38
$R_w(F^2)$,[a] %	16.47

[a] Quantity minimized = $R_w(F^2) = \sum[w(F_o^2 - F_c^2)^2]$; $R = \Delta/\sum(F_o)$, $\Delta = |F_o - F_c|$.

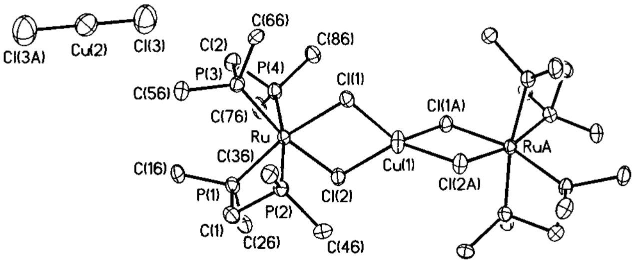
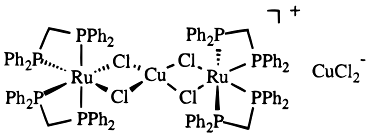


Figure 1. ORTEP diagram of the solid-state structure of **2**·solvent showing the atomic labeling scheme. The apparent solvent molecules and the phenyl groups, except the *ipso* carbon atoms, are omitted for clarity. The thermal ellipsoids are depicted at 30% probability.

We tested the catalytic reaction in the presence and absence of ambient laboratory light for 24 h and obtained identical results. Stirring a solution of *cis*-**1** without added copper(I) halide under ambient laboratory light resulted in the conversion to 60% *trans*-**1** after 24 h. However, with added CuCl or CuI under ambient light, only a small amount (<5%) of *trans*-**1** was formed. These results suggest that the presence of the copper(I) halide prevents formation of significant amounts of *trans*-**1**, presumably by reconversion of photochemically formed *trans*-**1** to *cis*-**1**.

Reaction of *trans*-1 with CuCl. A small amount (<5%) of a new phosphorus-containing product was also observed by ^{31}P NMR prior to workup when CuCl was used as the catalyst in eq 3. This product was obtained in high yield when a CH_2Cl_2 solution of *trans*-**1** or *cis*-**1** was stirred with excess CuCl at room temperature for 2 h. This complex was isolated and characterized as **2**.



2

Complex **2** was crystallized by diffusion of hexanes into a 1,2-dichloroethane solution to give yellow crystals whose structure was determined by single-crystal X-ray diffraction (Figure 1). The structure shows that **2** is a halide-bridged heterotrimetallic cationic complex in which the copper center has four chloride ligands bridging to the two ruthenium atoms. Although halide bridging ligands are common in coordination chemistry, halide-bridged heterobimetallic complexes are uncommon, and only several have been structurally

Table 2. Selected Bond Lengths in **2**·solvent (Å)

Ru−P(1)	2.303(2)	P(1)−C(1)	1.856(9)
Ru−P(2)	2.363(2)	P(1)−C(16)	1.842(5)
Ru−P(3)	2.312(2)	P(1)−C(26)	1.845(5)
Ru−P(4)	2.351(2)	P(2)−C(1)	1.853(8)
Ru−Cl(1)	2.470(2)	P(2)−C(36)	1.828(6)
Ru−Cl(2)	2.469(2)	P(2)−C(46)	1.820(4)
Cu(1)−Cl(1)	2.398(2)	P(3)−C(2)	1.856(8)
Cu(1)−Cl(1A)	2.398(2)	P(3)−C(56)	1.832(5)
Cu(1)−Cl(2)	2.398(2)	P(3)−C(66)	1.844(5)
Cu(1)−Cl(2A)	2.398(2)	P(4)−C(2)	1.822(9)
Cu(2)−Cl(3)	2.101(4)	P(4)−C(76)	1.80(1)
Cu(2)−Cl(3A)	2.101(4)	P(4)−C(86)	1.820(5)

Table 3. Selected Bond Angles in **2**·solvent (deg)

P(1)−Ru−P(2)	72.01(8)	C(26)−P(1)−Ru	119.3(2)
P(1)−Ru−P(3)	95.16(8)	C(16)−P(1)−Ru	126.1(2)
P(1)−Ru−P(4)	100.38(8)	C(26)−P(1)−C(16)	101.7(3)
P(3)−Ru−P(2)	102.30(8)	C(36)−P(2)−C(1)	106.4(4)
P(3)−Ru−P(4)	72.09(8)	C(46)−P(2)−C(1)	107.6(3)
P(4)−Ru−P(2)	170.41(8)	C(46)−P(2)−C(36)	99.9(2)
P(1)−Ru−Cl(1)	164.71(8)	C(56)−P(3)−C(2)	106.9(3)
P(1)−Ru−Cl(2)	93.61(8)	C(56)−P(3)−C(66)	100.8(3)
P(2)−Ru−Cl(1)	93.45(7)	C(66)−P(3)−C(2)	103.2(4)
P(2)−Ru−Cl(2)	92.34(8)	C(86)−P(4)−C(2)	106.6(4)
P(3)−Ru−Cl(1)	92.51(7)	C(86)−P(4)−C(76)	100.6(4)
P(3)−Ru−Cl(2)	164.69(8)	C(1)−P(1)−Ru	96.6(2)
P(4)−Ru−Cl(1)	94.56(7)	C(1)−P(2)−Ru	94.6(3)
P(4)−Ru−Cl(2)	93.99(8)	C(2)−P(3)−Ru	95.0(3)
Cl(2)−Ru−Cl(1)	82.03(7)	C(2)−P(4)−Ru	94.7(3)
Cl(2)−Cu(1)−Cl(1)	85.03(7)	C(36)−P(2)−Ru	123.2(2)
Cl(2)−Cu(1)−Cl(1A)	113.80(8)	C(46)−P(2)−Ru	123.1(2)
Cl(1A)−Cu(1)−Cl(1)	131.2(1)	C(56)−P(3)−Ru	127.1(2)
Cl(2A)−Cu(1)−Cl(1)	113.79(8)	C(66)−P(3)−Ru	120.4(2)
Cl(2A)−Cu(1)−Cl(1A)	85.04(7)	C(76)−P(4)−Ru	122.8(4)
Cl(2A)−Cu(1)−Cl(2)	134.9(1)	C(86)−P(4)−Ru	121.8(2)
Cl(3A)−Cu(2)−Cl(3)	180.0	Cu(1)−Cl(1)−Ru	96.42(7)
C(2)−P(4)−C(76)	109.0(4)	Cu(1)−Cl(2)−Ru	96.44(8)
C(16)−P(1)−C(1)	104.6(3)	P(2)−C(1)−P(1)	95.4(4)
C(26)−P(1)−C(1)	105.8(4)	P(4)−C(2)−P(3)	96.5(4)

characterized.[18−21] Complex **2** is the first example of a complex containing a dihalide bridge between ruthenium and copper centers. A previous study proposed a single bridging chloride on the basis of NMR evidence for $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})Cl_2Ru(\mu\text{-}Cl)\text{-}Cu(PCy_3)]$.[20] In complex **2**, the Cu atom is in a severely distorted tetrahedral environment with four equal Cu−Cl bond lengths of 2.398(2) Å. In comparison, the Cu−Cl bonds in $[\{(C_5H_{10}NO)_2Mo(\mu_2\text{-}S)_2Cu(\mu_2\text{-}Cl)\}_2]$ are 2.375(1) and 2.341(2) Å in length, while the Cu centers in this complex are much closer to a tetrahedral geometry than those in **2**.[22] The ruthenium centers in complex **2** are in a slightly twisted trigonal antiprismatic coordination, with Cl(1), P(3), and P(2) forming one face and Cl(2), P(4) and P(1) forming the opposite face. The Ru−Cl bonds in **2** (2.469(2), 2.470(2) Å) are slightly longer than the corresponding bonds in *cis*-**1** (2.440(2), 2.451(13) Å)[23], while the Cl−Ru−Cl angle is smaller in **2** (82.03(7)°) than in *cis*-**1** (84.1(5)°)[23]. The $[CuCl_2]^-$ counterion of **2** is linear with a Cu−Cl bond length of 2.101(4) Å, similar to the Cu−Cl bond length in $[(n\text{-}Bu)_4N][CuCl_2]$ (2.107(1) Å).[24] (See Tables 2 and 3 for selected bond distances and angles.)

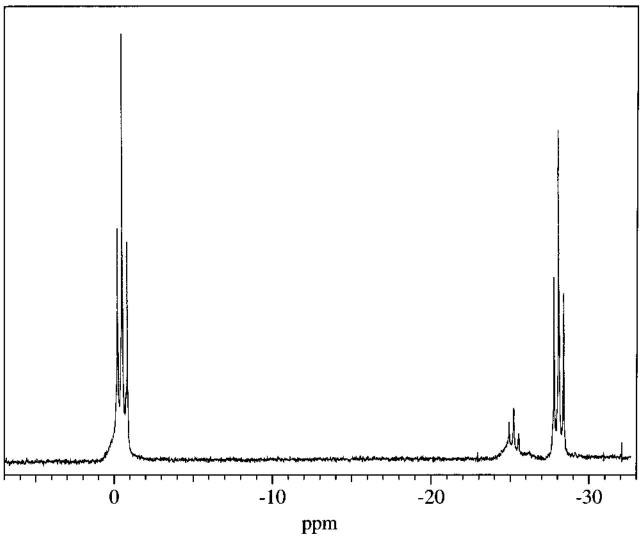
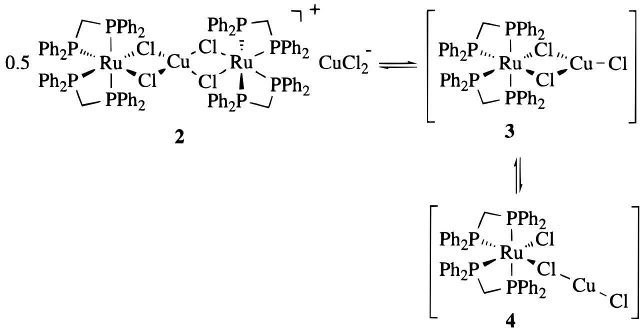


Figure 2. ^{31}P NMR spectrum of **2** in CD_2Cl_2.

Scheme 1



When pure crystalline **2** was dissolved in CD_2Cl_2, the ^{31}P NMR spectrum obtained suggested that several complexes were present in solution (Figure 2). Complex **2** is poorly soluble in most other weak donor solvents; however, the ^{31}P NMR spectrum of **2** in mixtures of CD_2Cl_2 and acetone or THF is similar to that in pure CD_2Cl_2. Complex **2** reacts with stronger donor solvents such as CH_3CN or CH_3NO_2. In CD_2Cl_2, the ^{31}P NMR spectrum consists of two major triplets (−0.5 and −28.2 ppm) and two smaller triplets (−0.4 and −25.3 ppm). In addition, there are broad peaks at 0 and −25 ppm which overlap the triplets. We attribute the four sharp triplets to the presence of two cis-substituted ruthenium complexes present in an approximately 4:1 ratio when **2** dissolves. Neither of these complexes is *cis*-**1**, and the small chemical shift differences between the sets of peaks indicate that they are structurally similar. We propose that these two major compounds are **2** and the intermediate **3** (Scheme 1). The molar conductivity (Λ_M) of an acetone solution of **2** is 207 Ω^{-1} cm^2 mol^{-1}, indicating that the major species in solution is the 1:1 electrolyte **2**. The broad peaks in the ^{31}P NMR spectrum may be due to species **4**, which would result if one of the Cu−Cl bonds in **3** breaks. The broad peaks could result from inequivalency of the phosphorus atoms in **4** or from chemical exchange with *cis*-**1**. Since **2** is a strong electrolyte, the relative concentrations of the species in Scheme 1 are expected to be independent of the amount of **2** added. A 10-fold increase in the amount of **2** dissolved does not change the ratio of **2** to the sum of **3** and **4** (integrated together in the ^{31}P NMR spectrum), consistent with the equilibria in Scheme 1.

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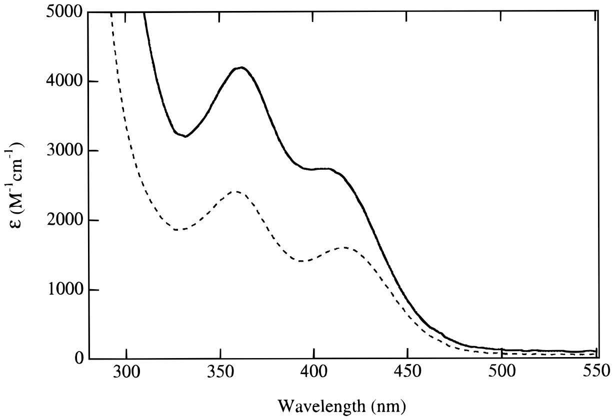


Figure 3. Absorption spectra of *cis*-**1** (- - -) and **2** (—) in CH_2Cl_2.

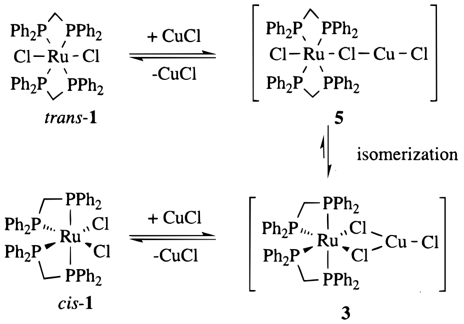
Addition of excess [*n*-Bu_4N]Cl or 2 M HCl(aq) to a solution of **2** resulted in complete conversion of all species present to *cis*-**1**. The added Cl^- presumably complexes the copper as $CuCl_2^-$, leaving *cis*-**1** as the only ruthenium-containing species. For this reason, when CuCl was used as a catalyst in eq 3, no **2** was isolated after workup with aqueous HCl. Subsequent addition of excess CuCl to a solution of **2** which had been treated with excess [*n*-Bu_4N]Cl results in the disappearance of peaks due to *cis*-**1** and reappearance of sharp peaks due to **2** and **3** as well as the broad peaks at 0 and −25 ppm in the ^{31}P NMR spectrum. These experiments demonstrate that *cis*-**1**, **2**, **3**, and **4** may be interconverted in the presence of CuCl and Cl^- and that the relative concentrations of these species in solution depend on the amount of CuCl and Cl^- present.

The progress of the reaction of *trans*-**1** with 1 equiv of CuCl in CD_2Cl_2 was followed by ^{31}P NMR. Since CuCl is poorly soluble, only a small amount dissolves initially and the reaction conditions are identical to the catalytic experiments. Upon addition of CuCl to the tube, the singlet in the ^{31}P NMR at −7.7 ppm due to *trans*-**1** broadens. In the early stages of the reaction, sharp resonances due to *cis*-**1** begin to appear, and eventually the resonances due to **2** and **3** also become apparent. When an identical experiment was carried out with *cis*-**1** and stoichiometric CuCl, reaction was very rapid in the NMR tube with complete disappearance of *cis*-**1** and formation of the equilibrium mixture of **2**−**4** within 5 min.

Complex *trans*-**1** isomerized to *cis*-**1** when a small amount of **2** was added to the solution. A solution of *trans*-**1** and 4 mol % **2** in CH_2Cl_2 was stirred at room temperature for 24 h, affording a solution which contained 90% *cis*-**1** and 10% *trans*-**1** by ^{31}P NMR. Adding a small amount of complex **2** to the isomerization reaction is analogous to adding catalytic CuCl. Intermediates **3** and **4** are formed directly in solution from **2**, introducing coordinated CuCl, which acts as a catalyst for the isomerization.

The UV−vis absorption spectrum obtained when **2** was dissolved in CH_2Cl_2 is similar to that of *cis*-**1** (Figure 3). It is likely that the bands in the spectrum of **2** are due to the same transitions observed for *cis*-**1**, with slight distortions due to the change in the ligand field around ruthenium upon coordination of the copper center. Since both **2** and **3** have very similar ligand environments at the ruthenium center, it is reasonable that both complexes exhibit similar visible transitions to *cis*-**1**. Solutions of **2** are stable under ambient laboratory light, consistent with the cis chloride ligands being locked in place on the ruthenium center by the copper, preventing photochemical isomerization.

Scheme 2



Discussion

We propose the following mechanism for the CuCl-catalyzed isomerization of *trans*-**1** to *cis*-**1**. As the CuCl dissolves, it coordinates to one of the chloride ligands in *trans*-**1**, yielding halide-bridged intermediate **5** (Scheme 2). We do not observe **5** in the ^{31}P NMR spectrum but observe a broadening of the singlet at −7.7 ppm. This broadening is specific to this peak and so is not due to nonspecific broadening as would be caused by paramagnetic Cu(II) impurities. It is possible that the broadening is caused by exchange between **5** and *trans*-**1**.

The ruthenium center in intermediate **5** is still trans substituted. Coordination of the CuCl is expected to weaken the Ru−Cl bond, facilitating isomerization to the more stable cis orientation at the ruthenium center. The Ru−Cl bond is lengthened in **2** compared to *cis*-**1**, consistent with a weakening of the Ru−Cl bond upon coordination of Cu. Thermodynamically, $RuCl_2(dppm)_2$ prefers the cis orientation. Meyer argued that this is because *cis*-**1** is stabilized by π-donation from the Cl through the Ru to a trans P, whereas this favorable interaction is not possible in the trans isomer.[14] We propose that **5** isomerizes to **3**, in which the ruthenium center has a cis geometry and the CuCl is coordinated to both chloride ligands. The intermediate **3** can then lose CuCl, presumably via **4**, to yield *cis*-**1**. This pathway is likely under catalytic conditions when there is a large excess of ruthenium species relative to CuCl. Under these conditions, any **3** which is formed probably reacts with *trans*-**1**, yielding *cis*-**1** and **5**. The equilibrium between **5** and **3** is expected to favor **3** due to both the favorable geometry of the ruthenium center in this complex and the stabilizing effect of coordination of the copper with both bridging chlorides. The effect of the CuCl is therefore to weaken the Ru−Cl bond in **5** and to stabilize intermediate **3**.

When stoichiometric amounts of CuCl are available, sufficient copper is present to complex all the available ruthenium species. We have shown that the reaction between *cis*-**1** and CuCl is rapid, so it is reasonable that **2** and **3** are the final products observed in the reaction between *trans*-**1** and stoichiometric CuCl. Because CuCl is poorly soluble, *cis*-**1** is observed first in this reaction followed by **2** and **3** as *trans*-**1** is consumed and *cis*-**1** is formed.

The copper(I) halide catalyzed isomerization of *trans*-**1** to *cis*-**1** provides an alternative, low-temperature route to the cis complex. Although a previous report indicated that complexes structurally related to *trans*-**1** such as *trans*-[$RuCl_2((o\text{-}C_6H_4(PMePh)_2)_2)$] can be isomerized to the corresponding cis isomer using excess triethylaluminum, this procedure involves air-sensitive reagents and proceeds via hydrido intermediates which must be hydrolyzed to regenerate the product.[25]

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[25] Grocott, S. C. *Inorg. Chem.* **1982**, *21*, 3526−3524.

Our method may allow for the convenient preparation of cis isomers of similar complexes which are difficult to isomerize thermally.

The results reported herein are important for understanding copper(I) halide catalyzed reactions involving *trans*-**1** and *cis*-**1**. It is likely that syntheses such as those shown in eqs 1 and 2 involve intermediates such as **2**−**5** in which the copper coordinates to the ruthenium halide complex. When the starting material is *trans*-**1** (as in eq 2), copper-catalyzed isomerization may generate cis-substituted intermediates in which the chloride ligands are more labile, facilitating reaction with the organostannane. In addition, since **2** is a soluble complex, it may be useful to use this directly as a reagent with organostannanes to make bisacetylide complexes and polymers.

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Supporting Information Available: An ^1H NMR spectrum of **2** (1 page). An X-ray crystallographic file, in CIF format, for complex **2** is available on the Internet only. Ordering and access information is given on any current masthead page.

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