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Reaction of organic halides with $[Cu^{I}(TMPA)CH_3CN]PF_6$

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Abstract

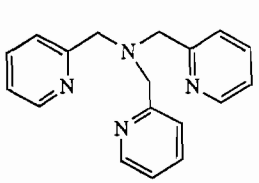
Under mild conditions, the copper(I) complex $[Cu^{I}(TMPA)CH_3CN]PF_6$ (TMPA = tris(2-pyridylmethyl)amine), reacts stoichiometrically with benzyl and allyl halides, and α-halo-ketones to produce near quantitative yields of carbon–carbon reductively coupled products bibenzyls, diolefins or diketones, respectively. The copper complex acts as the halide acceptor and the copper(II) complex $[Cu^{II}(TMPA)X]PF_6$ ($X = Cl^-$ or Br^-) is also isolated. No firm mechanistic conclusions can be drawn, but the intermediacy of oxidatively added RX products, i.e. organo–Cu(II) or Cu(III), is suggested.

Introduction

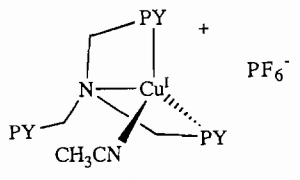
Transition metals in low oxidation states have been used extensively as reagents for reductive coupling of benzylic halides. Titanium [1], vanadium [2], chromium [3], tungsten [4] and nickel [5] have been utilized to activate the carbon–halogen bond in benzylic halides and may be prepared *in situ* by reducing the appropriate metal halide with strong reducing agents such as lithium aluminium hydride or lithium metal in the presence of naphthalene. Nickel(I) [6], cobalt(I) [7] and vanadium(II) [8] complexes or metal carbonyls of nickel [9], cobalt [10], iron [11], molybdenum [12] and tungsten [4], as well as metallic iron [13], have been employed for reductive coupling of benzylic mono- and polyhalides. However, most of the coupling reagents mentioned above suffer disadvantages of having moderate or low yields due to side reactions (e.g., the reduction of benzylic compounds to toluene derivatives) and the low-valent reagents prepared *in situ* from metal halides by using lithium aluminum hydride have the limitations of not being compatible with functional groups which react with lithium aluminum hydride (e.g., cyano and nitro groups).

Despite the fact that lithium organocuprates are widely used in synthetic organic chemical processes [14], there are only a few examples in the literature for activating the carbon–halogen bond with copper complexes. Homo- and cross coupling of alkyl and aryl halides can be facilitated by using metallic copper prepared from $CuI \cdot P(Et)_3$ and lithium metal in the presence of naphthalene [15]. A bis(diimine) copper(I) complex was employed to couple benzylic halides in photoassisted electron transfer reactions [16]. In addition, copper–amine complexes activate carbon–halogen bonds in polyhalomethanes, facilitating hydrogen atom abstraction from various hydrocarbons [17] and addition of carbon tetrachloride [18] and chloroform [19] to styrene.

In the course of our studies on mimicking dioxygen transporting enzymes with model copper complexes [20] we found that a copper(I) complex of TMPA (**1**, PY = 2-pyridyl) reacts with dichloromethane resulting in the formation of chloro–copper(II) compounds. This inspired us to investigate the reaction of $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) with a number of halogenated hydrocarbons.



TMPA



1

$[Cu^{I}(TMPA)CH_3CN]PF_6$

Results and discussion

Compound $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**), used here as the reductive coupling agent, was prepared

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as described elsewhere [20b, c]. The coupling reactions were carried out under mild conditions by stoichiometric addition of the benzylic halide to a stirred solution of **1** in deaerated acetonitrile.

$$\underset{\mathbf{1}}{ArCH_2X} + [Cu^{I}(TMPA)CH_3CN]PF_6 \xrightarrow[CH_3CN]{Ar}$$

$$\frac{1}{2}\underset{\mathbf{2}}{ArCH_2CH_2Ar} + \underset{\mathbf{3a}\ (X=Cl)\quad \mathbf{3b}\ (X=Br)}{[Cu^{II}(TMPA)X]PF_6}$$

X = Cl, Br

The reactions proceed smoothly at room temperature, generally going to completion in a few hours or less, and yield nearly pure homocoupled products in addition to the oxidized copper(II) halide complexes (**3a, b**).

The results of the reactions with benzylic mono- and polyhalides are summarized in Table 1 which serves to illustrate the selectivity and generally high yield of the reactions. Thus, benzyl bromide reacts rapidly at room temperature to given bibenzyl (**2**) in nearly quantitative yield along with $[Cu^{II}(TMPA)Br]PF_6$ (**3b**). Other benzylic monohalides such as bromodiphenylmethane, 9-bromofluorene, and (±)-1-bromophenylethane also undergo reductive homocoupling to afford the corresponding ethane derivatives (**4–6**) in 87–99% yield. Chlorotriphenylmethane, on the other hand, couples to give the unsymmetrical quinoid compound 1-diphenylmethane-4-trityl-2,5-cyclohexadiene (**7**). In general, these transformations were found to occur without appreciable side reactions; however, in the case of 9-bromofluorene, a trace amount of the corresponding reduction product, fluorene (**5b**), was observed along with the coupled product, bifluorene (**5a**).

In addition to the monohalides, benzylic di- and trihalides were also subjected to reaction with **1**, affording substituted ethenes. For example, α,α-dichlorotoluene gave almost exclusively the *trans*-isomer of stilbene (**8**) in 92% yield (a trace of the *cis*-isomer was observed by GC). Compound **3a** could also be isolated.

$$\underset{\mathbf{1}}{PhCHCl_2} + 2[Cu^{I}(TMPA)CH_3CN]PF_6 \xrightarrow[CH_3CN]{Ar}$$

$$\frac{1}{2}\underset{\mathbf{8}}{PhCH=CHPh} + \underset{\mathbf{3a}}{2[Cu^{II}(TMPA)Cl]PF_6}$$

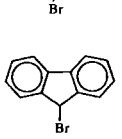
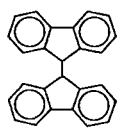
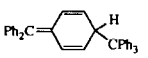
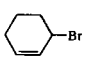
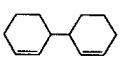
Reaction of 1 equiv. of α,α,α-trichlorotoluene with 3 equiv. of **1** resulted in the formation of a mixture of *cis*- and *trans*-1,2-dichloro-1,2-diphenylethene (**9**) (*cis*/*trans* = 80/20) with no diphenylacetylene detected by GC. The same reaction carried out with a Cu(I):trihalide ratio of 2:1 gave essentially the same product distribution in 99% yield (Table 1).

Allyl halides are also reactive toward **1** although possibly to a lesser extent than the benzylic compounds. Thus, 3-bromocyclohexene was coupled to give bi-2-cyclohexen-1-yl (**10**) in 68% yield.

Reacting $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) with phenacyl chloride, in which the carbon–halogen bond is 'activated' by the neighboring keto group, gives mainly an α,δ-diketo compound (**11b**) along with acetophenone (**11a**) as fully reduced side-product (Table 1).

A number of halogenated compounds were found to be unreactive toward $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**). These include primary, secondary and tertiary halides such as 1-bromopentane, bromocyclohexane and 2-bromo-2-methylpropane. The aromatic carbon–halogen bond was also unreactive toward the copper(I) reagent as evidenced by the failure of 4-bromotoluene to couple. In addition, the geminal dihalide 1,1-dichloro-3,3-dimethylbutane also did not undergo any coupling reaction with **1** which was surprising in light of the observation that dichloromethane readily reacts to give **3a** and an as yet undetermined organic product.

TABLE 1. Reductive coupling of benzyl and allyl halides, and α-haloketones by $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**)

Substrate	Product		Yield (%)
Ph-CH_2Br	Ph-CH_2-CH_2-Ph	**2**	91[a]
Ph-CH(Br)-Ph	Ph_2CH-$CHPh_2$	**4**	99[a]
		**5a**	96[b]
	Fluorene	**5**	3[b]
Ph-CH(CH_3)-Br	Ph-CH(CH_3)-CH(CH_3)-Ph	**6**	89[a]
Ph_3C-Cl		**7**	42[a]
Ph-$CHCl_2$	Ph-CH=CH-Ph (*trans*)	**8**	92[a]
Ph-CCl_3	Ph-C(Cl)=(Cl)C-Ph	**9**	99[a, c]
		**10**	68[a]
Ph-C(=O)-CH_2Cl	Ph-C(=O)-CH_3	**11a**	9[b], 36[e, b]
	Ph-C(=O)-CH_2-CH_2-C(=O)-Ph	**11b**	44[b], 0[e, b]
	Ph-C(=O)-CH=CH-C(=O)-Ph	**11c**	~3[d], 0[e, d]

[a]Isolated yield. [b]Determined by ^1H NMR. [c]*cis*/*trans* Ratio determined by GC was 4:1. [d]Determined by GC. [e]Solvent: 90% CH_3CN + 10% H_2O.

Mechanistic aspects

Considering the mechanistic studies on reductive coupling of organic halides with lithium diorganocuprates [14, 21] and other metal complexes [1–16, 22], there are two likely mechanistic pathways for the reductive coupling of allyl, benzyl and α-keto halides by $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**): these are *ionic* (oxidative addition) and *radical* (Scheme 1, eqns. (1) and (2)). Due to the fact that **1** has a relatively high negative redox potential, an electron transfer represents a reasonable way for the Cu^{I} donor to interact with the electron-deficient organic halide to form the radical ion pair **I** which is the common intermediate in both pathways. Cage collapse affords oxidative adduct **II** in eqn. (1), which is competitive with a diffusion process (eqn. (2)) resulting in the formation of organic radicals and Cu^{II} complexes. The stability and the lifetime of the caged ion pair then determine the dominant pathway (i.e. ionic or radical) in the course of the reaction. The oxidative addition product organo–Cu^{III} complex (**II**) would attack another RCH_2X molecule in a nucleophilic substitution reaction affording the coupled organic product and a dihalo–Cu^{III} complex (eqn. (3)) which reacts with Cu^{I} to yield the Cu^{II} product (eqn. (4)), and/or would be reduced by the $RCH_2^{\cdot}$ radical (eqn. (5)). The fate of the organic radical formed in the diffusion decay of **I** would be either dimerization (eqn. (6)) or oxidative addition to the Cu^{I} complex present (eqn. (7)*) to produce an alkyl–Cu^{II} complex (**III**) or the reduction of complexes **II** (eqn. (5)) and **III** (eqn. (9)). There are several examples in the literature supporting these hypotheses, showing that organic radicals readily add to copper(I) and copper(II) complexes [16, 21, 22a, 23, 24] and that they are also capable of reducing organometallic compounds [6e, 23a, 25].

In an attempt to isolate intermediates of the type **II** or **III** (Scheme 1) we reacted $[Cu^{I}(TMPA)CH_3CN]ClO_4$ (**1**-ClO_4) with *N*-bromophthalimide (Scheme 2). We were able to isolate a stable solid **12** corresponding to the type **III** intermediate in Scheme 1. Complex **12** may have been formed by the reaction of an intermediate addition product of **1** and *N*-bromophthalimide with more complex **1**, as shown. Compound $[Cu^{II}(TMPA)Br]ClO_4$ (**3b**-ClO_4) was also isolated from the reaction mixture (see 'Experimental'). The reaction shown in Scheme 2 could also occur via a free radical mechanism.

*Meyerstein and co-workers have described this kind of reaction as an equilibrium process, as well [23b].

$$RCH_2X + Cu^{I} \longrightarrow \underset{\mathbf{I}}{\{RCH_2^{\cdot}, Cu^{II}X\}} \begin{cases} \longrightarrow \underset{\mathbf{II}}{RCH_2Cu^{III}X} & (1) \\ \longrightarrow RCH_2^{\cdot} + Cu^{II}X & (2) \end{cases}$$

$$\underset{\mathbf{II}}{RCH_2Cu^{III}X} + RCH_2X \longrightarrow RCH_2CH_2R + Cu^{III}X_2 \quad (3)$$

$$Cu^{III}X_2 + Cu^{I} \longrightarrow 2Cu^{II}X \quad (4)$$

$$\underset{\mathbf{II}}{RCH_2Cu^{III}X} + RCH_2^{\cdot} \longrightarrow Cu^{II}X + RCH_2CH_2R \quad (5)$$

$$2RCH_2^{\cdot} \longrightarrow RCH_2CH_2R \quad (6)$$

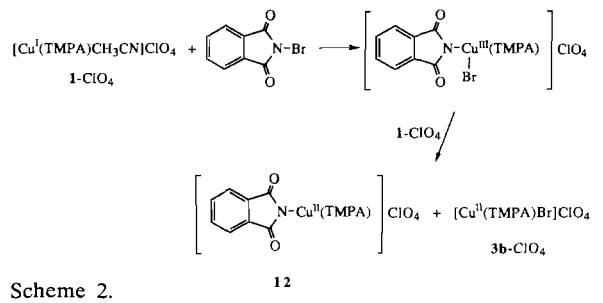
$$RCH_2^{\cdot} + Cu^{I} \longrightarrow \underset{\mathbf{III}}{RCH_2Cu^{II}} \quad (7)$$

$$\underset{\mathbf{III}}{RCH_2Cu^{II}} + RCH_2X \longrightarrow RCH_2CH_2R + Cu^{II}X \quad (8)$$

$$\underset{\mathbf{III}}{RCH_2Cu^{II}} + RCH_2^{\cdot} \longrightarrow Cu^{I} + RCH_2CH_2R \quad (9)$$

(R = aryl, alken-1-yl, acyl)

Scheme 1.



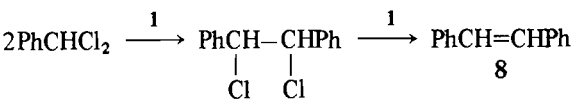
Scheme 2.

EPR measurements were carried out in order to provide evidence for the presence of the radical and/or copper(III) intermediates postulated above. Unfortunately, no EPR signal was observed in the course of the reaction of $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) with organic halides, which means that the lifetimes of these postulated paramagnetic intermediates are either too short to be detectable or there is a magnetic interaction between the paramagnetic centers in the solvent cage, causing line-broadening which makes them EPR undetectable.

When benzyl bromide was reacted with $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) in the presence of acrylonitrile, in addition to the coupled product **2**, 4-phenylbutanenitrile, 2-benzyl-4-phenylbutanenitrile and 4-cyano-6-phenylhexanenitrile were formed, indicating the intermediacy of either the benzyl radical and/or benzyl–copper complexes or both. Since both radicals [26] and organometallic compounds [22a, b; 6a, 27] react with alkenes, this method can not differentiate between the radical and oxidative addition pathways. More selective trapping methods should be used to elucidate this problem.

The compounds α,α-dichlorotoluene and α,α,α-trichlorotoluene can also be reductively coupled by $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) to form *trans*-stilbene (**8**) and a mixture of *cis* and *trans*-1,2-dichloro-1,2-diphenylethene (**9**), respectively (see above). One can think of two feasible pathways for the reductive coupling of benzylic polyhalides by transition metal complexes, either via a carbene–metal species or via a step-by-step dehalogenation. A carbene mechanism was assumed for the $Fe(CO)_5$ [11a], $Ni(COD)_2$, $Co_2(CO)_9$ [28], and the $W(CO)_6$ [4] promoted reductive coupling of gem-dihalides. On the other hand, it was suggested that the reaction with $Co_2(CO)_8$ [10] or metallic iron [29] proceeds via a step-by-step mechanism.

The reaction of α,α-dichlorotoluene with $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) was carried out in the presence of an excess of cyclohexene in order to try to trap any carbene intermediates. However, no cyclopropane derivative could be detected, suggesting that a step-by-step mechanism operates in the reaction.



Thus, a reductive coupling takes place in the first step followed by a reductive dehalogenation of the 1,2-dichloro-1,2-diphenylethane intermediate. Indeed, we found that 1,2-dichloro-1,2-diphenylethane reacts with $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) to yield *trans*-stilbene in 99% yield.

In the case of 9-bromofluorene and phenacyl chloride not only coupled products but the formation of hydrocarbons (fluorene and acetophenone, respectively) was also observed (*vide supra*). This phenomenon can be rationalized by (i) hydrogen atom abstraction from the solvent (or from the coupled product indicated by the formation of the ethene derivative (**11c**, Table 1)) by radical intermediates and/or (ii) there is a competition between the RCH_2^{+} and H^{+} which comes from the solvent (the carbon–hydrogen bond in CH_3CN is fairly acidic) to react with the $RCH_2Cu^{III}X$ intermediate in eqn. (3) (Scheme 1). Accordingly, when phenacyl chloride was reacted with $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) in the presence of water which is a better $H^{+}/H^{\cdot}$ donor than acetonitrile, the yield of acetophenone (**11a**) increased and no formation of coupled product was observed.

Conclusions

The cationic complex $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) is a strongly reducing Cu(I) compound* which is capable of the stoichiometric and highly efficient reductive coupling of benzyl and allyl halides and α-halo-ketones under mild conditions. While no firm mechanistic conclusions can be drawn, the intermediacy of organo–Cu(II) or Cu(III) species is suggested. The considerable current interest [31] in reductive coupling processes mediated by mild one-electron reducing agents prompts us to pursue related chemistry using **1** or new analogues; we are currently investigating such possibilities.

Experimental

Materials and methods

NMR spectra were recorded on a Varian XL-300 spectrometer using $CDCl_3$ as the solvent and Me_4Si as the internal reference. Gas chromatography was

*The redox potential of an analogous copper(II) complex, $[Cu(TMPA)Cl]PF_6$, was found to be -0.39 V vs. NHE in dimethylformamide [30].

carried out on a Hewlett-Packard 5890 gas chromatograph using a 30-meter HP5 (crosslinked 5% phenyl methyl silicone) capillary column. Mass spectra (EI) were recorded with a Hewlett-Packard 5970 mass selective detector interfaced to an HP 5980 gas chromatograph (12-m capillary column, crosslinked methyl silicone gum). IR spectra were taken with a Perkin-Elmer 283 spectrophotometer as KBr disks or neat liquids. Melting points were determined with a Buchi 510 capillary melting point apparatus and are uncorrected.

Organic halides were commercially available and were used as received unless otherwise noted. Acetonitrile (spectrophotometric grade), acrylonitrile and cyclohexene were used from freshly opened bottles. All coupling reactions were carried out at room temperature under an atmosphere of argon with the reagents used in the ratio of Cu:halogen ≈ 1:1. Products were identified by comparison of their physical and spectral properties with those of commercially available authentic samples or reported values. Except where stated otherwise, yields of organic products were determined by isolation with product purity judged by ^{1}H NMR and GC (further purification was generally not required as determined by these methods).

Reaction of dichloromethane with [Cu^I(TMPA)CH$_3$CN]PF$_6$ (1) in CH$_3$CN. Isolation of [Cu^{II}(TMPA)Cl]PF$_6$ (3a)

To a solution of 0.506 g (0.937 mmol) [Cu^I(TMPA)CH$_3$CN]PF$_6$ (**1**) in 20 ml of CH$_3$CN (under Ar) was added 10 ml of a 1:9 (vol./vol.) mixture of dichloromethane/CH$_3$CN. Upon addition of the dichloromethane, the bright orange Cu(I) solution began to turn green and the reaction mixture was stirred for *c.* 1 h. The product was precipitated with diethyl ether (200 ml) to give 0.482 g (96%) of [Cu^{II}(TMPA)Cl]PF$_6$ (**3a**) as a blue–green powder. Identification of the inorganic product was made on the basis of spectroscopic comparison (IR, UV–Vis) to an authentic sample of **3a**; the organic product was not identified.

General procedure for coupling of organic halides with [Cu^I(TMPA)CH$_3$CN]PF$_6$ (1)

Solid [Cu^I(TMPA)CH$_3$CN]PF$_6$ (**1**) was added to an evacuated and argon purged 50-ml Schlenk flask. A 100-ml Schlenk addition funnel was attached to the reaction flask and charged with 10 ml of CH$_3$CN which was degassed by bubbling with argon for 20 min. The acetonitrile was added to the Cu(I) complex and the resulting orange solution was stirred for 10 min. To the addition funnel was then added a solution of the organic halide in 20 ml of CH$_3$CN. After bubbling with Ar for 20 min, the halide solution was then added to the reaction flask dropwise, with stirring, causing a gradual color change of the mixture from orange to green. The reaction was judged to be complete when GC monitoring of the reaction mixture indicated that the starting halide was either completely consumed or showed no further change. Acetonitrile was removed *in vacuo* at room temperature and the organic product extracted from the solid mixture by elutriation with diethyl ether or benzene (3–20 ml). The resulting organic solution was filtered through a disposable nylon filter unit (Nalgene, 0.45 μm) and the solvent removed by rotary evaporation. The product was dried *in vacuo* and subjected to physical characterization by IR, GC, NMR and GC/MS.

Inorganic products were obtained in high yield (80–95%). [Cu^{II}(TMPA)Cl]PF$_6$ (**3a**) was isolated without further purification and identified by comparison of its spectral properties (IR, UV–Vis) with those of authentic material. In one case (see below) [Cu^{II}(TMPA)Br]PF$_6$ (**3b**) was purified by recrystallization and subjected to physical and spectroscopic characterization.

1,2-Diphenylethane (2)

Benzyl bromide (0.209 g, 1.22 mmol) was added to [Cu^I(TMPA)CH$_3$CN]PF$_6$ (**1**) (0.663 g, 1.25 mmol) in CH$_3$CN at room temperature as described above. The reaction was stopped after 20 min and worked up to give 0.102 g (92%) of white crystalline solid **2**; m.p. 50–51 °C (lit. 51.2 °C [32]). ^{1}H NMR (CDCl$_3$): δ 7.17–7.31 (m, 10 H), 2.92 (s, 4 H); ^{13}C NMR (CDCl$_3$): δ 141.75, 128.43, 128.31, 125.90, 37.94; NMR spectral data were consistent with those reported [33]. GC/MS (*m/z* (rel. abund.)): 182 (M^+, 18), 92 (10), 91 (100), 89 (5), 77 (6), 65 (35), 63 (8), 51 (13).

1,1,2,2-Tetraphenylethane (4)

Bromodiphenylmethane (0.263 g, 1.06 mmol) was allowed to react with **1** (0.573 g, 1.06 mmol) for 1 h according to the general procedure. Workup yielded 0.177 g (99%) of **4** as a cream-colored crystalline solid; m.p. 207–209 °C (lit. 208–209 °C [34]). ^{1}H NMR (CDCl$_3$): δ 6.97–7.22 (m, 20 H), 4.77 (s, 2 H); ^{13}C NMR (CDCl$_3$): δ 143.46, 128.49, 128.12, 125.83, 56.32. GC/MS (*m/z* (rel. abund.)): 168 (14), 167 (100), 165 (32), 152 (19), no M^+ peak observed.

9,9'-Bifluorene (5a)

Reaction of 9-bromofluorene (0.243 g, 0.991 mmol; purified by recrystallization from ethanol/water) with **1** (0.535 g, 0.991 mmol) for 2 h followed by the usual workup gave 0.178 g of a mixture of 9,9'-

bifluorene (**5a**, *c.* 97% by ^{1}H NMR) and fluorene (**5b**, *c.* 3% by ^{1}H NMR). Recrystallization from chloroform yielded 0.143 g (87%) of **5a** as white crystals; m.p. 243–244.5 °C (lit. 245–246 °C [35]). ^{1}H NMR ($CDCl_3$): δ 6.93–7.65 (m, 12 H), 4.82 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ 144.62, 141.48, 127.24, 126.67, 124.05, 119.61, 49.77; NMR spectral data were consistent with those reported [36].

meso/D,L-*2,3-Diphenylbutane (6)*

Reaction of (±)-1-bromo-1-phenylethane (0.190 g, 1.03 mmol) with **1** (0.559 g, 1.03 mmol) afforded 0.0962 g (89%) of a 1:1 mixture of *meso*-2,3-diphenylbutane (**6a**) and the enantiomers D,L-2,3-diphenylbutane (**6b**). No attempt was made to separate the isomers which were obtained as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 6.82–7.23 (m, 20 H, **6a**+**6b**), 2.84 (br m, 2 H, **6b**), 2.70 (br m, 2 H, **6a**), 1.18 (br m, 6 H, **6b**), 0.93 (br m, 6 H, **6a**); NMR spectral data were consistent with those reported [37]. GC/MS (*m/z* (rel. abund.)): essentially identical for **6a** and **6b**, 210 (M^+, 7), 106 (9), 105 (100), 104 (26), 103 (9), 91 (5), 79 (15), 78 (5), 77 (18), 51 (7).

1-Diphenylmethylene-4-trityl-2,5-cyclohexadiene (7)

Chlorotriphenylmethane (0.537 g, 1.93 mmol) was added to **1** (1.04 g, 1.93 mmol) in CH_3CN according to the general procedure. After stirring the reaction mixture at room temperature for 24 h, the volume of solution was reduced to 5 ml *in vacuo* resulting in the formation of a tan-colored precipitate. The solution was decanted and the solid washed with argon-saturated CH_3CN (2×10 ml) to remove the Cu(II) product. Drying *in vacuo* gave 0.197 g (42%) of **7** as an air-sensitive tan powder. ^{1}H NMR ($CDCl_3$): δ 6.92–7.34 (m, 25 H), 5.94–6.24 (m, 4 H), 5.11 (s, 1 H); NMR spectral data were consistent with those reported [38].

trans-Stilbene (8)

Reaction of α,α-dichlorotoluene (0.185 g, 1.15 mmol) with **1** (1.24 g, 2.30 mmol) for 4 h according to the general procedure gave 0.0956 g (92%) of **8** as colorless crystals: m.p. 117–119 °C (lit. 126–127 °C [39]). ^{1}H NMR ($CDCl_3$): δ 7.53–7.22 (m, 10 H), 7.11 (s, 2 H); ^{13}C NMR ($CDCl_3$): δ 137.34, 128.71, 128.66, 127.62, 126.53; NMR spectral data were consistent with those reported [37]. GC/MS (*m/z* (rel. abund.)): 180 (M^+, 92), 179 (100), 178 (63), 176 (11), 165 (51), 152 (17), 102 (15), 89 (33), 77 (17), 76 (29), 75 (10), 63 (22), 52 (10), 51 (35). Reaction of *meso*-1,2-dibromo-1,2-diphenylethane (0.172 g, 0.506 mmol) with **1** (0.547 g, 1.01 mmol) for 2 h also gave **8** (0.0901 g, 99%).

Reaction of α,α-dichlorotoluene with $[Cu^{II}(TMPA)CH_3CN]PF_6$ (1) in the presence of cyclohexene

A solution of 1.564 g (19.0 mmol) cyclohexene in 10 ml of CH_3CN was added, under argon, to 0.511 g (0.946 mmol) of $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**). The resulting orange solution was stirred for 30 min followed by addition of α,α-dichlorotoluene (0.0764 g, 0.474 mmol) in 10 ml of acetonitrile. The solution began to turn green as the halide was added and the mixture was stirred for 64 h at room temperature. Analysis of the reaction mixture by GC subsequently showed only the presence of the coupled product, *trans*-stilbene (**8**) (and cyclohexene).

cis/trans-1,2-Dichloro-1,2-diphenylethene (9)

Addition of α,α,α-trichlorotoluene (0.101 g, 0.518 mmol) to **1** (0.557 g, 1.03 mmol) according to the procedure given above (20 min) resulted in the formation of 0.0680 g (99%) of a mixture of *cis*-(**9a**) and *trans*-1,2-dichloro-1,2-diphenylethene (**9b**). GC analysis indicated that the *cis/trans* ratio was *c.* 80/20. ^{1}H NMR ($CDCl_3$): δ 7.30–7.70 (m, 5 H, **9b**), 7.14–7.25 (m, 20 H, **9a**). GC/MS (*m/z* (rel. abund.)): **9a**: 249 (M^+, 2), 248 (31), 213 (22), 212 (15), 179 (6), 178 (90), 177 (21), 176 (22), 151 (8), 93 (7), 89 (7), 88 (22), 76 (9), 75 (11), 74 (7), 63 (7), 51 (10), 50 (7), 44 (100); **9b**: 248 (6), 178 (28), 177 (3), 48 (3), 44 (100), no M^+ peak observed.

Bi-2-cyclohexen-1-yl (10)

Addition of 3-bromocyclohexene (0.320 g, 1.99 mmol) to **1** (1.08 g, 1.99 mmol) and reaction for 3 h yielded 0.110 g (68%) of **10** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.53–5.75 (m, 4 H), 1.26–2.17 (m, 14 H). GC/MS (*m/z* rel. abund.)): 162 (M^+, 0.3), 91 (6), 82 (6), 81 (100), 80 (67), 79 (34), 77 (12), 65 (5), 53 (15), 51 (5).

Reaction of benzyl bromide with $[Cu^{I}(TMPA)CH_3CN]PF_6$ (1) in the presence of acrylonitrile

A solution of benzyl bromide (0.092 g, 0.574 mmol) in 10 ml of CH_3CN was added, under argon, to a mixture of acrylonitrile (0.609 g, 11.5 mmol) and $[Cu^{I}(TMPA)CH_3CN]PF_6$ (**1**) (0.310 g, 0.574 mmol) in 10 ml of CH_3CN maintained at −39 °C. Following addition of the halide, the solution was allowed to warm to room temperature and was stirred for three days followed by the usual workup. Analysis of the product mixture by GC/MS showed, in addition to the starting halide and coupled product (**2**), the presence of addition products of acrylonitrile including 4-phenylbutanenitrile (*m/z* = 145, M^+), 4-cyano-6-phenylhexanenitrile (*m/z* = 198, M^+) and 2-benzyl-4-phenylbutanenitrile (*m/z* = 235 M^+).

Reaction of 2-chloroacetophenone with [Cu^{I}(TMPA)CH$_3$CN]PF$_6$ (1)

A solution of 2-chloroacetophenone (0.171 g, 1.11 mmol) in CH_3CN was added to **1** (0.598 g, 1.11 mmol) according to the general procedure. After stirring for 24 h followed by the usual workup, 0.909 g of a dark semi-solid material was isolated. Analysis by GC/MS and ^{1}H NMR indicated that the product was composed of a mixture of acetophenone (**11a**), 1,2-dibenzoylethane (**11b**), and the starting material, phenacyl chloride (*c.* 3% of 1,2-dibenzoylethene (**11c**) was detected by GC). The mole percent composition of the mixture was determined by ^{1}H NMR to be 21% acetophenone, 28% phenacyl chloride and 51% 1,2-dibenzoylethane. The yield of acetophenone (**11a**) was calculated to be about 9%, based on the starting material, while that of the coupled product, **11b**, was 44%. For **11a**: ^{1}H NMR ($CDCl_3$) (deduced from the spectrum of the mixture): δ 7.4–8.1 (m, 5 H), 2.61 (s, 3 H); GC/MS (*m/z* (rel. abund.)): 120 (M^+, 25), 106 (7), 105 (92), 78 (10), 77 (100), 74 (7), 52 (5), 51 (49), 50 (25), 43 (27), 39 (11), 38 (8). For **11b**: ^{1}H NMR ($CDCl_3$) (deduced from the mixture): δ 7.4–8.1 (m, 10 H), 3.47 (s, 4 H); NMR spectral data were consistent with those reported [40]; GC/MS (*m/z* (rel. abund.)): 238 (M^+, 15), 133 (9), 106 (8), 105 (100), 77 (62), 55 (5), 51 (25), 50 (7).

In a separate experiment, 0.156 g (1.01 mmol) of 2-chloroacetophenone in 10 ml of CH_3CN was added to a solution of **1** (0.548 g, 1.01 mmol) in 10 ml of a 10:1 (vol./vol.) mixture of CH_3CN/H_2O. The reaction mixture was stirred for 24 h and, after workup, gave 0.113 g of a yellow oil which was found to contain only the starting material and acetophenone (**11a**). The mole percent composition of the mixture was found to be approximately 45% phenacyl chloride and 55% acetophenone by ^{1}H NMR. The yield of acetophenone was 36% based on the phenacyl chloride starting material.

Isolation of [Cu^{II}(TMPA)Br]PF$_6$ (3b)

Following the reaction of 3-bromocyclohexene with **1** (see above), the crude Cu(II) product was dissolved in acetone (30 ml) and the solution layered with diethyl ether (100 ml). Storage of the mixture at 8 °C for several days resulted in the deposition of large emerald-green crystals. The material was recrystallized a second time from acetone/Et_2O and the product dried *in vacuo* to yield 0.911 g (79%) of [Cu^{II}(TMPA)Br]PF$_6$ (**3b**). *Anal.* Calc. for $C_{18}H_{18}BrCuF_6N_4P$: C, 37.35; H. 3.14; N, 9.68. Found: C, 37.96; H, 3.14; N. 9.75%. IR (Nujol; cm^{-1}): 3620(w, H_2O impurity), 3540(w), 1620(s, C=C), 1580(m), 8450(vs), 1380(s), 1320(s), 1300(m), 1270(s), 1220(w), 1160(s), 1095(s), 1055(vs), 1020(s), 1010(s), 995(m), 980(m), 960(s), 900(s), *c.* 835(vs, br, PF_6^-), 765(vs), 730(s), 650(m), 640(s), 555(vs). UV–Vis (CH_3CN: λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 256 (12 200), 324 (4170), 772 (sh, 91.7), 986 (206). Molar conductivity: $\Lambda_M = 152$ Ω^2 mol^{-1}. EPR: $g_{\|} = 1.950$, $A_{\|} = 86 \times 10^{-4}$ cm^{-1}, $g_{\perp} = 106 \times 10^{-4}$ cm^{-1}.

Reaction of N-bromophthalimide with [Cu^{I}(TMPA)CH$_3$CN]ClO$_4$ (1). Isolation of [Cu^{II}(TMPA)phthalimide]ClO$_4$ (12)

A solution of *N*-bromophthalimide (0.167 g, 0.740 mmol) in 30 ml of CH_3CN was added, under argon, to a 100-ml Schlenk reaction vessel containing 0.713 g (1.44 mmol) of [Cu^{I}(TMPA)ClO_4 (**1**-ClO_4) in 10 ml of CH_3CN. As the reaction progressed, the mixture changed from the bright orange color characteristic of **1** to green, and finally to a deep blue color. The resulting solution was stirred overnight and then carefully layered with argon-saturated diethyl ether (60 ml). After several days at room temperature, blue crystals were deposited on the sides of the reaction flask and the solution had become an emerald-green color. The solution was decanted and the crystals washed with Et_2O (75 ml) and dried *in vacuo* to give 0.306 g (71%) of **12** as a blue powder. *Anal.* Calc. for $C_{26}H_{22}ClCuN_5O_6$: C, 52.09; H. 3.70; N, 11.68. Found: C, 51.91; H, 3.70; N, 11.20%. IR (Nujol; cm^{-1}): *c.* 2900(vs, C–H), 2000(w, ClO_4^- overtone), 1730(w, C=O), 1645(s, C=O), 1600(s, C=C), 1570(m), 1450(vs), 1365(vs), 1300(s), 1170(m), 1160(m), 1065(vs, ClO_4^-), 1010(s), 975(m), 940(m), 890(m), 850(m), 835(m), 770(s), 760(s), 720(vs), 670(w), 645(m), 620(s). UV–Vis (CH_3CN; λ_{max}, nm (ϵ, M^{-1} cm^{-1})): 256 (13 700), 290 (4650), 699 (sh, 140), 783 (153).

The green solution removed from the phthalimide complex above was layered with diethyl ether (150 ml) and placed into the refrigerator. After several days light green crystals were formed which were air-dried to yield 0.314 g (75%) of [Cu^{II}(TMPA)Br]ClO_4, identified by comparison of its IR and UV–Vis spectra to those of [Cu^{II}(TMPA)Br]PF$_6$ (**3b**).

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