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Catalytic cyclopropanation of olefins using copper(I) diphosphinoamines

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ABSTRACT

Catalytic cyclopropanation reactions of olefins with ethyl diazoacetate were carried out using copper(I) diphosphinoamine $(PPh_2)_2N(R)$ (R = ^{i}Pr, H, Ph and $-CH_2-C_6H_4-CH=CH_2$) complexes at 40 °C in chloroform. High yields of the cyclopropanes were obtained in all cases. The rate of the reaction was influenced by the nuclearity of the complex and the binding mode of the ligand which was either bridging or chelating. Comparison of isostructural complexes shows that the rate follows the order R = ^{i}Pr > H > Ph, where R is the substituent on the N. However, cyclopropane formation versus dimerization of the carbene, and *trans* to *cis* ratios of cyclopropane was similar in all cases. The nearly identical selectivity for different products formed was indicative of a common catalytic intermediate. A labile "copper–olefin" complex which does not involve the phosphine or the counterion is the most likely candidate. The differences in the reaction rates for different complexes are attributed to differences in the concentration of the catalytically active species which are in equilibrium with the catalytically inactive copper–phosphinoamine complex. To test the hypothesis a diphosphinoamine polymer complexed to copper(I) was used as a heterogeneous catalyst. Leaching of copper(I) and deactivation of the catalyst confirmed the proposed mechanism.

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1. Introduction

Transition metal catalyzed cyclopropanation reaction of olefins proceeds via cycloaddition of a metal-bound carbene fragment to an olefin (Scheme 1) [1–3]. A variety of transition metals promote the reaction, although copper and rhodium appear to be the best. Copper-based systems are more attractive compared to those of rhodium from the cost perspective, and hence, have been extensively studied [4]. A variety of copper sources [5] are known to catalyze the cyclopropanation reaction including copper(I) complexes containing nitrogen [6] and phosphorus [2,6e,7–10] ligands.

It is generally assumed that in all reactions catalyzed by copper, unstable Cu(I) carbenoid intermediates $[L_nCu = C(R)R']^+$ are formed and these are trapped by the substrate alkene, resulting in cyclopropanes. In year 2000, Hofmann et al. [11] reported a remarkably stable fluxional copper α-carbonyl diazoalkane complex which was structurally characterized. Hofmann and coworkers also reported the intermediacy of a copper(I) carbene in a cyclopropanation reaction where the carbene carbon was spectroscopically characterized with a chemical shift of 229.9 ppm [12]. More recently Warren et al. have reported catalytic cyclopropanation using Cu(I) β-diketiminate: $[Me_2NN]Cu(\eta^2$-ethylene) complex [13]. Chelating diiminophosphorane and tripodal iminophosphorane copper and palladium complexes have been shown recently to efficiently catalyze the cyclopropanation of activated monosubstituted olefins [14].

From a mechanistic view point, nitrogen-based ligands have been examined in great detail [3,15] experimentally and through computation. But to the best of our knowledge, there have been few attempts to study the mechanism of the cyclopropanation reactions catalyzed by copper(I)–phosphine complexes. We report here a study of a wide variety of copper(I) diphosphinoamine complexes as catalysts in catalytic cyclopropanation of olefins. Different Cu(I) complexes of the four diphosphinoamine ligands $(PPh_2)_2N(R)$ (R = ^{i}Pr, dppipa; Ph, dppan; H, dppa; and $-CH_2-C_6H_4-CH=CH_2$, vbzpnp) have been used for catalytic cyclopropanation of styrene and cyclohexene using ethyl diazo acetate (EDA). These copper(I) complexes have been described in an accompanying paper in detail (Table 1) [16–18]. It was of interest to utilize these complexes as catalysts to find out how the substituent on the central nitrogen atom and the nuclearity influence the cyclopropanation reaction.

2. Results

2.1. Optimization of catalytic conditions

The monomeric complex of dppipa, $[Cu(dppipa)_2]ClO_4$ was chosen as the catalyst, for the optimization of reaction conditions.

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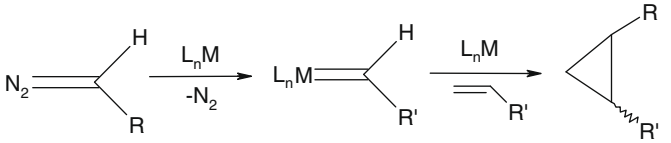


Scheme 1. Mechanism of metal-catalyzed cyclopropanation.

Initial attempts were made with 2.5 mol% of the copper complex in CH_2Cl_2 with 2 equiv. of styrene at room temperature. Complete consumption of the diazo compound was observed after 4 h with 54% yield of cyclopropane (Table 2, entry 1). A reaction in refluxing dichloromethane gave 50% cyclopropane in 2 h (entry 2).

To have a better idea of the progress of the reaction times, the same reaction was carried out in a NMR tube with $CDCl_3$ as solvent at 40 °C and the reaction was monitored by ^1H NMR spectroscopy at short intervals of time (entry 3). It was found that the results were similar to that obtained in the two-necked round bottom flask under nitrogen atmosphere. Thereafter the reactions were carried out in NMR tubes and monitored by ^1H NMR spectroscopy at 40 °C with an internal standard. The yields obtained by ^1H NMR spectroscopy measurements were further confirmed by by isolating the products and estimating the yield in a separate experiment.

The next reaction was attempted with 2.5 mol% of the copper complex in the presence of 4 equiv. of styrene (entry 4). The yield of the cyclopropane increased to 64% with an increased reaction time of 2 h 40 min. A further increase to 10 equiv. of styrene with 2.5 mol% of the catalyst enhanced the yield of cyclopropane to 78% (entry 5) with a total reaction time of about 3 h. With 10 equiv. of olefin, reducing the amount of copper complex to 1 mol% had a slight adverse effect (entry 6 and 7); the cyclopropane yield increased to 72% but reaction times were longer (entry 7). A further increase in the cyclopropane product (83%) was obtained with 0.5 mol% catalyst (entry 8). On the contrary, a similar increase was not observed when the catalyst was further reduced to 0.2 mol% (entry 10). The selectivity was very similar to that obtained with 0.5 mol% but the reaction time almost doubled.

Based on these observations, the optimized conditions were identified to be 0.5 mol% of the catalyst with 10 equiv. of styrene in $CDCl_3$ at 40 °C. The results were found to be reproducible (entry 8). The optimized reaction conditions were also employed for a large scale reaction carried out in a round bottom flask in refluxing dichloromethane with similar results (entry 9). The optimized conditions were then employed for all copper(I) diphosphinoamine complexes.

2.2. Reactions with copper(I) dppipa complexes

The results obtained in cyclopropanation reactions carried out with copper(I) dppipa complexes as catalysts are given in

Table 1
List of Cu(I) Complexes employed for catalytic cyclopropanation (P = PPh_2). dppipa = $(Ph_2P)_2N(^iPr)$, dppan = $(Ph_2P)_2N(Ph)$, vbzpnp = $(Ph_2P)_2N(C_6H_4–CH=CH_2)$, dppa = $(Ph_2P)_2N(H)$.

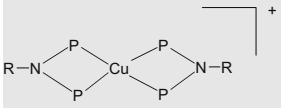
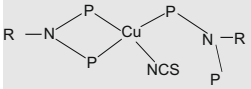
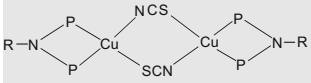
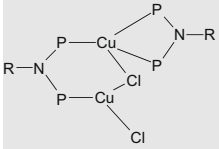
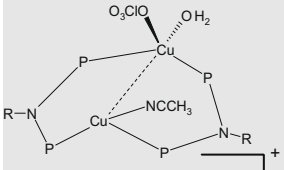
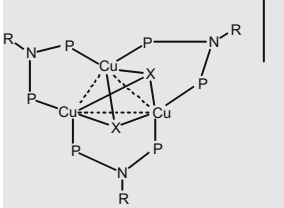
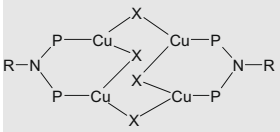
Complex	Substituents	Formula
	R = ^{i}Pr, X = ClO_4^- R = Ph, X = ClO_4^- R = $–CH_2–C_6H_4$ $H_4–$ CH=CH_2, X = ClO_4^- R = Ph, X = BF_4^-	$[Cu(dppipa)_2]ClO_4$ $[Cu(dppan)_2]ClO_4$ $[Cu(vbzpnp)_2]ClO_4$ $[Cu(dppan)_2]BF_4$
	R = Ph	$[Cu(dppan)_2(NCS)]$
	R = ^{i}Pr	$[Cu_2(dppipa)_2(SCN)_2]$
	R = ^{i}Pr, X = Cl	$[Cu_2(dppipa)_2Cl_2]$
	R = H	$[Cu_2(dppa)_2(CH_3CN)(OH_2)(OClO_3)]$ ClO_4
	R = ^{i}Pr, X = Cl R = ^{i}Pr, X = Br R = H, X = Cl R = H, X = Br	$[Cu_3(dppipa)_3Cl_2][CuCl_2]$ $[Cu_3(dppipa)_3Br_2][CuBr_2]$ $[Cu_3(dppa)_3Cl_2]Cl$ $[Cu_3(dppa)_3Br_2]Br$
	R = ^{i}Pr, X = Cl R = ^{i}Pr, X = Br R = Ph, X = Cl R = Ph, X = Br R = $–CH_2–C_6H_4–$ CH=CH_2, X = Cl	$[Cu_4(dppipa)_2Cl_4]$ $[Cu_4(dppipa)_2Br_4]$ $[Cu_4(dppan)_2Cl_4]$ $[Cu_4(dppan)_2Br_4]$ $[Cu_4(vbzpnp)_2Cl_4]$

Table 2
Cyclopropanation of styrene with $[Cu(dppipa)_2]ClO_4$ (dppipa = $(Ph_2P)_2N(^iPr)$.

Entry	[Cu] Mol%	Equiv. of olefin	Temperature (°C)	Total reaction time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	*trans*:*cis* (Alk.)
1[a]	2.5	2	23	240	54	74:26	46	58:42
2[a]	2.5	2	40	120	50	67:33	50	55:45
3[b]	2.5	2	40	120	47	69:31	53	57:43
4[b]	2.5	4	40	160	64	79:21	36	59:41
5[b]	2.5	10	40	185	78	74:26	22	60:40
6[b]	1.0	4	40	180	66	76:24	32	59:41
7[b]	1.0	10	40	240	72	77:23	28	66:34
8[b,c]	0.5	10	40	145	85	79:21	15	64:36
9[a]	0.5	10	40	150	83	77:23	17	64:36
10[b]	0.2	10	40	300	85	75:25	15	64:36

CP = Cyclopropane, Alk. = Alkene.
[a] In CH_2Cl_2 in a round bottom flask.
[b] In $CDCl_3$ in a NMR tube.
[c] Average of two runs.

Table 3. In general, the reaction times differed with different complexes but offered similar yields of cyclopropane with similar selectivity for the *trans* product (*trans*:*cis* = 85:15). Ability to recycle the catalyst was verified by a second addition of the diazo compound to the spent reaction mixture, after complete consumption of the diazo compound (entry 3).

The reaction carried out with cyclohexene was found to be much faster than the one carried out with styrene (entry 9–11). In terms of selectivity, the cyclopropane formation was less (79%) in comparison with in reactions attempted with styrene. Contrary to what was observed in the case of styrene, it was found that the total time taken for the reaction decreased in the subsequent runs, on addition of another equivalent of the diazo compound to the same reaction mixture.

All complexes studied were extremely fast in initiating the reaction except the *bis* chelated complex, $[Cu(dppipa)_2]ClO_4$ and the dimer bridged by chloride ions, $[Cu_2(dppipa)_2Cl_2]$ where induction times of 20 min and 15 min, respectively, were observed. In the case of other dppipa complexes, the reaction had already begun before the first spectrum could be recorded.

2.3. Reactions with copper(I) dppa complexes

The catalytic cyclopropanation was attempted with the perchlorate complex $[Cu_2(dppa)_2(CH_3CN)(OH_2)(OClO_3)]ClO_4$ and the halide complexes of dppa, $[Cu_3(dppa)_3X_2]X$ (X = Cl, Br) previously reported by Ellermann et al. [19]. The results of the catalytic reactions are shown in Table 4. The dimeric perchlorate complex was found to be extremely fast in comparison with all the dppipa complexes (Table 4, entry 1), though the selectivity obtained for the dppa complex was similar to that of the dppipa complex. The trimeric halide complexes, $[Cu_3(dppa)_3X_2]X$ (X = Cl, Br) (entries 3 and 4) were found to be slower than the dimeric perchlorate complex.

2.4. Reactions with copper(I) dppan complexes

The results obtained on carrying out cyclopropanation reactions with the dppan complexes are listed in Table 5. Although longer reaction times were associated with these complexes, the cyclopropanation reactions offered similar selectivity ratios with almost similar yields of cyclopropane in most cases. As seen earlier, the reactions with cyclohexene were faster than the reactions carried out with styrene.

2.5. Reactions with copper(I) bis(diphenylphosphino)-p-vinylbenzylamine complexes

Copper(I) complexes of vbzpnp [18] were also utilized to carry out cyclopropanation of styrene. The results are summarized in Table 6. These complexes were found to be sluggish compared to the complexes mentioned earlier but offered similar selectivity (entry 1 and entry 2). The copper(I) loaded polymer, Cu(I) complex of polyvbzpnp [18] was employed as a heterogeneous catalyst. Three cycles were carried out showing a drop in cyclopropane yield from 91% in the first cycle to 74% in the third cycle (entry 3–5).

Table 3
Data for cyclopropanation with other copper(I) dppipa [$(Ph_2P)_2N(^iPr)$] complexes. Reaction conditions: 0.5 mol% Cu with 10 equiv. of olefin in CDCl3 at 40 °C.

Entry	Catalyst	Olefin	Time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	*trans*:*cis* (Alk.)
1[a]	$[Cu(dppipa)_2]ClO_4$	St	145	85	79:21	15	64:36
2[b]	$[Cu_4(dppipa)_2Cl_4]$	St	85	85	75:25	15	59:41
3[c]	$[Cu3(dppipa)_3Cl_2][CuCl_2]$	St	105	86	76:24	14	63:37
4[d]	$[Cu_3(dppipa)_3Cl_2]$ $[CuCl_2]$	St	120	84	76:24	16	56:44
5	$[Cu_2(dppipa)_2Cl_2]$	St	240	86	75:25	14	56:44
6	$[Cu_4(dppipa)_2Br_4]$	St	150	82	77:23	18	58:42
7	$[Cu_3(dppipa)_3Br_2][CuBr_2]$	St	165	87	76:24	13	63:37
8	$[Cu_2(dppipa)_2(SCN)_2]$	St	85	80	81:19	20	60:40
9	$[Cu_3(dppipa)_3Cl_2][CuCl_2]$	Cy	60	79	76:24[f]	21	53:47
10[d]	$[Cu_3(dppipa)_3Cl_2]$ $[CuCl_2]$	Cy	45	79	75:25[f]	21	54:46
11[e]	$[Cu_3(dppipa)_3Cl_2][CuCl_2]$	Cy	20	78	76:24[f]	22	54:46

CP = Cyclopropane, Alk. = Alkene, Cy = Cyclohexene, St = Styrene.
[a] Entry 8 from Table 2.
[b] Average of three runs.
[c] Average of two runs.
[d] Second cycle.
[e] Third cycle.
[f] *exo*:*endo* ratio.

Table 4
Data for cyclopropanation with copper(I) dppa [$(Ph_2P)_2N(H)$] complexes. Reaction conditions: 0.5 mol% Cu with 10 equiv. of olefin in $CDCl_3$ at 40 °C.

Entry	Catalyst	Olefin	Induction time (min)	Total reaction time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	*trans*:*cis* (Alk.)
1[a]	$[Cu_2(dppa)_2(L)(L')(OClO_3)]ClO_4$	St	5	50	85	77:23	15	55:45
2[b]	$[Cu_2(dppa)_2(L)(L')(OClO_3)]ClO_4$	St	5	35	83	77:23	17	53:47
3	$[Cu_3(dppa)_3Cl_2]Cl$	St	20	150	86	75:25	14	57:43
4	$[Cu_3(dppa)_3Br_2]Br$	St	75	185	86	77:23	14	53:47
5	$[Cu_2(dppa)_2(L)(L')(OClO_3)]ClO_4$	Cy	15	40	77	79:19[d]	23	59:41
6[b]	$[Cu_2(dppa)_2(L)(L')(OClO_3)]ClO_4$	Cy	–[e]	20	77	78:22[d]	23	56:24
7[c]	$[Cu_2(dppa)_2(L)(L')(OClO_3)]ClO_4$	Cy	–[e]	15	75	76:24[d]	25	55:45

L = CH_3CN, L′ = OH_2, Cy = Cyclohexene, CP = Cyclopropane, St = Styrene Alk. = Alkene.
[a] Average of two runs.
[b] Second cycle.
[c] Third cycle.
[d] *exo*:*endo* ratio.
[e] Less than 5 min.

Table 5
Data for cyclopropanation with copper(I) dppan [$(Ph_2P)_2N(Ph)$] complexes. Reaction conditions: 0.5 mol% Cu with 10 equiv. of olefin in $CDCl_3$ at 40 °C.

Entry	Catalyst	Olefin	Time (min)	Induction time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	*trans*:*cis* (Alk.)
1	$[Cu(dppan)_2]ClO_4$	St	210	45	84	74:26	16	52:48
2	$[Cu(dppan)_2]BF_4$	St	210	75	83	75:25	17	55:45
3	$[Cu_4(dppan)_2Cl_4]$	St	120	15	82	77:23	18	59:41
4	$[Cu_4(dppan)_2Br_4]$	St	240	30	85	76:24	15	62:38
5	$[Cu(dppan)_2(NCS)]$	St	170	85	81	77:23	19	60:40
6	$[Cu_4(dppan)_2Cl_4]$	Cy	55	15	75	77:23[c]	25	58:42
7[a]	$[Cu_4(dppan)_2Cl_4]$	Cy	30	–[d]	75	76:24[c]	25	59:41
8[b]	$[Cu_4(dppan)_2Cl_4]$	Cy	30	–[d]	75	76:24[c]	25	59:41

Alk. = Alkene, Cy = Cyclohexene, CP = Cyclopropane, St = Styrene.
[a,b] Second and third cycle, respectively.
[c] *exo*:*endo* ratio.
[d] Less than 5 min.

Table 6
Data for cyclopropanation with copper(I) vbzpnp [$(Ph_2P)_2N(C_6H_4–CH=CH_2)$] complexes.

Entry	Complex	[Cu] mol%	Total time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	*trans*:*cis* (Alk.)
1	$[Cu(vbzpnp)_2]ClO_4$	0.5	220	84	76:24	16	59:41
2	$[Cu4(vbzpnp)_2Cl_4]$	0.5	350	82	78:22	18	56:44
3[a]	Cu(I) complex of polyvbzpnp[18]	1.7	4560 (76 h)	91	76:24	9	50:50
4[b]	Cu(I) complex of poly vbzpnp	–	2880 (48 h)	87	76:24	13	50:50
5[c,*]	Cu(I) complex of poly vbzpnp		9300 (>6d)	74	75:25	9	45:55

[*] 17% EDA left unreacted.
[a] First cycle.
[b] Second cycle.
[c] Third cycle.

2.6. Decay of Ethyl diazoacetate

In order to compare the rates of the reactions, the decay of EDA was monitored by ^1H NMR spectroscopy at regular time intervals. The resonance at 4.74 ppm corresponding to the –CH of the diazo compound was used to calculate the concentration of ethyl diazo acetate. This concentration of EDA was then plotted with respect to time. Decay of EDA with time for the three copper(I) dppa complexes is shown in Fig. 1 as a representative example.

As observed by other workers in this field [6e] the decay of the diazo reactant was found to follow a simple rate law. The concentrations were fit to a straight line by a plot of ln([EDA]) versus time. First order kinetics was observed in the case of decomposition of EDA (Supplementary information). The values of the rate constants were calculated from the slope of the straight line fit (Table 7). The errors for the rate constants were obtained from three independent reactions carried out with the chloride tetramer of dppipa and were estimated to be ±10%. The dimeric complex of dppa, $[Cu_2(dp-$

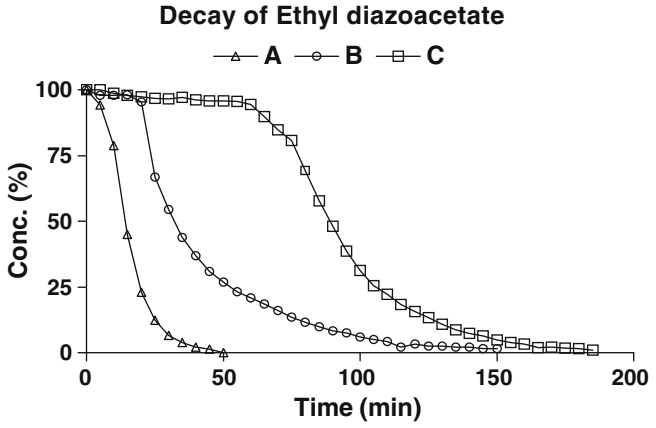


Fig. 1. Decay of EDA with time for dppa complexes; A = $[Cu_2(dppa)_2(CH_3CN)(O-H_2)(OClO_3)]ClO_4$, B = $[Cu_3(dppa)_3Cl_2]Cl$, C = $[Cu_3(dppa)_3Br_2]Br$.

Table 7
First order rate constants for the consumption of ethyl diazoacetate.

S. no.	Catalyst	First order rate constant/10^{-2} (min^{-1})
1	$[Cu(dppipa)_2]ClO_4$	4.13
2	$[Cu_2(dppipa)_2(SCN)_2]$	1.85, 7.76
3	$[Cu_4(dppipa)_2Cl_4]$	5.27
4	$[Cu_3(dppipa)_3Cl_2]$ $[CuCl_2]$	5.02
5	$[Cu_2(dppipa)_2Cl_2]$	2.10
6	$[Cu_4(dppipa)_2Br_4]$	2.98
7	$[Cu_3(dppipa)_3Br_2]$ $[CuBr_2]$	4.00
8	$[Cu_2(dppa)_2(CH_3CN)(OH_2)(OClO_3)]ClO_4$	11.2
9	$[Cu_3(dppa)_3Cl_2]Cl$	3.21
10	$[Cu_3(dppa)_3Br_2]Br$	3.32
11	$[Cu(dppan)_2]ClO_4$	2.28
12	$[Cu(dppan)_2(NCS)]$	2.06, 6.65
13	$[Cu_4(dppipa)_2Cl_4]$	5.76
14	$[Cu_4(dppipa)_2Br_4]$	2.14

$pa)_2(CH_3CN)(OH_2)(OClO_3)]ClO_4$ was found to have the largest rate constant ($11.2 \times 10^{-2}\ min^{-1}$). The thiocyanate complexes, $[Cu_2(dppipa)_2(SCN)_2]$ and $[Cu(dppan)_2(NCS)]$ exhibited a bimodal decay and two first order rate constants could be evaluated. Interestingly, one of the components was almost as high as the dimeric complex of dppa. Since the SCN complex can adopt dimeric and monomeric structures (*vide supra*), it is tempting to propose that the two components arise from the presence of the catalytic activities of the dimer and the monomer. The dimer had almost ten times greater reactivity than the monomer.

3. Discussion

Most studies on the mechanism of cyclopropanation have been based on nitrogen ligands rather than phosphorus ligand systems. This is probably because the transition state containing the copper–carbene is more stabilized in the presence of nitrogen ligands on copper [15c,15d,15o]. Chiral N-ligand systems have enabled enantioselective cyclopropanation. Most of the earlier studies carried out with copper(I)–phosphine complexes have shown only moderate yields [2,6e]. With the diphosphinoamine copper(I) catalysts investigated in the present study, good yields of the cyclopropanation product have been obtained from cyclohexene (~77%) and styrene (~85%). They are definitely better than copper(I) salts (Table 8).

3.1. Reactions with alternative copper(I) sources (Table 8)

Tetrakis(acetonitrile)copper(I) with different counter anions namely perchlorate and tetrafluoroborate were also investigated under similar conditions. Cyclopropanation reactions with the corresponding hexafluorophosphate complex has been reported [19]. Reactions with 0.5 mol% of *tetrakis*(acetonitrile)copper(I) perchlorate and tetrafluoroborate and 10 equivalents of styrene in $CDCl_3$ under the optimized reaction conditions discussed earlier (entry 1 and entry 2) gave about 88% and 90% of the cyclopropane in 4 h and 1 h, respectively. Surprisingly the reaction with the perchlorate complex took almost 2 h to start, whereas the tetrafluoroborate complex initiated the reaction almost instantaneously. The tetrafluoroborate complex (2 mol%) studied by Woodward and coworkers gave 60% cyclopropane product from styrene in 10 min at ambient temperature and 30% cyclopropane product from cyclohexene in 10 min under similar conditions (entries 3 and 4) [2]. The complex $[Cu(CH_3CN)_4]B(C_6F_5)_4$ [8] has been reported to yield around 71% of cyclopropane product of styrene with 49:51 ratio of *trans* to *cis* cyclopropane (entry 5) when used in 2 mol% concentration. Copper–nitrile strength was found to be an important factor influencing catalytic activity of copper(I) nitrile complexes. The more weakly the nitrile ligands are coordinated to the metal center, the better is the catalytic performance of the complex [8].

Monodentate phosphines like PPh_3, [2] PCy_3, [2] PPh_2–Ar, (Ar = *o*-Me_2N–(CH_2)–C_6H_4), [2] diphosphines like $(PPh_2)_2(CH_2)_2$ (dppe) [6e] have also been investigated for the catalytic reaction. With 2 mol% of the monophosphine catalyst, the cyclopropane was obtained in low yields (27–65%) (entries 6–9). The reaction with trimeric complex of *bis*(diphenylphosphino)methane (dppm) and copper(I) chloride, $[Cu_3(dppm)_3Cl_2]Cl$, was quite sluggish, even after 7 h 30 min cyclopropane was obtained in 80% yield and 4% of the ethyl diazoacetate was left unreacted (entry 10). Results with different copper(I) phosphite complexes [15b] are given in entries 11–14 and indicate higher activity. Copper(I) complex containing dihydridobis(pyrazolyl)borate in conjunction with various mono and diphosphines have been reported and the results are listed in entries 15–17. Cyclopropanes are obtained in 60–64% yield.

Table 8
Comparison with other copper(I) complexes reported in literature.

Entry	Catalyst	[Cu] mol%	Olefin	Reaction time (min)	CP (%)	*trans*:*cis* (CP)	Alk. (%)	Ref.
1[a]	$[Cu(CH_3CN)_4]ClO_4$	0.5	St	215	88	76:24	12	*
2[a]	$[Cu(CH_3CN)_4]BF_4$	0.5	St	65	90	65:35	10	*
3	$[Cu(CH_3CN)_4]BF_4$	2.0	St	10	60	62:38	30	[2]
4	$[Cu(CH_3CN)_4]BF_4$	2.0	Cy	10	30	85:15[b]	44	[2]
5[c]	$[Cu(CH_3CN)_4]B(C_6F_5)_4$	2.0	St	60	71	49:51	29	[8]
6	$[Cu(CH_3CN)(PPh_3)_2]BF_4$	2.0	St	135	55	71:29	31	[2]
7	$[Cu(CH_3CN)(PPh_3)_3]BF_4$	2.0	St	960	27	70:30	34	[2]
8	$[Cu(F\text{-}BF_3)(PCy_3)_2]$	2.0	St	270	29	80:20	49	[2]
9	$[Cu(CH_3CN)_2(PPh_2\text{-}Ar)_2]BF_4$	2.0	St	900	65	73:27	32	[2]
10[a]	$[Cu_3(dppm)_3Cl_2]Cl$	0.5	St	450	80	76:24	16	*
11	$CuClP(O^iPr)_3$	2.0	St	480	88	74:26	–	[15b]
12	$CuClP(O^iPr)_3$	2.0	Cy	480	28	87:13[b]	–	[15b]
13	$CuClP(OPh)_3$	2.0	St	480	84	71:29	-	[15b]
14	$CuClP(OPh)_3$	2.0	Cy	480	25	87:13[b]	-	[15b]
15	BpCu(dppe)	1.0	St	180	60	75:25	40	[6e]
16	$BpCu(Pcy_3)$	1.0	St	180	64	75:25	36	[6e]
17	$BpCu(PPh_3)_2$	1.0	St	180	64	75:25	36	[6e]

* This work St = Styrene, Cy = Cyclohexene, Cp = Cyclopropane, Alk. = Alkene Reactions carried out at RT with 5 equiv. of olefin except entries 1–2, 12–16 (with 10 equiv. of styrene).
[a] 40 °C.
[b] *exo*:*endo* ratio.
[c] Two equivalents of styrene, Ar = *o*-Me_2N–(CH_2)–C_6H_4, $(PPh_2)_2(CH_2)_n$ (n = 1;dppm, n = 2; dppe), Bp = dihydridobis(pyrazolyl)borate.

3.2. Differences in reactivity

Coordinative unsaturation at the metal center allows transition metal complexes to react as electrophiles (lewis acids) with diazo groups [15i]. Hence the ease of cyclopropanation will depend upon the ease with which the coordination site at the metal center is available for the incoming reactants [5i,15i,20]. This simple model is able to explain most of the observations made in this study. Thus copper(I) triflate [21] and hexafluorophosphates [19] complexes are highly reactive compared to the chloride complexes [21b].

3.2.1. Influence of phosphorus to copper ratio

The structure of the copper(I) complex plays a significant role in the reaction. The substituent present on the nitrogen atom of the PNP ligand and the 3D structure of the complex dictated by the anion, affect the initiation time and the over all rate of the reaction. In the two cases where initiation time was pronounced, the metal to phosphorus ratio was found to be low.

The perchlorate complex of dppipa, $[Cu(dppipa)_2]ClO_4$ was found to be less reactive in comparison with the halide complexes, $[Cu_3(dppipa)_3X_2][CuX_2]$ (X = Cl, Br) (Tables 2 and 3). This is because of the stability of the CuP_4 unit in the perchlorate complex. An induction period of 20 min was observed which is similar to the results obtained by Pérez et al. [6b,6e] i.e. the rate of the reaction was slower in the presence of excess ligand on the metal.

Among the halide complexes, the tetramers reacted faster than the trimers which were in turn faster than the dimer. This trend is also rationalized on the basis of the number of phosphorus ligands on the copper. More the number of phosphorus ligands, slower the reaction. The tetramers have phosphorus to metal ratio of 1:1, the trimer, 3:2 and the dimer 2:1.

A similar effect of the phosphorus to metal ratio on the cyclopropanation reaction is found to be applicable in dppan ligand system also. The perchlorate complex, $[Cu(dppipa)_2]ClO_4$ reacted slower than the chloride complex, as it has phosphorus to metal ratio of 4:1 whereas the chloride complex, $[Cu_4(dppipa)_2X_4]$ (X = Cl, Br) has metal to phosphorus ratio of 1:1.

3.2.2. Influence of counter anion

Among the halide complexes, the bromide complexes were slower than the corresponding chloride complexes. This implies that the reaction probably requires dehalogenation, the rate of which will be different for chlorides and bromides in order to initiate the reaction. Surprisingly the thiocyanate complex was found to be as fast as the chloride tetramer even though the phosphorus to metal ratio is 2:1. This could probably be due to the ease in breaking the strained chelate ligand on copper in comparison with the bridged ligand.

In the case of dppa complexes, though the ratio of the phosphorus to metal is 1:2 in perchlorate as well as the halide complex, $[Cu_2(dppa)_2(CH_3CN)(OH_2)(OClO_3]ClO_4$ and $[Cu_3(dppa)_3X_2]X$ (X = Cl, Br) respectively, the difference in the induction time and the rate of the reaction can be rationalized based on the coordination environment around copper. In the perchlorate complex, the acetonitrile present on copper is labile, resulting in a two coordinate copper complex leading to fast initiation and completion of the reaction. On the contrary, the halide being bound to copper, makes the reaction slower. Recently Cu(I) Bpy complexes have been used for catalytic cyclopropanation of styrene and influence of counter anion has been discussed [22]. The anion did not affect the binding strength of styrene, rather the rate of decomposition of EDA was lowered in the presence of either weakly coordinating anion (ClO_4^-) as that compared to in the presence of non-coordinating anions (PF_6^- or $CF_3SO_3^-$).

3.3. Comparison between isostructural complexes

The substituent on the nitrogen atom of the diphosphinoamine ligand influences the cyclopropanation reaction as subtle differences are seen in the induction time and the rate of the reaction on comparing the reactions with isostructural complexes. In the case of trimers, the dppipa complexes were faster than the dppa complexes. The dppipa complexes initiated the reaction almost instantaneously and exhibited higher reaction rates compared to the corresponding dppa complexes. On comparing the isostructural tetramers of dppipa and those of dppan, it was seen that bromide complex of dppipa complex was faster than the corresponding dppan complex. Also the perchlorate complex of dppipa, $[Cu(dppipa)_2]ClO_4$ was faster than the perchlorate complex of dppan, $[Cu(dppan)_2]ClO_4$.

In general, the dppipa complexes were the fastest with dppa perchlorate complex being an exception, which is by far the fastest. Electron donating groups (^{i}Pr) on the nitrogen will make the phosphorus a poorer π-acceptor. Electron-withdrawing groups (Ph) on the nitrogen will make the phosphorus a better π-acceptor for the same reason. This effect will become more pronounced if the copper is bound to the halide (π-donor) along with the phosphorus. Thus the presence of an electron-donating group on the nitrogen facilitates the cleavage of the Cu–P bond by making it weak (*vide infra*).

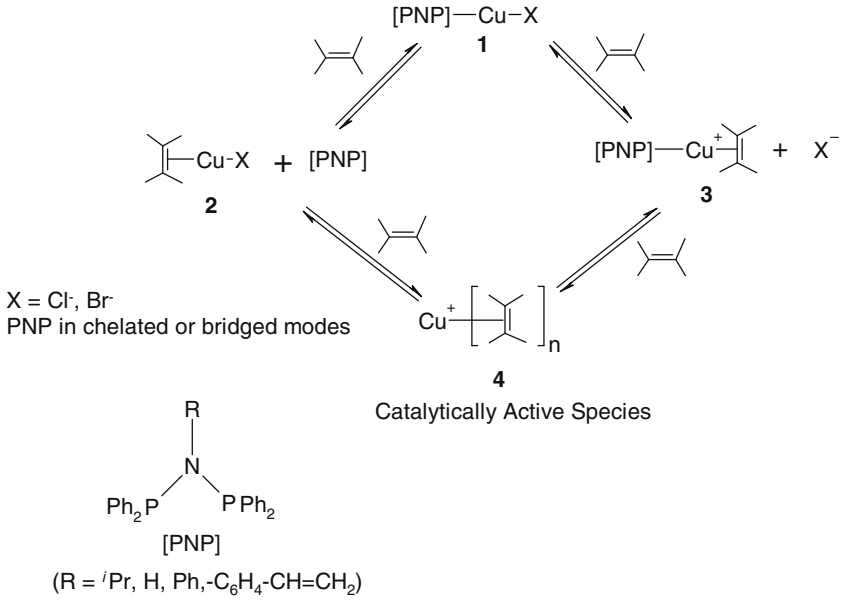
3.4. Mechanism of cyclopropanation

The most significant result obtained from comparing the three ligand systems was that the yield of the cyclopropanation product (~85% from styrene) as well as the *trans* to *cis* ratio of the cyclopropanes (~75:25) was similar in all cases. On the other hand, the reactions carried out with cyclohexene yielded ~77% cyclopropane with *trans* to *cis* ratio of ~76:24. These results show that it is the olefin that plays a role in the catalytically active species rather than the phosphine or the counter anion. If the ligand as well as the counter anion is not attached to the catalytically active metal center, then the active species is probably an olefin bound copper catalyst, since the yield of cyclopropane is dependent on the olefin.

Hence a tentative mechanism is proposed as shown in Scheme 2. It involves dissociation of the phosphine (**2**) and the loss of the halide (**3**) from the coordination sphere of the metal in **1**. Depending on the relative stability of the Cu–X and Cu–P bonds, one step will precede the other. Thus complexes with higher phosphorus to metal ratio take longer time for completion of the reaction. Apparently, when there is a dimer, the process is faster presumably due to inter-metal ligand transfer In the presence of excess olefin, a Cu–olefin complex **4** could be formed. Subsequent interaction of the copper–olefin species with a carbene source, leads to the formation of cyclopropane products. The steps leading to the formation of the olefin complex are reversible and result in a dynamic equilibrium between **1**, **2**, **3** and **4**. The reaction carried out with the trimeric copper(I) complex of dppm (Table 6, entry 9) also gave similar results supporting the idea that the phosphine has no role in the active species generating the cyclopropane.

3.5. Cyclopropanation using heterogeneous copper(I) catalyst; Cu(I) complex of polyvbzpnp [18]

To test the mechanistic hypothesis, a polymeric phosphine was used to generate an anchored catalyst. If a copper (I) olefin complex devoid of phosphines is the catalytically active species, the heterogenous catalyst [18] would not be stable would from a soluble catalyst. In support of this hypothesis, the catalyst underwent partial leaching of the metal in every cycle (Table 6). In the first two cycles, complete consumption of EDA could be realized but



Scheme 2. Proposed mechanism for generation of catalytically active species.

in the third cycle, even after 155 h of heating, 17% EDA was found to remain unreacted.

4. Concluding remarks

Copper(I) diphosphinoamine complexes have been studied for catalytic cyclopropanation of styrene and cyclohexene with ethyl diazoacetate. All complexes are reactive at 40 °C giving high yields of cyclopropane. The differences in the rates of the reactions are due to the different binding modes of the ligand controlled by the substituents on the nitrogen atom of the diphosphinoamine ligand. However, the selectivities are independent of the substituent since the catalytically active intermediate.

Since the yields of the products and *trans* to *cis* ratio of the cyclopropanes are very similar in all the cases investigated, the reaction probably proceeds through a common intermediate. Hence the active species is assigned to a labile copper–olefin complex. This is further confirmed by the behaviour of the heterogeneous copper(I) diphosphinoamine catalyst. As the active intermediate is phosphine free, it suffers from leaching problems during the cyclopropanation reaction. This also explains why it is not possible to use chiral phosphine complexes for enantioselective cyclopropanation [23]. The differences in the reaction times for different catalysts are attributed to differences in the concentration of the catalytically active species. Complexes with weaker Cu–P and Cu–X bonds lead to a faster rate. A large copper to phosphorus ratio helps in increasing the reaction rate. Similarly a dimeric starting complex formed by the bridging phosphinoamine leads to a faster reaction as it has labile Cu–P bonds. The advantage of using a phosphinoamine complex instead of simple copper(I) salts arises from the increased stability of copper(I) in the reaction medium. The short bite ligand is good enough to stabilize the copper(I) but labile enough for generating an active species making it an ideal catalyst.

5. Experimental

5.1. General remarks

Dichloromethane, chloroform, petroleum ether (b.p. 60–80 °C) and acetonitrile were purified and dried under nitrogen atmosphere by conventional methods [24]. All manipulations were carried out under an atmosphere of purified N_2 using standard Schlenk techniques. Copper(I) complexes of *bis*(diphenylphosphino)isopropylamine (dppipa), *bis*(diphenylphosphino)amine (dppa) and *bis*(diphenylphosphino)aniline (dppan) are described elsewhere [16–17]. Synthesis of and *bis*(diphenylphosphino)-*p*-vinyl benzylamine and it's copper(I) complexes have been previously reported [18].

5.2. Physical measurements

All ^1H, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 400 Avance spectrometer, in $CDCl_3$ as the solvent, with tetramethylsilane (TMS) as the internal reference. The kinetics experiments were conducted using "MULTIZG" program, which allowed recording of ^1H NMR spectra at short time intervals.

5.3. Typical procedure for catalytic cyclopropanation

Neat N_2=CHCOOEt (10.5 μl, 0.1 mmol) was added to a NMR tube containing the catalyst (0.5 mol%) and olefin (1.0 mmol) in $CDCl_3$ (0.3 ml). The sample was maintained at 40 °C and spun inside the NMR probe. ^1H NMR spectra were recorded at regular intervals. The reaction was continued until the –CH proton of ethyl diazoacetate disappeared. The percentage yields of cyclopropanes, alkenes and their respective *trans* to *cis* ratios were calculated from the appropriate integrals and were reproducible to ±5%.

5.4. Reactions carried out in a two-necked round bottom flask

To 15 ml of CH_2Cl_2 in a 100 ml double necked round bottom flask, was added the catalyst (0.5 mol%) followed by styrene (1.1 ml, 10 mmol). Then ethyl diazo acetate (0.1 ml, 1 mol) was added and the solution refluxed. ^1H NMR spectra of aliquots from the reaction mixture were recorded at regular intervals. The reaction was continued until the peak due to the diazo "CH" disappeared completely.

5.5. Reactions with an anchored copper

To 15 ml of $CHCl_3$ in a 100 ml double necked round bottom flask, was added the catalyst (1.7 mol%). The polymer was allowed

to swell for about half an hour. Then styrene (11 ml, 100 mmol) and ethyl diazo acetate (1.0 ml, 10 mmol) were added and the solution was heated at 40 °C. ^{1}H NMR spectra of aliquots from the reaction mixture were recorded at regular intervals. After completion of the first cycle, evidenced by the complete disappearance of EDA, the reaction mixture was centrifuged and washed well with diethyl ether. The residue was utilized for the second cycle by adding fresh lots of styrene and EDA as mentioned above. The reaction progress was followed in a similar fashion.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.041.

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