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## Olefin cyclopropanation catalyzed by new diiminophosphorane and triiminophosphorane complexes of copper and palladium

Laurence Beaufort, Albert Demonceau and Alfred F. Noels\*

Laboratory of Macromolecular Chemistry and Organic Catalysis (CERM), University of Liège, Sart-Tilman (B6a), 4000 Liège, Belgium

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Abstract—Chelating diiminophosphorane and tripodal iminophosphorane copper and palladium complexes are found to efficiently catalyze the cyclopropanation of activated monosubstituted olefins with ethyl diazoacetate. Cycloolefins, and linear  $\alpha$ -olefins are somewhat less reactive. The diastereoselectivities of the reactions are moderate and no major differences were seen when comparing the bidentate chelating ligand to the tripodal ligands.

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## 1. Introduction

Organic chemists have always been fascinated by cyclopropanes because the smallest cycloalkane is present as a basic structural element in a great variety of natural and synthetic components of notable interest.<sup>1,2</sup> Cyclopropanes, besides their utility as such, can also be used as synthons in the molecular construction. They are versatile intermediates and can be converted into a variety of useful products by cleavage of the strained three-membered ring. This has led to the development of many methods for cyclopropanation reactions, including the Simmons–Smith reaction<sup>3,4</sup> and the now quite popular transition metal-catalyzed reactions of diazo compounds with olefins (Scheme 1).<sup>2,5</sup>

Control of the stereochemistry of this reaction is an important objective in organic synthesis and to date, the need for cheap, readily available, and highly diastereoselective cyclopropanation catalysts remains, however, largely unmet and the trans to cis (or *syn* to *anti*) selectivities remain usually modest with most Cu-based catalysts. This results from the fact that the stereocontrol of the intermolecular cyclopropanation reaction is most often controlled by the particular olefin-diazocompound combi-

nation, more bulky ester groups favoring the formation of the trans product. Recent developments have highlighted the use of nitrogen ligands in homogeneous catalysis, including enantioselective cyclopropanation catalyzed by transition metals.<sup>6,7</sup> This resulted in the emergence of copper complexes containing a large variety of ligands<sup>8</sup> that include inter alia Schiff bases,<sup>9,10</sup> oxazolines,<sup>11,12</sup> semicorrin,<sup>13</sup> and tris(pyrazolyl)<sup>14,15</sup> ligands for the cyclopropanation reaction.

The present article reports the first results of a work aimed at assessing the potential utility of a series of transition metal complexes based on chelating diiminophosphorane ligands and on triiminophosphorane ligands (their tripodal analogues) as catalysts for the cyclopropanation of olefins with ethyl diazoacetate (EDA) as the carbene source (Scheme 1). Iminophosphoranes are predominantly two electron  $\sigma$ -donors with only minor  $\pi$ -acceptor properties. They feature a short P–N bond and act as neutral monodentate ligands via the lone pair at the nitrogen centre. Further, iminophosphoranes where the carbon backbone bridges the two or three nitrogen atoms (such as those reported in this study) are expected to be sterically demanding ligands since their bulky phosphino substituents



Scheme 1.

Keywords: Cyclopropanation; Alkenes; Diazoester; Iminophosphorane; Tripodal ligand.

<sup>\*</sup> Corresponding author. Tel.: +32 4 3663463; fax: +32 4 3663497; e-mail: af.noels@ulg.ac.be

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are close to the metal centre. The triiminophosphorane ligands utilized in this work constitute a new family of tripodal ligands, the synthesis of which will be reported elsewhere (Scheme 2).<sup>26</sup>



#### Scheme 2.

The iminophosphorane ligand being quite flexible, the symmetry induced by the ligand seems to strongly depend on the coordination sphere of the metal.<sup>16</sup> The diiminophosphorane ligands formally form 16 electron complexes with Cu(I)- and Pd(II) whereas tripodal iminophosphoranes are expected to form 18 electron complexes provided ligation to all three nitrogen atoms takes place. Because these ligands can act in different coordination modes, the different occupancy of the metal coordination sphere might thus, bring about different geometry and have an influence on the catalytic behavior of the metal complexes. Indeed, if complexes of four-coordinate copper are most often tetrahedral, they can also be square-planar whereas sixcoordinate copper complexes are octahedrally disposed. The coordination chemistry of iminophosphoranes and of imino-aza-P(V) ligands has recently been reviewed.<sup>17</sup> To date, however, there is only one report in the literature on the use of diiminophosphorane ligands in olefin cyclopropanation.<sup>16</sup>

#### 2. Results and discussion

## 2.1. Diiminophosphorane complexes of Cu and Pd

The diiminophosphorane ligands 1-4 were prepared as previously reported by reacting a dibromotriaryl-phosphorane (Ar<sub>3</sub>PBr<sub>2</sub>, prepared in situ) with *o*-phenylene-

Table 1. Styrene cyclopropanation with Ph(N=PR3)2-Cu and Pd catalysts

diamine in the presence of triethylamine.<sup>16</sup> The corresponding air stable metallic complexes **5–8** were formed by reacting the four different ligands **1–4** with the appropriate metallic salt, respectively, CuOTf, Cu(OTf)<sub>2</sub> (OTf= trifluoromethanesulfonate anion) or PdCl<sub>2</sub> in dichloromethane (Scheme 3).

#### Scheme 3.

Screening cyclopropanation experiments with the complexes were performed under typical reaction conditions as already reported,<sup>18</sup> using a syringe pump for diazoester addition (EDA) and with styrene or cyclooctene as model substrates for activated and non-activated olefins, respectively. In order to minimize carbene coupling, a large excess of styrene has been used; the molar ratio Cu:EDA:styrene being 1:100:1000 and its addition occurs very slowly by means of a drip. The tests have been realized at two different temperatures, 60 °C and rt and the reaction products (*cis* and *trans* cyclopropanes, diethyl maleate, and fumarate) identified by CPC. Table 1 summarizes the results obtained with styrene.

It follows that, as usual, various parameters that include the catalyst structure, the substrate and the reaction temperature affect to some extent the rates and the yields of the reactions, as well as their diastereoselectivities (cis/trans or *exolendo* ratio).

As a rule, the cyclopropanation reactions take place with

<i>T</i> (°C)	Ligand PR <sub>3</sub> <sup>a</sup>	Metal	Cyclopropanation <sup>b</sup>		Dimerisation	
			Yield (%)	cis/trans	Yield (%)	Maleate/fumarate
60 °C	PCp <sub>3</sub>	Cu(II)	99	0.65	0.5	0.94
		Cu(I)	95	0.63	5	1.49
		Pd(II)	93	0.50	7	0.15
	Ph <sub>2</sub> Cy	Cu(II)	95	0.61	5	1.30
	2 0	Cu(I)	98	0.66	2	1.22
	PPh <sub>3</sub>	Cu(II)	96	0.54	4	0.72
	2	Cu(I)	99	0.45	0.5	0.27
		Pd(II)	98	0.55	2	0.45
	PCy <sub>3</sub>	Cu(II)	98	0.70	2	0.63
		Cu(I)	87	0.73	12	0.71
rt <sup>c</sup>	PCp <sub>3</sub>	Cu(II)	79	0.92	18	1.01
	1.5	Pd(II)	82	0.46	18	0.13
	Ph <sub>2</sub> Cy	Cu(II)	90	0.31	7	1.29
	PPh <sub>3</sub>	Cu(II)	89	0.42	9	3.89
	2	Pd(II)	74	0.62	25	0.67
	PC <sub>V3</sub>	Cu(II)	90	0.62	8	1.07
	2.2	Cu(I)	88	0.85	12	1.72

<sup>a</sup> Abbreviations: Cp, cyclopentyl; Cy, cyclohexyl.

<sup>b</sup> Experimental conditions: Cu complex, 0.01 mmol; styrene, 2 mL; ethyl diazoacetate (EDA), 1 mmol diluted by the olefin up to 1 mL; addition time, 3 h. Yields based on EDA.

<sup>c</sup> rt, room temperature.

high yields (>95%) at 60  $^{\circ}$ C, whatever the initial oxidation state of copper. There is a general agreement that EDA reduces Cu(II) to Cu(I) species and that in both cases, the active form of copper is the +1 oxidation state.<sup>8,19</sup> Only a small amount of carbene dimers (ethyl maleate and ethyl fumarate) is formed as by-products. On the whole, the alteration of the phosphine part of the ligand does not much influence the cyclopropanation yields, although it does affect the diastereoselectivity of the reaction. This is mostly noticeable with the copper(I) catalysts for which the ratio cis/trans varies from 0.45 to 0.73 at 60 °C (i.e., about a 30-40% fraction of *cis* isomers), depending on the selected phosphine. Such values come within the range of results obtained with the vast majority of Cu-based catalysts reported up to now.9 Even if the stereoselectivity of the cvcloaddition remains modest, there seems to exist a direct relationship between the steric bulk of the phosphine and the relative amount of cis cyclopropane synthesized, which increases following the series  $PPh_3 < PPh_2Cy \approx PCp_3 <$ PCy<sub>3</sub>. No such trend is seen for carbene dimers.

The reactions also take place at rt with the copper and palladium complexes though the reaction time for diazoester decomposition needs then to be lengthened, and it takes around 20 h for the reaction to be complete instead of 3 h at 60 °C. The yields remain very good, although slightly lower than those obtained at higher temperature.

The same copper- and palladium-based catalysts have been applied to the cyclopropanation of cyclooctene, a non activated olefin (Scheme 4). The results of the cyclopropanation reactions at two different temperatures are reported in Table 2.



#### Scheme 4.

At 60 °C, good cyclopropanation yields are obtained with both metal complexes, though slightly inferior to those observed with styrene. With both metals, the *exo*cyclopropane is preferentially formed, especially with Pd-based catalysts, the copper(II) complexes forming relatively more *endo*-isomer. Here also all metal complexes remain active for EDA decomposition at rt, although the duration of the reaction time needs again to be considerably increased. The cyclopropanation yields fall from 90% for a reaction performed at 60 °C to 60% at rt with the less efficient Cu-based system. The simultaneous increase of maleate and fumarate formation that is observed is concomitant with a fall of the cyclopropanation yields. Moreover, the issue of the cyclopropanation reaction in term of selectivity is similar to that obtained at higher temperature.

It appears from these preliminary results that the structural features of the ligand used in the cyclooctene or styrene cyclopropanation reactions do not modify the outcome of the reactions to a large extent, neither in terms of stereoselectivity nor of yield. On the other hand, replacing copper for palladium, mostly brings about some modification of the ratio of the isomers formed. In this context, the diiminophosphoranes complexes of palladium even if they are slightly more selective than the corresponding copper triflate based complexes, are also slightly less efficient cyclopropanation catalysts, especially with cyclooctene.

## 2.2. Triiminophosphorane complexes of Cu and Pd

Recent advances in olefin cyclopropanation catalyzed by metal complexes have highlighted the interest of tridentate ligands for obtaining highly active and selective catalysts. It is the case namely for complexes based on pyridinebisoxazoline (pybox) and on homoscorpionate ligands (pyrazolylborates, Tp, see Scheme 5), some of which are capable of inducing large enantiomeric excesses in the conversion of alkenes into cyclopropanes while also favoring cis-isomer formation.<sup>15,20,21</sup> The necessity of being able to promote reactions of highly enantioselective and *cis*-selective cyclopropanation is illustrated inter alia by the recent synthesis of a powerful inhibitor of the inverse transcriptase (HIV-1).<sup>22</sup>



Table 2. Cyclooctene cyclopropanation with Ph(N=PR<sub>3</sub>)<sub>2</sub>-Cu and -Pd catalysts

<i>T</i> (°C)	Ligand <sup>a</sup>	Metal	Cycle	Cyclopropanation		Dimerisation	
			Yield (%)	endo/exo	Yield (%)	Maleate/ fumarate	_
60 °C	$Ph(N=PCp_3)_2$	Cu(II)	92	0.41	7	1.36	5
		Pd(II)	83	0.16	17	0.38	5
	$Ph(N=PPh_3)_2$	Cu(II)	89	0.50	10	1.41	4
	. 572	Pd(II)	89	0.19	11	0.94	48
rt <sup>b</sup>	$Ph(N=PCp_3)_2$	Cu(II)	73	0.39	27	1.46	22
	15/2	Pd(II)	68	0.20	32	0.38	22
	Ph(N=PPh <sub>3</sub> ) <sub>2</sub>	Cu(II)	60	0.47	39	1.60	22

<sup>a</sup> Experimental conditions: complex, 0.01 mmol; cyclooctene, 2 mL; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 3 h. <sup>b</sup> rt, room temperature.

<i>T</i> (°C)	Ligand <sup>a</sup>	Metal	Cyclopropanation <sup>b</sup>		Dimerisation	
			Yield (%)	cis/trans	Yield (%)	Maleate/fumarate
60	CH <sub>3</sub> -C-(CH <sub>2</sub> NPPh <sub>3</sub> ) <sub>3</sub>	Cu(II)	97	0.57	3	1.33
	5 . 2	Pd(II)	81	0.56	19	0.59
	$CH_3-C-(CH_2NPCp_3)_3$	Cu(II)	88	0.47	12	1.95
	$Ph-C-(CH_2NPPh_3)_3$	Cu(II)	97	0.54	3	1.40
	2 5/5	Pd(II)	86	0.52	14	0.73
	$Ph-C-(CH_2NPCp_3)_3$	Cu(II)	93	0.50	7	1.32
rt <sup>c</sup>	$CH_3-C-(CH_2NPPh_3)_3$	Cu(II)	84	0.60	15	1.76
	CH <sub>3</sub> -C-(CH <sub>2</sub> NPCp <sub>3</sub> ) <sub>3</sub>	Cu(II)	86	0.12	12	0.90

Table 3. Styrene cyclopropanation with tripodal ligand-based catalysts

<sup>a</sup> Abbreviations: Cp, cyclopentyl; Cy, cyclohexyl.

<sup>b</sup> Experimental conditions: complex, 0.01 mmol; styrene, 2 mL; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 3 h.

<sup>c</sup> rt, room temperature.

There are some coordinating similarities between the pyrazolyborate 1 ligands shown in Scheme 5 and the triiminophosphoranes 2. Each of these ligands looks like a hand formed by three 'fingers' relatively independent from each other, although one might expect a somewhat greater flexibility for the triiminophosphoranes. Each 'fingers' contains a  $sp^2$  nitrogen atom that will coordinate to the transition metal through its lone electron pair. The proposed tridentate chelation is based on their spectroscopic data as no suitable crystals of any complexes have been obtained so far.

Pérez and co-workers,<sup>14,15,20,23,24</sup> and Penoni and co-workers<sup>25</sup> have demonstrated the potential of copper complexes bearing homoscorpionate (Tp) ligands in carbene reactions. Hence, this justifies the interest of exploring the catalytic activity of the new triimino-phosphorane ligand system in olefin cyclopropanation. The triiminophosphorane ligands were prepared as reported and the corresponding metallic complexes were formed by reaction of the ligand with the appropriate metallic salt in a dichloromethane solution.<sup>22</sup> Screening cyclopropanation experiments were performed under the same reaction conditions as reported for the diiminophosphorane complexes<sup>18</sup> and an overview of the activity/selectivity pattern of Cu- and Pd-complexes ligated to such tripodal ligands is reported hereafter.

The results for styrene cyclopropanation at two different temperatures are summarized in Table 3. It comes out that these triiminophosphorane-based complexes present a good catalytic activity, the yields vary from 81 and 99% and the secondary products (ethyl maleate and ethyl fumarate) are formed in low amounts when the reactions are performed with copper at 60 °C. The yields obtained with the Pd-based complexes are somewhat lower and from that on, an increased formation of carbene dimers can be observed. No significant influence of the substituent (methyl or phenyl group) at the sp<sup>3</sup> carbon bearing the three functionalized tethers is seen.

The diastereoselectivity of the reaction at 60  $^{\circ}$ C is not exceptional and does not vary much from one ligand to the other. In the whole, the cis- and trans-cyclopropanes are formed in an average ratio 35:65 whatever the ligand utilized. The ligand structure seems thus, to have relatively little influence on the outcome of the cyclopropanation reaction even if the stereoselectivity of the reactions can be

significantly different to that observed with the corresponding bis-iminophosphorane complexes. This concurs with what has already been reported by Pérez and co-workers,<sup>15, 20</sup> and according to these authors, the catalyst structure has little influence on the stereoselectivity of the reaction. This fact has been rationalized assuming that the high reactivity of the metal–carbene complex results from a transition state (A) (Scheme 6) in which the olefin remains always at a relatively important distance from the metal centre, which prevents it from being significantly affected by the steric bulk of the ligand. For that reason, the steric influences are not decisive in the induction of the diastereoselectivity.





At rt, the results are slightly less satisfactory regarding the yield of the cyclopropanation. On the other hand, in the case of the  $CH_3-C-(CH_2NPCp_3)_3$  ligand, the copper complex tends to form predominantly the trans-isomer in a more significant way than at higher temperature. Furthermore, the stereoselectivity is opposite to that, which is observed with the corresponding bis-Cp-iminophosphorane (cis/trans ratios=0.12 vs 0.92, see Table 1).

In order to study the influence of the substrate and of the stereo-electronic effects in these cyclopropanation reactions, differently substituted styrene derivatives and some aliphatic or aromatic olefins have been tested with the metal complex  $[CH_3-C-(CH_2NPCp_3)_3Cu(OTf)_2]$ . The results are reported in Table 4.

As a whole, the yields of the cyclopropanation reaction of the styrene derivatives are good to excellent (entries 1-7), with the exception of 4-*t*-butylstyrene and to a lesser extent of 4-methylstyrene. It should be noted that 4-methoxy as well as 4-chloro, and 4-trifluoromethylstyrenes give high yields of cyclopropanation products. Electron-rich and electron-depleted styrenes are thus, suitable targets for the carbene (or carbenoid) species formed in situ. The

Table 4. Cyclopropanation of various olefins with EDA and CH<sub>3</sub>–C–(CH<sub>2</sub>NPCp<sub>3</sub>)<sub>3</sub>Cu(OTf)<sub>2</sub>

Entry	Substrate		Cyclopropanation <sup>a</sup>	Dimerisation (%)
		Yield (%)	cis/trans ratio	
1	Styrene	88	0.54	12
2	4-Chlorostyrene	93	0.45	7
3	4-Methoxystyrene	98	0.50	2
4	4-t-Butylstyrene	62	0.47	16
5	4-Methylstyrene	78	0.49	21
6	α-Methylstyrene	89	0.80	10
7	4-Trifluoromethylstyrene	91	0.49	9
8	1-Octene	52	0.51	48
9	Cyclooctene	77	0.65	23
10	1-Decene	68	0.61	32
11	Diethyl fumarate	2		nd <sup>b</sup>
12	Phenylacetylene	21	—	79

<sup>a</sup> Experimental conditions: complex, 0.005 mmol; olefin, 1 mL; ethyl diazoacetate, 1 mmol diluted by the olefin up to 1 mL; addition time, 3 h; temperature, 60 °C.

<sup>b</sup> nd, not determined.

copper-catalyzed reactions of ethyl diazoacetate with linear alkenes or cycloalkenes are more difficult but proceed in relatively good yields, although as expected, the activated alkenes (styrenes) are always more reactive than the nonactivated ones (1-octene, cyclooctene, 1-decene).

Globally, all the diasteroselectivities of the cyclopropanations obtained with the different olefins remain more or less in the same range of cis/trans ratio but for  $\alpha$ -methylstyrene where it reaches the value of 0.8. This styrene derivative is known to give frequently ratio of isomeric cyclopropanes close to 1.

Despite the fact that the steric requirements for di- and triiminophosphorane complexes are quite different, the resulting stereoselectivities remain relatively close (although sometimes significantly different, however), and are difficult to rationalize. We have then performed competition experiments with *para*-substituted styrenes to obtain some further informations on the electronic effects of these ligands in the cyclopropanation reaction.

Four different complexes have been employed as the

precatalyst in the competitive cyclopropanation of an equimolar mixture of two styrenes, the non-substituted  $C_6H_5CH=CH_2$  and a *para*-substituted styrene of general formula  $XC_6H_4CH=CH_2$  (Scheme 7). The ratio of the resulting cyclopropanes **11a**,**b**:**12a**,**b** were determined by gas chromatography. The results are summarized in Table 5.

In all cases, the cyclopropanation reaction favors the electron rich derivatives, whatever the kind of copper complex used (bearing a di- or a triiminophosphorane type ligand), that is, the *p*-methoxy- and *p*-tertbutylstyrenes, whereas the electron-withdrawing groups such as Cl and CF<sub>3</sub> clearly disfavor the cycloaddition. This confirms the electrophilic character of carbenes (carbenoids) formed during the cyclopropanation reaction and is consistent with the observation that the carbene addition on electron poor olefins such as diethyl maleate or diethyl fumarate is only poorly effective, as depicted in Table 4.

Furthermore, the complexes ligated to cyclopentyl-triiminophosphoranes always appear to be more selective than their bis-iminophosphorane counterparts, the reverse



Scheme 7.

Table 5. Competition experiments<sup>a</sup> with para-substituted styrenes

Catalyst		)]			
	p-OMe/H	<i>p-t</i> Bu/H	p-Cl/H	<i>p</i> -CF <sub>3</sub> /H	
Ph-1,2-(N=PPh <sub>3</sub> ) <sub>2</sub> Cu(OTf) <sub>2</sub>	1.66	1.67	0.72	0.32	
Ph-1,2-(N=PCp <sub>3</sub> ) <sub>2</sub> Cu(OTf) <sub>2</sub>	1.63	1.54	0.79	0.49	
$CH_3-C(CH_2N=PCp_3)_3Cu(OTf)_2$	2.07	1.86	0.84	0.52	
Ph-1,2-(N=PPh <sub>3</sub> ) <sub>3</sub> Cu(OTf) <sub>2</sub>	1.38	1.46	0.83	0.21	

<sup>a</sup> Experimental conditions: complex, 0.005 mmol; olefin, 1 mL of an equimolar mixture; ethyl diazoacetate, 1 mmol diluted by the equimolar mixture of olefins up to 1 mL; addition time, 3 h; temperature, 60 °C.

trend being observed with the phenyl-substituted ligands. On the other hand, the phenyl-bisiminophosphoranes show the reverse trend and select preferentially the electron-rich olefins when compared to their triiminophosphorane analogs. This constitutes a further indication that the metal complexes of bis- and triiminophosphoranes yield different active species in situ.

In conclusion, the present investigations have shown that the Cu- and Pd- di- and triiminophosphoranes are good to excellent catalysts for olefin cyclopropanation. However, despite the bulkiness of the iminophosphoranes used in this study, the stereoselectivities of the cyclopropanation reactions remains modest.

## 3. Experimental

# **3.1.** General procedure for the cyclopropanation experiments

Cyclopropanation reactions were performed in small 10 mL two necked flasks fitted by a three way stopcock and by a septum. In this flask,  $1 \times 10^{-5}$  mol of the copper complex are introduced. The flask is then placed under inert atmosphere by three consecutives vacuum-argon cycles. To the catalyst, 2 mL of the dried, distillated, and degassed olefin are then added. The flask is heated to 60 °C in an oil bath (excepted for the reactions carried out at rt). In a 1 mL seringe, 0.125 g of the diazocompound are weighted and diluted up to 1 mL with the olefin. The diazoester is slowly added to the alkene solution via a syringe pump, the duration of the addition is 3 h at 60 °C. The kinetics of ethyl diazoacetate decomposition is followed by volumetry through  $N_2$  evolution. To this end, the reaction flask is connected via the three way stopcock to a water column through a metallic canula. At the end of the reaction, the reaction mixture is analyzed by gas chromatography and the reaction products identified and quantified by comparison with authentic samples.

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