Polyoxometalates: Powerful Catalysts for Atom-Efficient Cyclopropanations

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Abstract: The polyoxometalate-based catalytic cyclopropanation of olefins by ethyl diazoacetate (EDA) is reported. The outstanding catalyst productivity (TONs up to 100,000) and the use of equimolar EDA/olefin ratio confer to the methodology a high sustainability. Preliminary mechanistic investigations are also discussed.

Keywords: cobalt; copper; cyclopropanes; diazo compounds; homogeneous catalysis; polyoxometa-lates

Oxo clusters of early transition metals in their highest oxidation state, polyoxometalates or POMs, are receiving much attention due to the great versatility of their molecular structures and properties. They display numerous applications, amongst which catalysis surely occupies the first place.^[1,2] Most applications of POMs in catalysis refer to acid catalysis due to the superacidity of heteropolyacids^[3] or oxidation catalysis,^[4] based on the intrinsic redox properties of POMs^[5] or the incorporation of active transition metals.^[6,7] Besides these traditional fields and the great challenges still being pursued, like water oxidation,^[8-10] the last few years have witnessed new fields of applications. POM-based organometallic assemblies have been described, either electrostatic or covalent, aiming at synergistically enhancing the activity of the organometallic catalyst,^[11-13] or that of the POM,^[14] or at facilitating the recovery of the organometallic catalyst.^[15] The ability of vacant POMs to accommodate almost any cation of the periodic table opens the scope of reactions to Lewis acid cataly-sis^[16-18] or coupling reactions.^[19,20] As underlined in the literature.^[21] POMs exhibit remarkable features as all-inorganic ligands, oxidatively, thermally and hydrolytically stable, providing pH control. The high oxidation state metal-oxo function^[22-25] can be electronically stabilised by adjusting the fine balance of π -donor oxo ligands and π -acceptor metallic backbone. Accordingly, oxygenation catalysis from transition metalsubstituted POMs (TMSPs) has been extensively illustrated. However other group transfers like carbene^[26,27] or nitrene transfers^[28] from similar TMSPs are curiously almost absent from the POM literature. This prompted our impetus to explore this still fallow domain, in line with the emergence of new types of reactions catalysed by POMs.

Carbene transfer reactions to olefins afford cyclopropanes, an important class of building blocks in organic synthesis, due to the high reactivity of the three-membered ring.^[29-31] Ring-opening and ring-expansion reactions of cyclopropanes have been emerging as useful methods to synthesise biologically and pharmaceutically active substances.^[32,33] This can explain why the scientific community currently devotes great efforts in developing efficient and selective methodologies to synthesise this kind of compounds.^[34] Metalloporphyrin complexes are well known to catalyse cyclopropanation using diazo derivatives as carbene sources^[35,36,37] and the robustness of this class of complexes allows high turnover numbers. Moreover, the introduction of stereogenic centres into the skeleton of porphyrins afforded in several cases impressive enantiomeric excesses.^[38] Some of us

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have also recently reported^[39] on the catalytic activity of chiral cobalt(II) porphyrins in the asymmetric cyclopropanation of olefins by ethyl diazoacetate (EDA). Unfortunately, a practical application of porphyrin-based homogeneous catalytic cyclopropanations is hampered by the difficulty in recovering and recycling the catalyst, an essential condition for an eco-compatible synthetic strategy.

Some parallels have been drawn between the tetraaza macrocycle of a porphyrin and the tetraoxo coordination environment provided by a mono-vacant Keggin or Dawson POM. This, together with the robustness of the all-inorganic POM ligand, has inspired the early work on TMSPs.^[40-42] Following on, theoretical calculations have shed light on the differences of their electronic structures and on the limits of this analogy.^[43] At variance with metalloporphyrins, POMs can be in principle easily removed from a catalytic mixture by precipitation with a suitable cation. The replacement of an organic cation by an alkaline one causes the precipitation of the POM from organic solvents, or allows its extraction in water. Alternatively, it can be separated by nano-^[15] or membrane-filtration.^[44] This should provide the organic products free of any metal traces.

For all the above-mentioned considerations, we decided to investigate the catalytic activity of polyoxometalates in cyclopropanations and the data reported herein show that this new POM-based methodology affords the desired products in high yields, outstanding turnover numbers and elevated atom efficiency.

To study the relationship between the structural features of POMs and their catalytic activity, we compared the reactivity of $[PW_{11}O_{39}M(OH_2)]^{5-}$ (1,^[45] M = Co^{2+} ; 2,^[46] M = Cu^{2+}) with that of the Krebs-type POM $[Bi_2W_{20}O_{70}Co_2(H_2O)_6]^{10-}$ (3).^[47] As each cobalt cation in the latter complex bears three water molecules instead of a single one, its catalytic activity could be improved, as already suggested.^[47–49] One asset of multi-vacant POMs is their ability to coordinate several active metallic sites, so that synergistic effects could arise, provided that they are not too distant from each other. We thus included the study of $[\gamma-SiW_{10}O_{36}Cu_2(N_3)_2]^{6-}$ (4).^[19,20,50,51]

The $[PW_{11}O_{39}Co(OH_2)]^{5-}$ $(1.39 \times$ (1) anion 10^{-2} mmol), initially available as a cesium salt, has been transferred from an aqueous solution (10 mL) into non-polar benzene solvent (10 mL) containing an excess of tetrahexylammonium bromide (THABr) (Cs/THABr = 1:1.65). After separation of the aqueous phase, a stream of dry dinitrogen was passed through the organic phase for 20 min, upon which a colour change from violet to green was observed in agreement with the procedure described in the literature for the formation of the unsaturated TM derivatives $[XW_{11}O_{39}M]^{n-}$.^[52] Then 100 equivalents of α -methylstyrene and 20 equivalents of ethyl diazoacetate



Scheme 1. Cyclopropanation of α -methylstyrene by EDA catalysed by 1 or 2.

(EDA) were added and the resulting yellow solution was refluxed until complete consumption of EDA. The reaction was monitored by IR, following the disappearance of the N₂ stretching of EDA band at 2112 cm⁻¹. The formation of cyclopropanes was confirmed by GC-MS analysis on the mother solution and by ¹H NMR analysis of the crude using 2,4-dinitrotoluene as internal standard.^[53] The reaction catalysed by **1** yielded 30% of *cis* and *trans* ethyl 2methyl-2-phenylcyclopropanecarboxylate with the diastereoisomeric ratio *cis/trans* = 36:64.

The reaction in Scheme 1 was also run in the presence of $[PW_{11}O_{39}Cu(OH_2)]^{5-}$ (2) that was dissolved in benzene using the same procedure as described above. The ¹H NMR analysis^[54] of the reaction mixture revealed the presence of 20% of cyclopropanes in a *cis/trans* ratio of 42:58.

Cyclopropane formation, even if in low yields, encouraged us to study the catalytic activity of structurally different POMs. In particular, we investigated the activity of POMs bearing two metallic centres such as $[Bi_2W_{20}O_{70}Co_2(H_2O)_6]^{10-}$ (3) and $[\gamma$ -SiW₁₀O₃₆Cu₂(N₃)₂]⁶⁻ (4). The catalytic activity of the latter in the oxidative alkyne-alkyne homocoupling^[50] and in the 1,3-dipolar cycloaddition of organic azides to alkynes^[19,55] was reported in the literature by Mizuno et al.

The Krebs-type POM $[Bi_2W_{20}O_{70}Co_2(H_2O)_6]^{10-}$ (3),^[47] initially prepared as a sodium salt has been transferred in dichloroethane as already described. Conversely, the availability of **4** as a tetrabutylammonium salt (TBA)₄[γ -H₂SiW₁₀O₃₆Cu₂(N₃)₂],^[50] allowed us to solubilise it directly in the reaction solvent. It is worth noting that the two cobalt centres are not connected in complex **3**, whereas two μ_2 - η^1 , η^1 N₃ ligands bridge the two copper centres in **4**. The catalytic activity of **3** and **4** was tested and the results are listed in Table 1. It should be noted that benzene was replaced by dichloroethane as the reaction solvent to ensure a complete solubilisation of the catalysts.

As described in the footnote to Table 1, ethyl diazoacetate was slowly added to the olefin/catalyst mixture to reduce the homocoupling formation of fumarate and maleate which are responsible for the low reported cyclopropane yields. The IR analysis, performed at the end of the EDA addition, showed the absence of the N_2 band of the diazo compound for

Table 1. Cyclopropanation reactions catalysed by **3** or **4**.^[a]

Entry	Product	Yield [%] ^[b]	cis/trans ^[c]
1	H ₃ C COOEt	58 ^[d] 90 ^[e]	28:72 ^[d] 49:51 ^[e]
2	CI COOEt	74 ^[d] 94 ^[e]	32:68 ^[d] 49:51 ^[e]
3	Ph COOEt	72 ^[d] 95 ^[e]	-
4	H ₃ C COOEt	40 ^[d] 80 ^[e]	26:74 ^[d] 34:66 ^[e]
5	CI COOEt	70 ^[d] 98 ^[e]	38:62 ^[d] 38:62 ^[e]
6	COOEt	67 ^[d] 98 ^[e]	38:62 ^[d] 31:69 ^[e]
7		25 ^[d] 33 ^[e]	35:65 ^[d] 44:56 ^[e]
8	COOEt	37 ^[d] 63 ^[e]	35:65 ^[d] 35:65 ^[e]

- ^[a] General procedure for the reaction: catalyst $(6.9 \times 10^{-3} \text{ mmol})$ was dissolved in 1,2-dichloroethane (9 mL) with olefin and then 1 mL of a dichloroethane solution of EDA was added by a syringe pump over 100 min at 75 °C; mol ratio catalyst/EDA/olefin = 1:40:100.
- [b] Determined by ¹H NMR with respect to EDA using 2,4dinitrotoluene as the internal standard. The only byproducts were fumarate and maleate for entries 1–6 and triethyl cyclopropane-1,2,3-tricarboxylate for entries 7 and 8. Catalyst 3 was eliminated using the procedure described for 1 and 2; however, to eliminate 4 the reaction mixture was evaporated to dryness, benzene was added and the obtained solid was filtered off before adding the internal standard to the filtrate.
- ^[c] Determined with a Shimadzu GCMS-QP5050 A instrument, equipped with an Equity 5 column.
- ^[d] **3** as catalyst.
- ^[e] **4** as catalyst.

every reaction reported in Table 1. In general, product yields of 4-catalysed cyclopropanations are higher than those of reactions run in the presence of 3. However, in these latter cases the diasteroselection is slightly better.

The data collected suggest that the reaction efficiency does not depend on the steric hindrance around the double bond of the olefin. In fact, similar yields are observed for styrenes with or without a substituent in the α -position of the double bond (compare entry 2 with entry 5). The cyclopropanation occurred also using indene (entry 6) or dienes (entries 7 and 8) as unsaturated substrates but, as expected, the cyclopropanation of dienes yielded the desired product in moderate yields. Nevertheless, it should be pointed out that the cyclopropane of 2,5-dimethyl-2,4hexadiene is an important precursor to the synthesis of chrysanthemic acid,^[56] a pyrethroid compound employed as household insecticide.

It worth noting that, having eliminated the catalyst, the 4-catalysed cyclopropanation of indene (Table 1, entry 6) afforded the corresponding cyclopropanes in a quantitative yield as a *cis/trans* mixture.

All the catalytic reactions described up to now were carried out with 2.5 mol% catalyst. Although this is a suitable amount on a laboratory scale, a lower catalyst loading would be preferable for industrial applications.

We have thus studied the influence of catalyst loading on the cyclopropanation of α -methylstyrene catalysed by **4** taken as a model case. Moreover, to enhance the atom efficiency of the cyclopropanation, all the reactions were run using an equimolar EDA/ olefin ratio. The results are reported in Table 2.

Very interestingly, the catalyst was still active after a catalytic reaction. In fact, the reaction of α -methylstyrene with EDA, performed with a mol ratio 4/ EDA/olefin=1:100:100, yielded a complete conversion of the diazo compound into the corresponding cyclopropane for three consecutive runs. The GC-MS analysis of each run revealed the presence of cyclopropanes in comparable diastereoisomeric ratios (first run 47:53, second run 47:53, third run 48:52).

As displayed in Table 2, lowering of the catalyst loading caused a decrease in the cyclopropane yield. However, this effect can be offset by increasing the

Table 2. Optimisation of the catalyst **4** loading for the reaction of α -methylstyrene with EDA.^[a]

Entry	4 (mol%)	$t [h]^{[b]}$	Yield[%] ^[c]	cis/trans ^[d]	TON
1	1	_	84	45:55	100
2	0.1	_	77	46:54	1,000
3	0.01	-	63	43:57	10,000
4	0.002	1	57	44:56	50,000
5	0.001	3	48	44:56	100,000

^[a] General procedure for the reaction: a 1,2-dichloroethane solution of **4** was added to 9 mL of a 1,2-dichloroethane α -methylstyrene (0.69 mmol) solution and then 1 mL of a 6.90×10^{-4} M solution of EDA (0.69 mmol) was added by a syringe pump over 100 min at 75 °C.

- ^[b] Further time required after the complete EDA addition to reach the complete conversion of starting EDA.
- ^[c] Determined by ¹H NMR (2,4-dinitrotoluene as the internal standard).
- ^[d] Determined with a Shimadzu GCMS-QP5050 A instrument, equipped with an Equity 5 column.

concentration of the substrates. Employing a molar ratio 4/EDA/olefin=1:100,000:100,000 and a concentration 50-fold higher than that of entry 5 (Table 2) a cyclopropane vield of 95% was finally achieved. These last experimental conditions were employed using the same olefins as reported in Table 1 and the results are listed in Table 3.

Overall, the reaction proceeds efficiently for the majority of the examined substrates, nevertheless, the cyclopropanation of dienes afforded the products only in modest yields. In these latter cases the GC-MS analysis of the crude reaction mixture revealed the formation of triethyl cyclopropane-1,2,3-tricarboxylate as a by-product.^[57] On the other hand, the modest yield reported in entry 2 is due to the forma-

Table 3. Cyclopropanation reactions catalysed by 4.^[a]

Entry	Product	<i>t</i> [h] ^[b]	Yield [%] ^[c]	cis/trans ^[d]
1	H ₃ C COOEt	5.30	95	45:55
2	CI COOEt	5.30	66	49:51
3	Ph COOEt	4.40	98	_
4	H ₃ C COOEt	4.40	86	40:60
5	CI COOEt	3.90	97	45:55
6	COOEt	4.00	96	36:64
7		3.30	30	41:59
8	COOEt	4.00	60	43:57

[a] General procedure for the reaction: 0.25 mL of a $6.9 \times$ 10^{-4} M 1,2-dichloroethane solution of 4 $(1.72 \times$ 10^{-4} mmol) was added to 5 mL of 1,2-dichloroethane containing the olefin (17.2 mmol) and then 1.81 mL of EDA (17.2 mmol) was added by a syringe pump over 75°C; 4/EDA/olefin = 100 min at mol ratio 1:100,000:100,000.

- Reaction time required to reach the complete conversion of starting EDA.
- [c] Determined by ¹H NMR using 2,4-dinitrotoluene as the internal standard.
- [d] Determined with a Shimadzu GCMS-QP5050 A instrument, equipped with an Equity 5 column.

tion of coupling by-products maleate and fumarate. Even if a poor diasteroselection was observed, to the best of our knowledge, a TON of 100,000 for homogeneous catalytic cyclopropanation has never been reported up to now.^[58] Besides, the atom efficiency of the reaction, already associated to the formation of molecular nitrogen as by-product, is enhanced by using an equimolar ratio EDA/olefin. A large excess of the olefin is often required to avoid the formation of undesired products due to decomposition of the diazo compound.^[59-61] Obviously, this is not in accord with the industrial request for sustainable processes, especially when expensive olefins are involved.

Some control experiments have been carried out to reveal insights into the mechanism of the reaction. Firstly, the 4-catalysed reaction between α -methylstyrene and EDA (4/EDA/olefin=1:40:100) was monitored by UV-vis spectroscopy. The absorption band at 360 nm attributed to the Cu(II) \leftarrow N₃-LMCT gradually decreased suggesting that the azido ligand was released during the reaction. Furthermore, a concomitant decay of the *d*-*d* transition band at 700 nm suggests that Cu(II) in 4 is probably reduced to Cu(I) during the catalytic cycle (see Supporting Information).^[50] The pre-catalyst nature of **4** is also supported by the induction period observed in the cyclopropanation of 4-chloro- α -methylstyrene (4/EDA/olefin = 1:1,000:1,000) monitoring the consumption of the diazo compound by IR spectroscopy (N₂ stretching at 2112 cm^{-1}). To control the EDA decrease all the reactants were dissolved together in the reaction solvent. As reported in Figure 1 in the first 5 min the EDA conversion was 6% while in the successive 10 min the EDA conversion was almost complete.

Then a 1,000:1,000 mixture EDA/olefin was readded and the reaction proceeded completely in only five minutes without any induction period. This last trend was observed after another EDA/olefin addi-



Figure 1. EDA percentage vs time in the catalytic reaction $cat/EDA/\alpha$ -methylstyrene = 1:1,000:1,000.

tion. If the catalytic mixture was opened to air before re-adding the EDA/olefin mixture, a very slow EDA conversion was observed indicating the extreme airsensitive nature of the active catalytic species.

To acquire more information on the nature of the active species, the solution after a catalytic reaction was evaporated to dryness and, under nitrogen, benzene was added to separate the organic products by filtration. The IR analysis, run under nitrogen, of the solid brownish residue dissolved in dichloroethane confirmed the absence of the azide band at 2077 cm⁻¹. The IR spectrum also revealed the retention of a POM framework, with intense bands characteristic of the metal-oxo framework around and below 1000 cm⁻¹, and the presence of a new and intense band at 1739 cm⁻¹ that can be assigned to a carbonyl group, which does not correspond to the cyclopropane -COOEt moiety (1721 cm⁻¹). It is worth noting that recovery of the copper-based POM under air led to a greenish solid, whose IR pattern is nevertheless similar to the above-mentioned one (see Supporting Information). The air-exposed species showed a decreased catalytic efficiency. Indeed, the cyclopropanation of α -methylstyrene, carried out using a mol ratio cat/EDA/olefin=1:40:100, afforded the desired cyclopropane in only 25% yield (compare with Table 1, entry 1).

In conclusion, we have described a new method to synthesise cyclopropanes in high yields using polyoxometalates as catalysts. The potentiality of this class of catalysts confers a high sustainability to the synthesis of useful fine chemicals such as cyclopropanes. The impressive TON observed and the use of equimolar amounts olefin/diazo compound defines our methodology as an environmentally benign technology. Moreover, when the cyclopropane is obtained in quantitative yield, the reaction mixture can be used for further transformations without any purification process.

Experimental Section

General Procedure for Cyclopropanation Reactions

In a typical experiment run with a mol ratio 4/EDA/olefin = 1:40:100, the olefin (0.69 mmol) and the catalyst (0.69 × 10^{-2} mmol) were dissolved in 9 mL of 1,2-dichloroethane. Then, 1 mL of a 1,2-dichloroethane solution of EDA (0.28 mmol) was added by syringe pump in 100 min at 75 °C. The reaction was followed by IR spectroscopy measuring the diazo characteristic absorbance at 2110 cm⁻¹. The reaction was considered to be finished when the absorbance of the EDA was below 0.03 (by using a 0.5 mm-thickness cell). The solution was analysed by GC-MS to determine the cyclopropanes *cis:trans* ratio. The reaction mixture was evaporated to dryness, benzene was added and the obtained solid was filtered off. The filtrate was evaporated to dryness and

the residue analysed by ¹H NMR with 2,4-dinitrotoluene as an internal standard. The same experimental procedure was employed to perform the reactions reported in Table 3 except that the ¹H NMR analysis was run in the presence of **4** (see footnotes for quantities). The collected analytical data for cyclopropanes are in agreement with those reported in the literature (see Supporting Information).

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