ELSEVIER

Journal of Organometallic Chemistry 627 (2001) 159–166

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Copper(I) complexes with the hexaazafulleroid $C_{60}(NR)_6$, derived from (2*S*,4*S*)-4-azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)pyrrolidine as multitopic ligand. Catalytic properties in oxidation of sulfides

Marta Iglesias, Berta Gómez-Lor, Amelia Santos *

Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

Received 12 December 2000; received in revised form 4 February 2001

Abstract

Reactions in a molar ratio 1:6 of the hexaazafulleroid $C_{60}(NR)_6$ (**1**), derived from the chiral azide (2*S*,4*S*)-4-azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)pyrrolidine (**2**), with the copper(I) complexes $[Cu(MeCN)_4]ClO_4$ and $[CuCl(cod)]_2$ (cod = 1,5-cyclooctadiene) lead to the polymetallated species $C_{60}[(NR)Cu(MeCN)_2(ClO_4)]_6$ (**3**) and $C_{60}[(NR)CuCl(cod)]_6 \cdot 2CuCl$ (**4**), respectively, which have been characterised by IR, ^{1}H- and ^{13}C-NMR spectroscopies and by mass spectrometry techniques (ES-, FAB- and MALDI-MS). The performance of both complexes as catalysts in the oxidation of alkylphenylsulfides [methylphenylsulfide, (2-ethylbutyl)phenylsulfide] was evaluated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: [60]Fullerene; Hexaazafulleroid; Cu(I) complexes; (2*S*,4*S*)-4-Azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)pyrrolidine; Oxidation catalysts

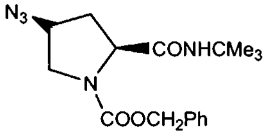
---

1. Introduction

Catalysis can be considered as a potential field of application of the fullerenes, since these carbon cages can be used as support in binding active metal centres [1]. Two main transition metal-fullerene binding types have been described: (a) direct coordination of the metal to the olefinic C=C bonds at 6:6 junctions to form η^2-coordination complexes and (b) coordination to ligating groups of addends previously attached to fullerene [2]. The symmetrical distribution of the 30 localised C–C double bonds on the spherical [60]fullerene surface leads to facile multiple addition reactions and renders highly probable the octahedral array of six addends. This fact has been demonstrated in the six-fold η^2-complex $C_{60}[Pt(PtEt_3)_2]_6$ [3].

We have recently reported on the synthesis of the polysubstituted fullerene $C_{60}(NR)_6$ (**1**) by reaction of [60]fullerene with the chiral azide (2*S*,4*S*)-4-azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)-pyrrolidine (**2**) [4]. This hexaazafulleroid reacts with $[Rh(CO)_2Cl]_2$ to yield a complex of composition $C_{60}[(NR)Rh(CO)_2Cl]_6$, which could be used as a catalyst in the hydrogenation of prochiral alkenes.

We report here on the reactions of the polyazafulleroid **1** with the Cu(I) complexes $[Cu(MeCN)_4]ClO_4$ and $[CuCl(cod)]_2$ (cod = 1,5-cyclooctadiene) as well as the catalytic properties of the complexes in oxidation reactions of organic sulfides.



2

---

* Corresponding author. Tel.: +34-91-3349030; fax: +34-91-3720623.

E-mail address: amelia.santos@icmm.csic.es (A. Santos).

PII: S0022-328X(01)00732-X

2. Results and discussion

2.1. Reaction of $C_{60}(NR)_6$ (**1**) with $[Cu(MeCN)_4]ClO_4$

Reaction of $C_{60}(NR)_6$ (**1**) with $[Cu(MeCN)_4]ClO_4$ in a molar ratio 1:6 in acetonitrile at the reflux temperature leads to formation of $C_{60}[(NR)Cu(MeCN)_2(ClO_4)]_6$ (**3**), which was isolated as a brown product in a relatively high yield (76%). IR spectrum shows all characteristic bands of the substituents at the pyrrolidine ring of the NR addends, and those of the remaining MeCN and ClO_4^- ligands, but modified by coordination effect. The most notable feature in this spectrum is the splitting of the asymmetrical stretching vibration ν_3, which appears as a doublet at 1104 and 1083 cm^{-1}, as a consequence of the lowering of symmetry from T_d to C_{3v} in a unidentate coordination of ClO_4^-. The same effect was observed for ν_4, which splits into two bands at 628 and 618 cm^{-1}, whereas ν_2 becomes active and appears at 930 cm^{-1} as a weak band. All these frequencies are in the same range as other tetracoordinated Cu(I) complexes containing a unidentate perchlorate ligand [5]. On the other hand, the most modified IR bands of the $C_{60}(NR)_6$ ligand are those corresponding to ν(CO) and δ(NH) vibrations of the substituents $COOCH_2Ph$ and $CONHCMe_3$ groups at the pyrrolidine rings of the NR addends. So the ν(CO) frequencies of the groups ester (1694 cm^{-1}) and amide (1675 cm^{-1}) in $C_{60}(NR)_6$ give rise only to one strong, broad band centred at 1680 cm^{-1} in complex **3** and δ(NH) is shifted from 1520 in the free ligand to 1534 cm^{-1} in complex **3**. All these effects confirm the coordination of Cu(I) to the amide nitrogen of NR addends.

The ^{1}H-NMR spectrum of complex **3** in CD_3CN solution, as that of the free $C_{60}(NR)_6$ ligand, shows broad overlapped signals for the different protons of the pyrrolidine rings of the six NR addends of the ligand. Only proton signals of the benzyl and *t*-butyl groups of the NR addends, and the methyl signal of the MeCN ligands appear as neat resonances. All these signals are observed as broad singlets or multiplets, which could be due to partial oxidation of Cu(I) in solution. Complex **3** is almost insoluble in common organic solvents and we have obtained the solid-state ^{13}C CP/MAS-NMR spectrum of a powdered sample. This spectrum shows broad signals and downfield shifts of the resonances with respect to those of the free ligand are observed as a general trend, the phenomenon being more pronounced for the carbons close to the coordinating atoms. The sp^2 fullerene carbons are hidden by the intense, broad phenyl signal of the NR addends. The amide and ester carbonyl carbons appear as well defined signals nearly at the same positions as in the free ligand and the most modified signal is that corresponding to the quaternary carbon of *t*-butyl, directly bonded to the amide nitrogen, which appears at δ 50.39 in $C_{60}(NR)_6$ and at δ 46.20 in complex **3**. Carbons of MeCN are observed at δ 2.44 and 118.00, respectively.

2.2. Reaction of $C_{60}(NR)_6$ (**1**) with $[CuCl(cod)]_2$

Reaction of $C_{60}(NR)_6$ with $[CuCl(cod)]_2$ in a molar ratio 1:3 (1:6 with respect to Cu) in acetonitrile at the reflux temperature gives rise to a product of composition $C_{60}[(NR)_6CuCl(cod)]_6 \cdot 2CuCl$, **4**, which was isolated as a brown solid in a moderate yield (56%) after concentration and precipitation with Et_2O, 30% of $C_{60}(NR)_6$ was recovered from the reaction solution after precipitation of **4**. As in complex **3**, the IR spectrum of **4** shows modifications for the ester and amide ν(CO) stretching bands and for δ(NH) of amide with respect to the free ligand, which are indicative of coordination through the N of amide group. Both ν(CO) frequencies appear as a broad and strong band with the maximum at 1690 cm^{-1}. This band can include the ν(C=C) frequency of cyclooctadiene, since it covers the range 1595–1770 cm^{-1}. δ(NH) shifts toward the higher frequencies with respect to that of free ligand and appears at 1527 cm^{-1}.

In the ^{1}H-NMR spectrum (CD_3CN), broad signals for the pyrrolidine protons and neat resonances due to CH_2Ph and CMe_3 groups are observed. In this case two signals appear for CMe_3, at δ 1.27 and 1.21. This fact could be due to the presence of two different coordination modes for Cu in complex **4**. The solid-state ^{13}C-NMR spectrum of complex **4**, as those of complex **3** and the free $C_{60}(NR)_6$ ligand, show well defined broad signals. The amide and ester carbonyl signals appear again nearly at the same positions as in the free ligand and the sp^2 fullerene- and the phenyl carbons of the NR addends give also an intense overlapped signal. The most downfield shifted signal is also in this complex, that corresponding to the quaternary carbon of *t*-butyl, directly bonded to the amide nitrogen, which shifts to δ 44.20 (δ 50.39 in the free ligand). The asymmetric carbon N*C**HCO signal is also slightly shifted from δ 58.31 in the free ligand to 59.95 in complex **4**. The olefinic and alkyl carbons of cyclooctadiene appear as shoulders at δ 72.00 and 32.15, respectively.

We have proposed for complex **3** a simple tetrahedral coordination of Cu(I) to each NR addend through the nitrogen of the amide group and to a unidentate perchlorate and two acetonitrile ligands. Since $[CuCl(cod)]_2$ does not react with [60]fullerene under the reaction conditions, the presence in complex **4** of two additional CuCl requires four bridging chlorides between four Cu(I) and two coordination modes should coexist at the metal simultaneously. Four of the eight Cu(I) should have a simple tetrahedral coordination to a NR addend as in complex **3** and to chloride and the bidentate cod ligand. The remaining four Cu(I) require

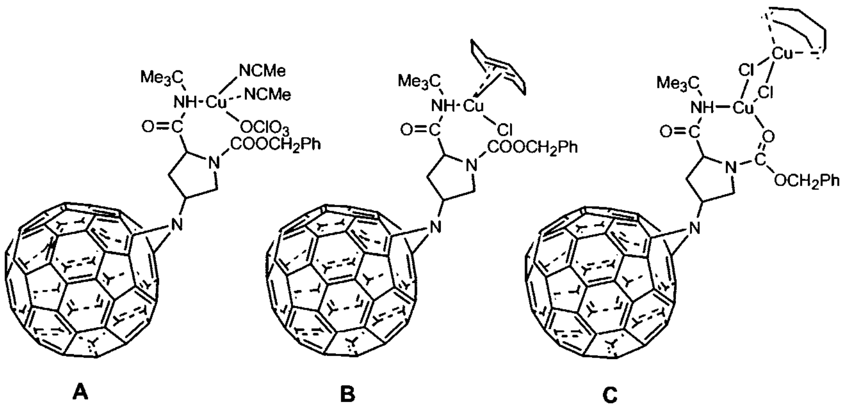


Fig. 1. (A) Coordination mode for complex **3**. (B) and (C) Coordination modes for complex **4**.

Table 1
Principal peaks observed in the different mass spectra of complex **3** [a]

ES	FAB	MALDI	Tentative assignment
	57		CMe_3
	77		Ph
	91		CH_2Ph
244			$(HN{=}R–cbz)Cu^+$
303			$[(R–bz–CMe_3)Cu(MeCN)_2]^+$
	324		$[(HN{=}R–CMe_3)Cu]^+$
	331		$[(HNR{=}R–bz)Cu(MeCN)]^+$
	365		$[(HN{=}R–CMe_3)Cu(MeCN)]^+$
456			$[(HN{=}R)Cu(II)(MeCN)Cl]^+$
	722		$C_{59}N$
		897	$\{C_{60}(6NR–3bz–3cbz–2CMe_3–4CONHCMe_3)[CuCl(MeCN)_2]_2\}^{2+}$
1892			$\{C_{60}(6NR–cbz)[Cu(MeCN)_2]_6(ClO_4)(ClO_3)_4\}^{2+}$
2064			$\{C_{60}(6NR–6cbz–3NHCMe_3–3CMe_3)[Cu(MeCN)_2]_4(ClO_4)(ClO_3)_2Cl\}$
2385			$\{C_{60}(6NR–6cbz–2NHCMe_3–3CMe_3)[Cu(MeCN)_2]_4(ClO_4)_2(ClO_3)Cl\}$
		2688	$\{C_{60}(6NR–6cbz–NHCMe_3–3CMe_3)[Cu(MeCN)_2]_5(ClO_4)_2(ClO_3)_2Cl\}$
2929			$\{C_{60}(6NR–6cbz–4CMe_3)[Cu(MeCN)_2]_6(ClO_4)_2(ClO_3)_3Cl\}$
		3005	$C_{60}[(NR)Cu(MeCN)_2]_3(NR–NH_2CMe_3)_3(ClO_4)(ClO_2)\}^+$
		3321	$C_{60}[(NR)Cu(MeCN)_2]_4(NR–NH_2CMe_3)_2(ClO_4)_2(ClO_2)\}^+$
		3638	$\{C_{60}[(NR)Cu(MeCN)_2]_5(NR–NH_2CMe_3)(ClO_4)_3(ClO_2)\}^+$
		3955	$\{C_{60}[(NR)Cu(MeCN)_2]_6(ClO_4)_4(ClO_2)\}^+$

[a] Only the most significant peaks were included.

another coordination mode in which two bridging chlorides are bonded to two pairs of metal atoms. Each of them completes its coordination, respectively, by bonding to a cyclooctadiene bidentate ligand or to N- and O-donor atoms of the amide and ester groups of NR addends. Fig. 1 shows the coordination mode for complex **3** and both possible coordination modes, which would explain the composition of complex **4**.

2.3. Mass spectrometry studies

Different mass spectrometry techniques have been applied previously for characterisation of functionalised fullerene derivatives with increasing complexity, since characterisation of these derivatives is usually hampered by problems derived from poor solubility, lability of compounds and spectral complexity that arise from lowering of the symmetry. Frequently MS analysis of C_{60} derivatives with high molecular weight leads to considerable fragmentation and molecular ions are often not observed [6].

In order to gain more information on the new complexes we have performed a detailed mass spectrometry study using several ionisation techniques such as electrospray (ESMS), fast-atom bombardment (FAB-MS) and matrix-assisted laser desorption/ionisation (MALDI-MS). The peak corresponding to the molecular ion could not be detected in any of these experiments and a considerable fragmentation pattern was observed instead. However, a lot of information could be obtained from this study.

Table 2
Principal peaks observed in the different mass spectra of complex **4** [a]

ES	FAB	MALDI	Tentative assignment
	57		CMe_3
	77		Ph
	91		CH_2Ph
	109		Cod
161			$[(HN{=}R–CMe_3–H)Cu(II)]^2$
176			$[(HN{=}R–cbz–H)Cu(II)(cod)]^{2+}$
	237		$[(HN{=}R–CMe_3–bz)Cu]^+$
244			$[(HN{=}R)Cu(II)(cod)]^2$
	709		$\{C_{60}[(NR–cbz–CMe_3)Cu(II)Cl][(NR–bz–CMe_3)CuCl_2Cl(cod)]\}^{2+}$
		961	$\{C_{60}(2NR–bz–cbz–NHCMe_3–CONHCMe_3\}$
1168			$\{C_{60}(6NR–3bz–4cbz–4NHCMe_3)Cu_2Cl_2\}^{2+}$
	1371	1369	$\{C_{60}(NR–cbz–NHCMe_3)_6\}$
1593			$\{C_{60}(2NR–bz–NHCMe_3–CONHCMe_3)[(NR)CuCl(cod)]_4\}^{2+}$
		1734	$\{C_{60}(6NR–5cbz–3NHCMe_3–2CONHCMe_3)[CuCl(cod)]\}$
		2051	$\{C_{60}(6NR–3cbz–2bz–4CONHCMe_3)[CuCl(cod)]_2\}$
		2368	$\{C_{60}(4NR–2cbz–4CONHCMe_3)[(NR)(CuCl(cod)]_2\}$
		2686	$\{C_{60}(3NR–2bz–cbz–2NHCMe_3–CONHCMe_3)[(NR)CuCl(cod)]_3\}$
2808			$\{C_{60}(6NR–4bz–cbz–2NHCMe_3)[CuCl(cod)]_4\}^+$
		3322	$C_{60}[(NR–bz–CMe_3)CuCl(cod)]_4(2NR–bz–CMe_3)[CuCl_2Cl(cod)]_2\}^+$

[a] Only the most significant peaks were included.

2.3.1. MS spectra of complex *3*

Table 1 shows the principal peaks observed in the ES-, FAB- and MALDI-MS spectra of complex **3**, and tentative assignments.[1]

With the ESMS technique the molecular peak is not observed because of its high molecular weight ($>$ 4000). However, significant fragments with high m/z values, derived from them by loss of groups easily removable in addends, have been observed. Besides fragments of low m/z values, corresponding to Cu complex species bonded to residual coordinating $CONH_2$ or $CONHCMe_3$ at the R or N=R groups separated from fullerene, are observed as peaks with high intensity.

A series of low intensity peaks with $m/z > 720$ are observed at 1893, 2065, 2385 and 2929. All these peaks can be assigned to C_{60} fullerene containing the six NR addends partially broken by loss of cbz, $NHCMe_3$ and/or CMe_3 groups, which remain coordinated to Cu through $CONHCMe_3$ or $CONH_2$ coordinating groups.

In the FAB-MS spectrum of complex **3**, with m-NBA (3-nitrobenzyl alcohol) as matrix, a peak at m/z 722 is observed, and could be assigned to $C_{60}H_2$ or to $C_{59}N$. Heterofullerene $C_{59}N^+$ peaks have been observed in the FAB-MS spectra of some bisazafulleroid derivatives [7]. The most intense peaks have a $m/z < 720$ and correspond to fragments of the NR addends, such as CMe_3, CH_2Ph, pyrrole or phenyl. With moderately low intensity appears a series of peaks which can be assigned to fragments of the NR addend containing Cu and sometimes other ligands, such as peaks at m/z 324, 331 and 365 assigned to the species $[(HN{=}R–CMe_3)Cu]^+$ and $[(HN{=}R–bz)Cu(MeCN)]^+$and $[(HN{=}R–CMe_3)Cu(MeCN)]^+$, respectively.

The MALDI-MS spectrum of **3** shows a series of peaks with high m/z values related with the expected molecular ion $\{C_{60}[(NR)Cu(MeCN)_2(ClO_4)]_6\}^+$ (4086), the highest of them being assigned to the species $\{C_{60}[(NR)Cu(MeCN)_2]_6(ClO_4)_3(ClO_3)_2\}^+$ that can be considered as a molecular ion, derived from the molecular species by loss of a ClO_4^- and two additional oxygens ($M - ClO_4^- - 2O = 3955$).

2.3.2. MS spectra of complex *4*

Table 2 shows the principal peaks observed in the ES-, FAB- and MALDI-MS spectra of complex **4**, and tentative assignments.[1]

In the ESMS spectrum of **4,** a series of peaks with high m/z values in the range 1100–3000 are observed and were assigned to fullerene containing from two to six fragmented NR addends and CuCl(cod) or $Cu(\mu\text{-}Cl)_2Cu(cod)$ units coordinated to the remaining $CONH_2$ or $CONHCMe_3$ groups at the pyrrolidine ring of NR.

The most intense peaks are found at m/z values between 105 and 245, which can be assigned to species related to free cyclooctadiene or fragments of NR addends, which can be coordinated to residual Cu

---

[1] Generally, we have selected only the most intense peak of each cluster. In this notation HN=R represents the NR addend separated from fullerene without additional hydrogen and (HN=R–cbz) represents the same fragment after loss of the carbobenzoxy group ($COOCH_2Ph$=cbz) and hydrogen, generating a double C=N bond at the pyrrolidine ring. Similarly, ($HN{=}R–NHCMe_3$) represents the HN=R fragment after loss of $NHCMe_3$ and H, generating a double C=C bond at the pyrrolidine ring.

complex units when the fragment contains coordinating $CONH_2$ or $CONHCMe_3$ groups.

The FAB-MS spectrum of complex **4**, with *m*-NBA as matrix, is notably different from that of **3** and shows discrete peak clusters in the m/z range 720–1500, some of them with relatively high intensities. The most intense peaks with $m/z < 720$ correspond also to fragments of the NR addends, such as CMe_3, dihydropyrrole, pyrrole, Ph, (HN=R–cbz–$CONHCMe_3$), CH_2Ph, (cod), (HN=R–bz–$NHCMe_3$), (HN=R–$CONHCMe_3$) and (HN=R). Remaining peaks with $m/z < 720$ can be assigned to NR fragments coordinated to Cu or to doubly charged species containing fullerene and NR fragments, some of them coordinated to Cu.

A fullerene cluster with maximum at m/z 720 does not appear and a series of clusters with m/z between 720 and 1389 were assigned to metallated or non-metallated species containing from two to six fragmented NR addends attached to fullerene. Although fragments with m/z 377 and 279, corresponding to these last species, were not observed, CMe_3, $NCMe_3$ and cod appear as high intensity peaks.

MALDI-MS spectrum of **4** shows peaks with high m/z values closer to molecular ions than those in the ES- and FAB-MS spectra, and some fragmentation peaks are also observed. The peak with a higher m/z (3322) can be derived from complex **4** by loss of all benzyl and CMe_3 groups of the six NR addends, which remain coordinated to four [CuCl(cod)] and two [Cu(μ-Cl)$_2$Cu(cod)] units, giving rise to the species $C_{60}\{(NR–bz–CMe_3)[CuCl(cod)]\}_4\{(2NR–bz–CMe_3)[Cu(\mu\text{-}Cl)_2Cu(cod)]_2\}^+$.

Especially interesting is a peak at m/z 1369, since it could correspond to C_{60} attached to six fragmented NR addends originated by loss of all $\{(NHCMe_3)CuCl(cod)\}$, $\{(NHCMe_3)CuCl_2Cu(cod)\}$ and cbz units from the initial complex **4**.

2.4. Thermal analysis

Thermal analyses of both complexes (N_2 flow, 22–800°C) are very different. Complex **3** decomposes exothermically at a relatively low temperature (211°C) after endothermic loss of residual moisture, solvating Et_2O and all MeCN ligands. This strong exothermic effect can be due to oxidative decomposition, with partial oxidation, of the organic substrate by perchlorate and the residue after this process fit well with CuCl, formed from reduction of ClO_4^-.

Complex **4** shows a very different thermal behaviour. Two overlapped exothermic peaks centred at 235 and 260°C are observed after two weak and overlapped endothermic peaks in the range 22–180°C. The initial weight loss (6%) corresponds to approximately two cod molecules for the composition $C_{60}[(NR)[CuCl(cod)]_4[(NR)CuCl_2Cu(cod)]$ (FW 4066) (calc. 5.3%). The total weight loss between 180°C and the end of both exothermic peaks at 290°C is 37%. On the other hand, between 180°C and the temperature corresponding to the end of the first step and maximal slope of the TG curve (238°C) the weight loss is 10% and could correspond to the remaining four cod molecules (calc. 10.6%). The total weight loss in the range 22–238°C corresponds to the elimination in two steps of all six cod ligands (calc. 16.0%). In this case the exothermic nature of both overlapped exothermic effects could be due to the formation of new strong Cu–N or Cu–O bonds in the rearrangements occurring after loss of the cod ligands, which could also mask the endothermic breaking of some C–O or C–N labile bonds in NR addends. Effectively the observed weight loss between 238 and 290°C (26%) corresponds well to $4cbz + 2bz + 6CMe_3$ groups of NR addends (calc. 26.3%). After 290°C four gradual and smooth weight loss steps take place with end temperatures 400°C (8%), 515°C (12%), 585°C (18%) and 620°C (18%). In this same temperature range two exothermic peaks appear in the DTA curve, centred at 490 and 600°C. The different weight loss steps observed in the TG curve in this last range could be attributed to the successive elimination of $2COO + 6CONH$ (calc. 8.7%), [6NR–6cbz–$6CONHCMe_3$] (calc. 12.1%), C_{60} (calc. 17.7%) and CuCl (calc.19.5%). The first elimination of two cod ligands could originate an exothermic rearrangement, with simultaneous breaking of the bonds of Cu with the remaining cod ligands. This should originate a new exothermic rearrangement, which leads to break the most labile C–O and C–N bonds of the NR addends. The presence of two bonding types in complex **4** (Fig. 1) could explain this behaviour. So CO*O*–CH_2Ph or *N*–*C*OOCH$_2$Ph bonds of carbobenzoxy groups would be preferentially broken depending on coordination or non-coordination of its carboxylate oxygen to Cu in the coordination types (C) and (B), respectively.

2.5. Catalytic properties of complexes 3 and 4 in oxidation of organic sulfides

In order to determine the performance of fullerene–Cu complexes as catalysts, the oxidation of organic sulfides [methylphenylsulfide, (2-ethylbutyl)phenylsulfide] was evaluated. The activities and selectivity attained are collected in Table 3, Figs. 2 and 3. The selectivity curves given in the figure show that the sulfoxide is a primary and unstable product, while the corresponding sulfone appears as a secondary and stable product.

The experimental conditions were established by varying the oxidant, pH of aqueous NaOCl solution and temperature. First, hydrogen peroxide (H_2O_2) was examined as oxidant in acetonitrile and little formation of sulfoxide was detected at ambient temperature in spite of the excess amount of oxidant used. NaOCl (pH 11.3) was employed as an oxidant in the present study since we have obtained high yields at low temperature. The promoter (NMO) is used to stabilise the Cu(III)-oxo species (catalytic active intermediate) formed in the oxidation cycle. Finally, low temperature (0°C) was chosen when a small molecule was oxidised; when a large molecule was oxidised no reaction was observed and the reaction temperature was raised to room temperature to increase the reaction rate.

The oxidations were usually carried out in the presence of catalytic amounts of the catalyst (0.5% based on

Table 3
Oxidation of methylphenylsulfide catalysed by fullerene–Cu complexes

Cat.	*T* (°C)	% conv. (h)	SO (%)	SO_2 (%)	TON [a]
3	r.t.	100 (0.5)	0	100	300
	0	54 (2) [b]	28	26	128
4	r.t.	100 (0.5)	0	100	273
	0	63 (3) [b]	24	44	60

[a] mmol subs./mmol cat. min.

[b] Total conversion was achieved in 3–4 h.

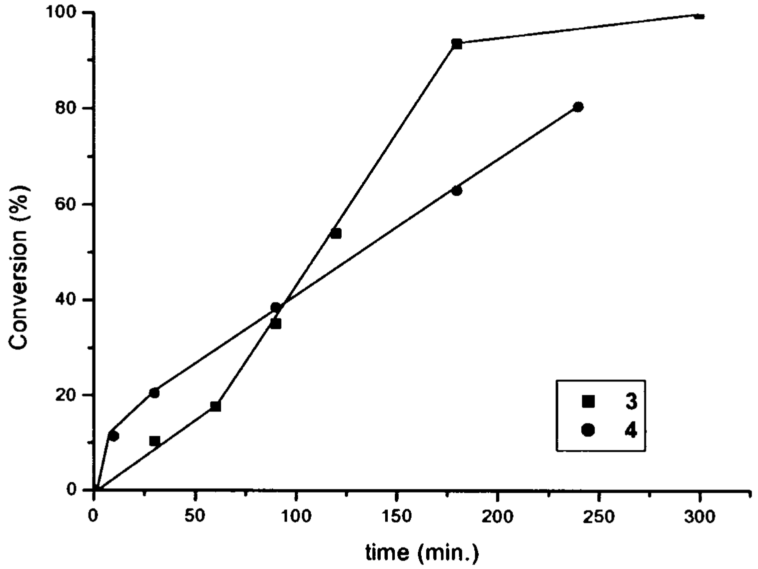


Fig. 2. Kinetic profile of oxidation of methylphenylsulfide with fullerene–Cu catalysts.

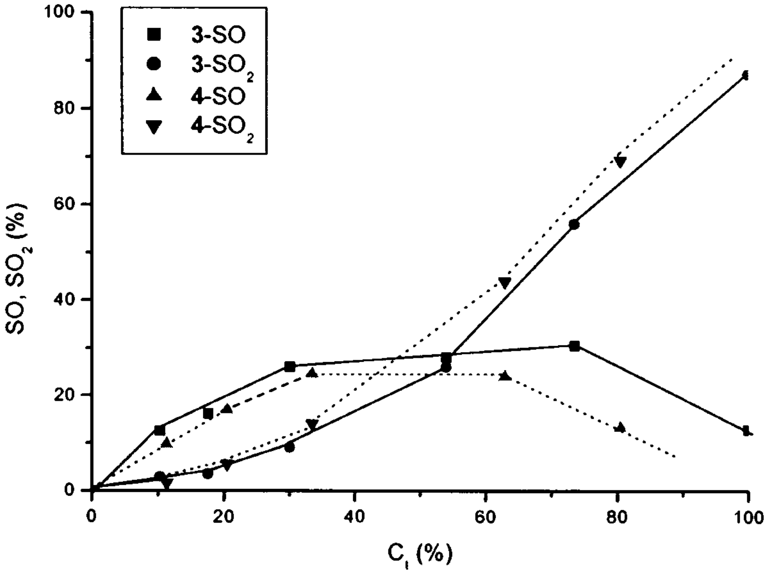


Fig. 3. Selectivity curves for the oxidation of methylphenylsulfide with fullerene–Cu complexes ($T = 273$ K).

experimental metal content) and 4-methylmorpholine *N*-oxide monohydrate (0.05 mmol) by using NaOCl as sacrificial oxidant in dichloroethane. A series of blank experiments revealed that each component is essential for an effective catalytic reaction.

The complexes showed a similar activity and chemoselectivity when methylphenylsulfide was used as substrate. Furthermore, products of the oxidation of the (2-ethylbutyl)phenylsulfide were not detected at 0°C and when the reaction takes place at room temperature only sulfone was obtained. The complexes appeared to be stable under experimental conditions (as the catalysts were found to be reactive for further catalytic runs).

3. Experimental

All synthetic operations were performed under a dry N_2 atmosphere, using conventional Schlenk techniques. Solvents were distilled over appropriate drying agents. $C_{60}(NR)_6$ [4], $[Cu(MeCN)_4]ClO_4$ [8] and $[CuCl(cod)]_2$ [9] were prepared according to reported procedures. Elemental analyses were performed at the ICMM (CSIC), using the atomic absorption technique (Perkin–Elmer 1100 B) for analysis of Cu. IR spectra were recorded with a Nicolet 20 SXC FT-IR spectrophotometer using KBr disks. NMR spectra in solution were recorded on Bruker AC-200 or Bruker AMX-300 spectrometers. High-resolution solid-state ^{13}C CP/MAS-NMR spectra of powdered samples were performed at the ICMM. These spectra were recorded at 100.63 MHz, 6.5 μs 90° pulse width, 1 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with a FT unit. The spinning frequency at the magic angle (54°44′) was 10 KHz. The FAB and MALDI mass spectra were performed at the UAM (SIdI), using *m*-NBA (3-nitrobenzyl alcohol) and dithranol (1,8,9-anthracene triol) as matrix, respectively. The ES mass spectra, were performed at the Centro de Química Orgánica 'Manuel Lora Tamayo' (CSIC), using a Hewlett–Packard 1100 MSD mass spectrometer (ESI-MS, APCI-MS) with positive mode and methanol as solvent. Differential thermal analysis (DTA) and thermogravimetric (TG) curves were obtained using a Stanton STA 781 simultaneous thermal analyser. Samples were heated in a N_2 flow (50 ml min^{-1}) at 10°C min^{-1} heating rate in the temperature range 25–800°C, using alumina as reference.

3.1. Reaction of $C_{60}(NR)_6$ (**1**) with $[Cu(MeCN)_4]ClO_4$. Formation of $C_{60}[(NR)Cu(MeCN)_2(ClO_4)]_6$ (**3**)

A mixture of **1** (50 mg, 0.019 mmol) and $[Cu(MeCN)_4]ClO_4$ (37 mg, 0.114 mmol) in acetonitrile were sonicated for 5 min and heated at the reflux temperature for 12 h. After partial evaporation of the solvent a brown solid was separated by addition of Et_2O, which was filtered off, washed three times with the same solvent and dried under vacuum (60 mg, 76%). Anal. Found: N, 9.99; Cu, 9.22. Calc. for $C_{60}(NR)_6[Cu(MeCN)_2(ClO_4)]_6 \cdot Et_2O$ ($C_{190}H_{184}Cl_6Cu_6N_{30}O_{43}$, 4169.66): N, 10.08; Cu, 9.14%. Elemental analysis of C and H gave too low values in several experiments, probably because of perchlorate, which could originate an anomalous combustion. IR (KBr, cm^{-1}): 3416sh, 3338m br, 2960m, 2922m, 2850sh, 2288vw ν(CN), 2250vw ν(CN), 1682s br, 1534m, 1444m, 1408ms, 1351m, 1262w, 1210mw, 1104vvs $\nu_{as}(ClO_4)$, 1083vvs $\nu_{as}(ClO_4)$, 930w $\delta_d(ClO_4)$, 752w, 738w, 692w, 628m $\delta_{as}(ClO_4)$, 618m $\delta_{as}(ClO_4)$. ^1H-NMR ($CHCl_3$-*d*, 200 MHz), only some signals are clearly observed at δ 7.39 (br m, 5H *Ph*), 5.20–5.00 (m, 2H, OCH_2Ph), 4.35 (br m), 2.06 (br s, 6H, MeCN), 1.30 (br s, 9H, CONHCMe_3). Solid-state ^{13}C-NMR CP/MAS spectrum: δ 169.88 (*C*ONHR), 155.08 (*C*OOCH$_2$Ph), 147.20 (s), 143.00sh, 144.00–135.20 (br s, with a maximum at 136.63, C_{60} sp^2 carbons + C_{ipso} Ph), 128.38 (br s, *o*-, *m*-, *p*-*Ph*), 118.10 (s, Me*C*N), 67.01 (sh, OCH_2Ph), 59.95 (s, NC^*HCO), 56.60 (s, CH_2N), 51.46 (s, *CH*–N–C_{60}), 46.20 (s, *C*Me$_3$), 36.57 (sh, CH_2), 28.41 (s, CMe_3), 2.44 (s, *Me*CN).

3.2. Reaction of $C_{60}(NR)_6$ (**1**) with $[CuCl(cod)]_2$. Formation of $C_{60}[(NR)CuCl(cod)]_6 \cdot x2CuCl$ (**4**)

A mixture of **1** (50 mg, 0.019 mmol) and $[CuCl(cod)]_2$ (24 mg, 0.038 mmol) in acetonitrile was sonicated for 5 min and heated at reflux temperature for 12 h. After partial evaporation of the solvent a brown solid was separated by addition of diethyl ether, which was filtered off, washed three times with the same solvent and dried in vacuum (42 mg, 56% with respect to ligand). 15 mg of $C_{60}(NR)_6$ were recovered from filtrate after solvent evaporation. Anal. Found: N, 6.19; Cu, 12.02. Calc. for $C_{60}(NR)_6[CuCl(cod)]_6 \cdot 2CuCl$ ($C_{210}H_{210}Cl_8Cu_8N_{18}O_{18}$, 4066.01): N, 6.20; Cu, 12.50%. Elemental analysis of C and H gave also too low results in several experiments, probably because of an anomalous combustion. IR (KBr, cm^{-1}) 3408sh, 3330m br, 2957m, 2922mw, 2850sh, 1690vs br, 1527m, 1442m, 1404ms, 1344m, 1210m, 1168mw, 1112mw, 970vw, 752w, 738w, 690mw. ^1H-NMR (CH_3CN-*d*, 300 MHz), only some signals are clearly observed at δ 7.38 (br m, 5H *Ph*), 5.16–5.01 (m, 2H, OCH_2Ph), 1.27, 1.21 (2br s, 3H + 6H, CONHCMe_3). Solid-state ^{13}C-NMR CP/MAS spectrum: δ 170.36 (*C*ONHR), 154.83 (*C*OOCH$_2$Ph), 147.10 (s), 142.40 (s), 138.00–133.10 (br s, with a maximum at 135.66, C_{60} sp^2 carbons + C_{ipso} Ph), 128.14 (br s, *o*-, *m*-, *p*-*Ph*), 72.00 (sh, cod sp^2 carbons), 64.50 (br s, OCH_2Ph), 59.95 (s, NC^*HCO), 53.60 (s, CH_2N), 50.97 (s, *CH*–N–C_{60}), 44.20 (s, *C*Me$_3$), 36.50 (s, *CH*$_2$), 32.15 (sh, cod *CH*$_2$ carbons), 27.92 (s, C*Me*$_3$).

*3.3. Thermal analysis of complexes **3** and **4***

Thermal analyses of both complexes were performed in an N_2 flow (50 ml min^{-1}) at 10°C min^{-1} heating rate until 800°C.

The DTA curve of **3** shows a low-temperature endothermic peak centred at 70°C, accompanied by a 3.4% weight loss in the TG curve. A second endothermic effect centred toward 130°C, followed by a strong exothermic peak at 211°C are also observed, accompanied, respectively, by 12 and 74% weight loss, being the residue at 211°C only 9.3% from the initial weight. Other two moderately exothermic peaks centred at 300 and 420°C, are finally observed, both accompanied by ca. 5% weight loss in the TG curve. For a composition $C_{60}(NR)_6[Cu(MeCN)_2(ClO_4)]_6 \cdot Et_2O$ (FW 4169.66), the first endothermic peak can be attributed to loss of diethylether (calc. 1.8%) and additional moisture and the second, to loss of 12 MeCN molecules (calc. 11.8%). The strong exothermic effect can be due to combustion or oxidative decomposition of organic residue by action of perchlorate and the residue at this temperature can be partially oxidised copper or residual Cu chlorides.

DTA and TG curves of **4** show in the range 22–180°C two weak endothermic effects, accompanied by 6% weight loss. An exothermic process follows, with a maximum of weight loss at 238°C. The DTA curve shows two overlapped exothermic peaks, centred at 235 and 260°C, which could be considered as concluded at 290°C, with total weight loss 36%. From this temperature four gradual and smooth weight loss steps take place with the end temperatures 400°C (8%), 515°C (12%), 585°C (18%) and 620°C (18%). In this same temperature range two exothermic peaks appear in the DTA curve, centred at 490 and 600°C. For a composition $C_{60}(NR)_6[CuCl(cod)]_6 \cdot 2CuCl$ (FW 4066.01) the different weight loss steps observed in the TG curve could be attributed to the successive elimination of 2cod (calc. 5.3%), 4cod + 4cbz + 2bz + 6CMe$_3$ (calc. 36.9%), 2COO + 6CONH (calc. 8.7%), [6NR–6cbz–6CONH-CMe$_3$] (calc. 12.1%), C_{60} (calc. 17.7%) and CuCl (calc. 19.5%). Thus the exothermic peak maximum at 238°C corresponds to the elimination in two steps of all six cod ligands (calc. 16%).

*3.4. Catalytic properties of complexes **3** and **4***

All oxidation reactions were carried out by the same procedure. The catalyst (0.05 mmol) was added to a dichloroethane solution of the substrate (sulfide, 1 mmol) and 4-methylmorpholine *N*-oxide monohydrate (NMO, 0.05 mmol). The mixture was allowed to the desired temperature and the oxidant NaOCl (pH 11.3, 1.9 mmol) was added. Chemical yields were measured by gas chromatography with a chiral glass capillary column (mixture of methylsilicone (OV-1701) and methylsilicone - heptakis - [2,3 - dipentyl - 6 - (*t* - butyldimethylsilyl)]-β-cyclodextrin as stationary phase) [10].

Acknowledgements

The authors are grateful for the financial support from Dirección General de Investigación Científica y Técnica of Spain (Project PB97-0002-C02-02 and MAT97-1016-c02-02). B.G.L. acknowledges the CAM for a postdoctoral fellowship.

References

[1] (a) M. Wohlers, B. Herzog, T. Belz, A. Bauer, Th. Rühle, R. Schlögl, Synth. Met. 77 (1996) 55. (b) Th. Braun, M. Wohlers, T. Belz, R. Schlögl, Catal. Lett. 43 (1997) 175. (c) R. Yu, Q. Liu, K.-L. Tan, G.-Q. Xu, S.Ch. Ng, H.S.O. Chan, T.S.A. Hor, J. Chem. Soc. Faraday Trans. 93 (1997) 2207.

[2] A.L. Balch, M.M. Olmstead, Chem. Rev. 98 (1998) 2123.

[3] P.J. Fagan, J.C. Calabrese, B. Malone, J. Am. Chem. Soc. 113 (1991) 9480.

[4] M. Iglesias, B. Gómez-Lor, A. santos, J. Organomet. Chem. 599 (2000) 8.

[5] N.M.N. Gowda, S.B. Naikar, G.K.N. Reddy, Adv. Inorg. Chem. Radiochem. 28 (1984) 255.

[6] D. Felder, H. Nierengarten, J.-P. Gisselbrecht, C. Boudon, E. Leize, J.-F. Nicoud, M. Gross, A. Van Dorsselaer, J.-F. Nierengarten, New J. Chem. 24 (2000) 685.

[7] I. Lamparth, B. Nuber, G. Schick, A. Skiebe, T. Grösser, A. Hirsch, Angew. Chem. Int. Ed. Engl. 34 (1995) 2257.

[8] I. Csöregh, P. Kierkegaard, R. Norestam, Acta Crystallogr. B 31 (1975) 314.

[9] B.W. Cook, R.G.J. Miller, P.F. Todd, J. Organomet. Chem. 19 (1969) 421.

[10] E. Miranda, F. Sánchez, J. Sanz, M.I. Jiménez, I. Martínez-Castro, J. High Resolut. Chromatogr. 21 (1998) 225.