

# New mono- and polyazafulleroids $C_{60}(NR)_n$ ( $n = 1, 2, 4, 6$ ) derived from a chiral azide containing *N*- and *O*-donor groups, and reactivity with $[RhCl(CO)_2]_2$

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## Abstract

Reactions in a 1:1 molar ratio of the chiral azide (2*S*,4*S*)-4-azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)pyrrolidine ( $N_3R$ ,  $R = C_{17}H_{23}N_2O_3$ , **I**) with  $C_{60}$  in ClPh, in the temperature range 100–132°C, lead to mixtures of mono- and polyazafulleroid species of general formula  $C_{60}(NR)_n$  ( $n = 1, 2, 4$ ), with a composition depending on the reaction conditions, and with a yield in the most substituted polyazafulleroids that increases with the concentration of reactants. However the reaction in a 1:6 molar ratio (fullerene–azide **I**) leads only to hexaazafulleroids  $C_{60}(NR)_6$ . All mono- and polyazafulleroids  $C_{60}(NR)_n$  react with  $[Rh(CO)_2Cl]_2$  to give complexes of composition  $C_{60}(NR)_n[Rh(CO)_2Cl]_n$ , which could be used as catalysts in asymmetric hydrogenation of prochiral olefins. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** [60]Fullerene; Monoazafulleroid; Polyazafulleroids; Rh complexes; (2*S*,4*S*)-4-Azido-1-benzyloxycarbonyl-2-(*t*-butylaminocarbonyl)-pyrrolidine; Asymmetric catalysis

## 1. Introduction

The reactions of organic azides with [60]fullerene have been widely studied, especially those that give rise to monocycloadducts as the majority reaction products [1]. The multifunctionality of fullerenes usually results in the formation of numerous inseparable products and special attention has to be paid to find the reaction conditions that lead to relatively simple reaction mixtures. In all known monoimino derivatives  $C_{60}N-R$  the N atom binds to two adjacent carbons of a [6,6] or [5,6] juncture of  $C_{60}$ . The resulting [6,6] or [5,6] transannular bonds could be open or closed, but only the closed [6,6]- (**I**) (fulleroaziridine) and the open [5,6]-bridged adducts (**II**) (azafulleroid) (Fig. 1) have been hitherto found.

The preferential formation of monoadducts of the type **I** or **II** seems to depend on the reaction conditions and the nature of the substituent R in the azide. So in reactions in a molar ratio of approximately 1:1

fulleroaziridines (**I**) are the main products in conditions which lead to formation of a nitrene intermediate from azide by photolysis or thermal activation (140–160°C) and with alkoxy carbonylazides  $ROOCN_3$  [1b–j] or tetrafluoroarylazides [1k], whereas with alkyl or aryl

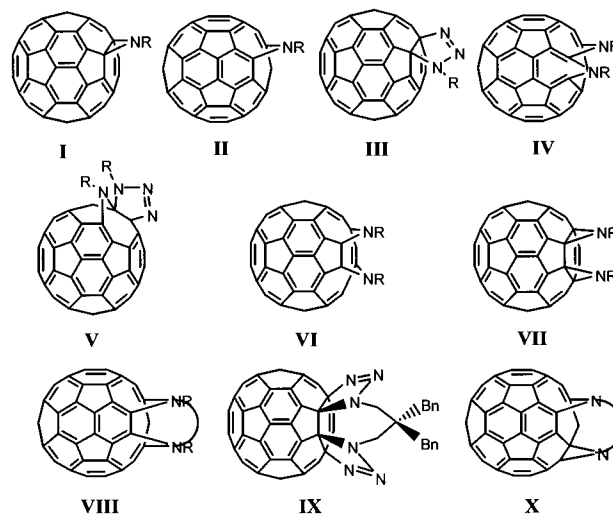


Fig. 1. Different mono- and bis-adduct types derived from reaction of  $C_{60}$  with mono- and diazides.

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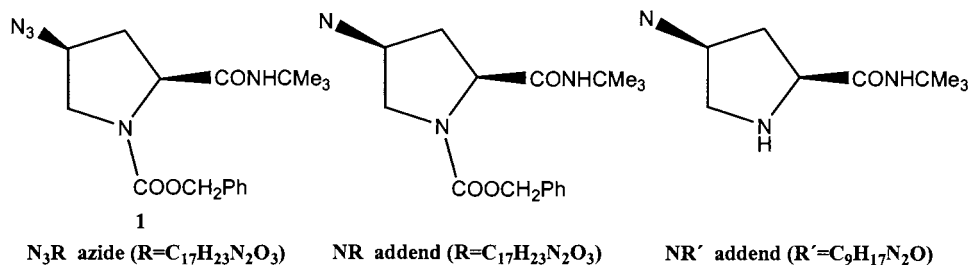


Fig. 2. Azide **1** and different types of addends derived from it.

azides and at lower temperatures (100–136°C), the formation of azafulleroids results is favoured [1a,l,m,2a]. The formation of azafulleroids through a triazoline adduct (**III**) as intermediate has been demonstrated by Schick et al. [1e,g,2a]. Some fulleroaziridines with alkoxy carbonyl substituents isomerize to oxazole adducts by heating [1d]. Photochemical rearrangement of an azafulleroid to fulleroaziridine has also been reported [1j].

Some reactions of  $\text{C}_{60}$  with an excess of azide have also been studied [2]. So the reaction with an excess of the azide SEMN<sub>3</sub> [SEM =  $-\text{CH}_2\text{O}(\text{CH}_2)_2\text{SiMe}_3$ ] in ClPh at 136°C for 12 h, gives rise to a mixture containing the bisazafulleroid adduct of type **IV** (Fig. 1) as the main product (60%) along with the triazoline (**III**) (30%) and aziridine (**I**) (10%) adducts. Products of type **V**, formed by addition of the azide  $\text{MeOOCCH}_2\text{N}_3$  to the corresponding azafulleroid **II**, give rise to the bisadduct **IV** by heating to reflux in toluene and have been proposed as possible intermediates [2a]. Bisadduct **IV** can be described as a double azafulleroid with the two N atoms bonded to the three carbons of two consecutive (5,6) junctions of the same pentagon. Another bisadduct of type **VI** has been isolated, which can be described as a double azafulleroid with both N atoms bonded to four carbons of two alternate (6,6) junctions of a hexagon. These adducts have been prepared regioselectively from the reaction of the aziridine adducts  $\text{C}_{60}\text{NCOOR}$  ( $\text{R} = \text{Et}, \text{'Bu}$ ) (**I**) with two equivalents of the corresponding azide at 60°C in 1-chloronaphthalene and ulterior heating in toluene reflux, and are the major products of the reaction of  $\text{C}_{60}$  with two equivalents of azide in 1-chloronaphthalene at 60°C followed by heating in toluene reflux [2b,c]. On the other hand, the reaction of  $\text{C}_{60}$  with two equivalents of  $\text{EtOOCN}_3$  in the conditions of formation of the nitrene intermediate gives rise to a mixture of isomers consisting of the bisadduct of the type **VI** (21%) and other seven different bisaziridine adducts, all components of which could be separated by HPLC and characterised [2c]. Bisadducts of the type **VI** give rise under FAB MS conditions to azafullerene  $\text{C}_{59}\text{N}^+$ , whereas those of the type **V** do not give this heterofullerene under the same conditions [2b]. When the open bisadduct of type **VI** with  $\text{R} = \text{'Bu}$  is treated with trifluoroacetic acid in toluene at room

temperature, a closed new bisadduct type, **VII**, with  $\text{R} = \text{H}$ , is formed, in which both nitrogen atoms remain bonded to the same carbons, but as in a bisaziridine adduct [2c].

Reactions of  $\text{C}_{60}$  with diazides have also been studied [3]. So the reaction with  $\text{N}_3(\text{CH}_2)_n\text{N}_3$  ( $n = 2, 3$ ) or  $\text{N}_3\text{C}(\text{COOEt})_2\text{N}_3$  gives a new type of open bisadduct, **VIII**, in which the two nitrogen atoms are bonded to four carbons of alternate (5,6) junctions of a pentagon [3a,b]. A mixture of bisadducts of types **VII** (18%), and **VIII** (11%), together with a bistriazoline adduct of type **IX** (25%), is formed by reaction of  $\text{C}_{60}$  and 2,2-dibenzyl-1,3-diazidopropane (1.5 equivalents) in refluxing ClPh for 8 h [3c]. Chiral bisazafulleroids of type **VII** are also formed in the reactions of  $\text{C}_{60}$  and the  $\text{C}_2$  chiral 1,4-*tert*-alkoxy-2,3-bisazidobutanes [3d]. However, reactions with bisazides tethered by polyglycol or polyglycol diacetate chains give rise to bisazafulleroids of type **IV** [3e]. Recently the photochemical rearrangement of a new bisazafulleroid of type **VIII** to give an azaziridinefullerene of type **X** has been shown [3f].

We describe here the reactions of  $\text{C}_{60}$  with the chiral azide (2*S*,4*S*)-4-azido-1-benzoyloxycarbonyl-2-(*t*-butylaminocarbonyl)pyrrolidine (**1**), which give rise to derivatives  $\text{C}_{60}(\text{NR})_n$  with one or several R groups attached to fullerene through the remaining nitrogen of azide (Fig. 2).

## 2. Results and discussion

### 2.1. Synthesis and characterisation of the $\text{C}_{60}(\text{NR})_n$ derivatives ( $n = 1$ (**2**), $n = 2$ (**3**), $n = 4$ (**4**) and $n = 6$ (**6**))

Reactions in a 1:1 molar ratio of [60]fullerene with the chiral azide **1** in chlorobenzene at the reflux temperature lead to reaction mixtures that contain mono- and polysubstituted derivatives, the composition of which depends on the concentration of the reactants. These reactions occur slowly and only after 3 days the presence of the azide cannot be detected by TLC. The reaction mixtures obtained were treated after evaporation of solvent by flash column chromatography (silica gel, mixtures of hexane–ethyl acetate). Elution with

different hexane–ethyl acetate mixtures leads to isolated fractions that contain the mono- and disubstituted species  $C_{60}(NR)$  (**2**) and  $C_{60}(NR)_2$  (**3**). Finally, the elution with pure ethyl acetate yields the more substituted species  $C_{60}(NR)_4$  (**4**). The composition of the different reaction mixtures obtained for concentrations of  $1.11 \times 10^{-3}$ ,  $3.32 \times 10^{-3}$  and  $5.55 \times 10^{-3}$  M are given in Table 1. A higher concentration favours the formation of polysubstituted products **3** and **4**, which are probably mixtures of isomers.

The reaction at a lower temperature (100°C) and a concentration of  $3.32 \times 10^{-3}$  M yields the products **2**, **3** and **4** in different proportions with respect to those of the reactions above described, together with a new product of composition  $C_{60}(NR)(N_3R)_2$  (**5**), which is probably an aza-bistriazoline-fullerene. The triazoline species, resulting from a [3 + 2]-addition of azide to fullerene and formed in reactions at 60°C in a high yield, are intermediates in the formation of aza-fulleroids [1g,2a]. The IR spectrum of **5** shows an additional weak band of free azide at  $2094\text{ cm}^{-1}$ . Since free azide was not detected in the reaction solution by TLC nor in the IR spectrum of the crude reaction product, this could be formed in a reverse reaction from a triazoline species in the separation process.

The unprecedented formation of higher substitution derivatives such as **3**, **4** and **5** in relatively high yields in 1:1 reactions at low concentrations, performed in similar conditions to those reported [1,2] is to be noted. On the other hand, the different types of bisadducts previously described are preferentially formed in reactions with an excess of azide [2].

From this results it is to be expected that the reaction at 130°C in similar conditions of concentration, but in a molar ratio 1:6 ( $C_{60}$ –azide **1**) could give rise to more substituted polyazafulleroid species in a high yield. This was effectively confirmed by the experimental results, and a unique fraction of composition  $C_{60}(NR)_6$  (**6**) was isolated from this reaction in a 74% yield.

All these products, isolated by evaporation of solvents after chromatography, show a strong tendency to retain chlorinated solvents and water and only by prolonged evacuation can correct analytical data for them be obtained. The colour varies from dark brown, for

the monoadduct **2**, to caramel–brown for the polysubstituted species, being progressively more clear for species containing an increasing number of addends attached to fullerene. IR spectra of all  $C_{60}(NR)_n$  products are very similar, as they correspond to species with only a different number of NR groups bonded to fullerene.

Except for the amide proton, the  $^1\text{H-NMR}$  spectrum of  $C_{60}(NR)$  (**2**) exhibits well-defined signals for the remaining different protons of the NR group [R =  $C_4H_6N(CO_2CH_2Ph)(CONHMe_3)$ ]. In the  $^{13}\text{C-NMR}$  ( $CDCl_3$ ) spectrum of this compound, 32 signals, 28 of them with double intensity, are observed in the range  $\delta$  148–132 ppm for the  $C_{60}$  carbons, as corresponding to a monoazafulleroid species with only  $sp^2$  fullerene carbons. Signals for all remaining carbons of NR are also observed. In the  $^1\text{H-NMR}$  spectra of the polysubstituted species  $C_{60}(NR)_n$  ( $n = 2, 4, 6$ ) a broadening of signals corresponding to the pyrrolidine CH and  $CH_2$  protons is observed, which increases with the number of substituents. So in the spectrum of  $C_{60}(NR)_6$  (**6**) only overlapped broad signals in the range 4.6–2.0 ppm are observed for these protons. Broad signals, but with defined maxima, are observed also for the  $PhCH_2$  and  $CMe_3$  protons of the NR groups in this same product. No well-defined signals are observable for the fullerene carbons in the solid-state  $^{13}\text{C-NMR}$  spectra of the polysubstituted species **3** and **6**, in which the intensities of the aromatic and aliphatic carbons signals of R increase dramatically with the number of R groups attached to fullerene, whereas those of the amide and ester carbonyl signals increase only moderately. However no signals towards 80 ppm, characteristic of aziridine  $sp^3$  fullerene carbons [1b,c,e], are observed in these spectra. The  $^{13}\text{C-NMR}$  spectrum of **6** in  $CDCl_3$  is totally similar to that obtained in the solid state. We can conclude that the products **3**, **4** and **6** are probably mixtures of isomers of polyazafulleroids of composition  $C_{60}(NR)_n$  with  $n = 2, 4$  and  $6$ , respectively. This could account for the broadening of signals observed for the CH and  $CH_2$  protons of the pyrrolidine ring and for the fullerene carbons in the  $^1\text{H-}$  and  $^{13}\text{C-NMR}$  spectra, respectively, compared with the signals observed in the corresponding spectra of **2**.

Table 1  
Reactions in a 1:1 molar ratio of  $C_{60}$ –azide **1**, in ClPh

Reaction	Reaction conditions			$C_{60}(NR)_n$ products: $n = 1, 2; n = 2, 3; n = 4, 3$ (% calculated with respect to $C_{60}$ )
	Concentration ( $\text{mol l}^{-1}$ )	$T$ ( $^\circ\text{C}$ )	$t$ (days)	
I	$1.11 \times 10^{-3}$	130	4	$C_{60}$ (38%) + <b>2</b> (34%) + <b>3</b> (23%) + <b>4</b> (5%)
II	$3.32 \times 10^{-3}$	130	4	$C_{60}$ (35%) + <b>2</b> (26%) + <b>3</b> (35%) + <b>4</b> (6%)
III	$5.55 \times 10^{-3}$	130	4	$C_{60}$ (61%) + <b>2</b> (10%) + <b>3</b> (13%) + <b>4</b> (16%)
IV	$3.32 \times 10^{-3}$	100	3	$C_{60}$ (54%) + <b>2</b> (12%) + <b>3</b> (18%) + <b>4</b> (4%) + $C_{60}(NR)(N_3R)_2$ ( <b>5</b> ) (12%)

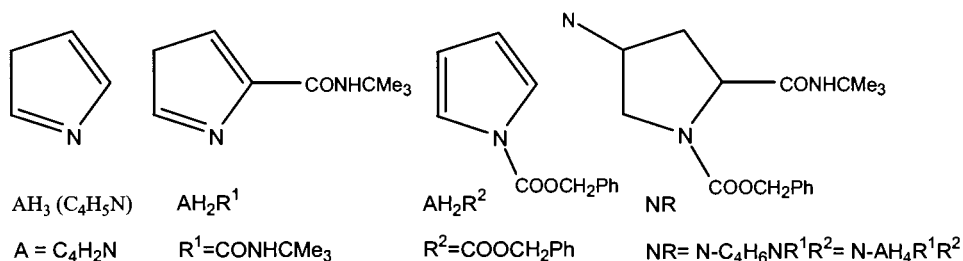


Fig. 3. Basic structures for abbreviated designation of MS fragments.

Mass spectra of **2**, **4** and **6** were performed using the fast cesium ion bombardment (LSI MS) technique and *m*-nba as matrix. Fig. 3 shows a series of basic structures for abbreviated designation of possible FAB MS fragments. In the region with  $m/z^+$  lower than 320 [ $NH_3R^+$ ,  $C_{17}H_{26}N_3O_3$ ] clusters corresponding to different fragments of NR and matrix appear, their more significant peaks corresponding to  $CMe_3$  [57.02], Ph [77.01],  $C_7H_7$  [91.03], [107.04],  $AH_4R^1$  [167.20],  $N-AHR^1$  [179.16],  $NH_2-AH_3R^2$  [221.18] and  $H_3N^+ - AH_4R^1R^2 = H_3N^+ - R$  [320.19]. In the region with  $m/z$  between 320 and 720 ( $C_{60}$ ) several peaks appear which can be assigned to fragments derived from fullerene, some of which could contain residual N from NR groups. These peaks appear at 529.43 ( $C_{44}$ ), 545.43 ( $C_{44}NH_2$ ), 647.45 ( $C_{54}$ ), 662.48 ( $C_{54}N$ ), 671.99 ( $C_{56}$ ), 695.99, 696.99 ( $C_{58}$ ), 697.99 ( $C_{57}N$ ), 719.99 (8.93,  $C_{60}$ ), 720.99 (9.21,  $C_{60}H^+$ ). The peaks at  $m/z = 696$ , 672 and 647 are clearly derived from 'shrink-wrapping fragmentation' of  $C_{60}$  core by successive elimination of  $C_2$  with retention of the fullerene structure. The high energy required for this process implies a previous elimination of all exohedrally bound groups [2b]. The peak at  $m/z = 698$  (observed in the MS spectra of **4** and **6**), corresponding to the heterofullerene species  $^{12}C_{57}^{14}N^+$ , could imply the presence of bisadducts of the type **VI** or mixed 5–6/6–6 trisadducts [2b,c]. Bisadducts of type **IV** and monoadducts **I** and **II** do not give rise to  $^{12}C_{57}^{14}N^+$  heterofullerene species under FAB conditions [2b]. In the region with  $m/z > 720$  peaks of relatively high intensity appear at 722.00 [6.4,  $^{12}C_{59}^{14}N^+$ ] in the MS spectra of **4** and **6**, which can also correspond to a heterofullerene species. Several peaks in the  $m/z$  range 734–739 can be due to  $^{12}C_{60}^{14}NH$  [735.21] (**4**, **6**) and  $^{12}C_{59}^{14}N_2H^+$  or  $^{12}C_{60}^{14}NH_2^+$  [736.00] (**2**, **4**, **6**) species. Peaks related with  $C_{60}(NH_2)_2$  [752.02] (**4**, **6**) and  $C_{60}(NH_2)_3$  [768.02] (**4**) species are also observed. Indeed, a series of peaks at  $m/z$  between 770 and 1038 appear, which can be due to fullerene attached to different residual fragments of the addend, such as  $C_{60}N-AH_3-CH_3^+$  [816.07] (**4**, **6**)  $C_{60}N-AH_2-CHO$  [828.06] (**4**) or  $C_{60}N-AH_3-CONH_2$  [845.06] (**4**, **6**). Only in the MS spectrum of **4** are observed peaks of relatively high intensities, at  $m/z = 1355.42$ , 1673.62 and 1990.90 [ $M^+$ ], corresponding to species  $C_{60}(NR)_n$  with

$n = 2, 3, 4$ , respectively, and a peak at  $m/z = 1038.12$ , corresponding to  $C_{60}(NR)$  is also observed in the MS spectra of **4** and **6**. Although no molecular peak is observed in the FAB spectrum of  $C_{60}(NR)$  (**2**), the API ES positive MS of this product, in MeCN as solvent, shows a peak at  $m/z = 1079.3$ , corresponding to the solvate  $C_{60}(NR) \times MeCN$ , and another peak at  $m/z = 834.3$ , assignable to fullerene bonded to a fragment of R, with the composition  $C_{60}(NAH_5CHO)$ .

From all this study we can conclude that in reactions in a 1:1 molar ratio of  $C_{60}$  with the azide **1** in chlorobenzene reflux (4 days) and at low concentration ( $1.11 \times 10^{-3}$  and  $3.32 \times 10^{-3}$  M), mixtures containing mono- bis- and tetraazafulleroid species were obtained; the last in a low yield. At a higher concentration ( $5.55 \times 10^{-3}$  M) and under the same conditions, the proportion of the species containing more addends increases, the most abundant of them being that of composition  $C_{60}(NR)_4$  (**4**). The FAB mass spectrum of this product shows peaks at  $m/z$  corresponding to  $C_{60}(NR)_4$  [ $M^+$ ],  $C_{60}(NR)_3$ ,  $C_{60}(NR)_2$  and  $C_{60}(NR)$ , so as to  $C_{59}N$  and  $C_{57}N$ . These  $C_{59}N$  and  $C_{57}N$  fragments could imply the presence of at least one group of two addends on alternating C–C bonds of the same hexagon of fullerene, as shown in Fig. 1 (**VI**) [2b,c]. This possibility is reinforced by the presence of signals at  $\delta = 113.39$  and 119.46 in the  $^{13}C$ -NMR solid-state spectrum of  $C_{60}(NR)_2$  (**3**), the range in which appear one of the characteristic signals of the bisazafulleroids of type **VI** [2b], the other characteristic signal of this species being possibly included in the broad signal centred at 127.96 ppm. Signals at 114 and 128 ppm have been assigned to the carbons bonded to nitrogen in the bisazafulleroids of this type [2b].

The reaction with an excess of azide **1** (1:6) leads to the expected polysubstituted product  $C_{60}(NR)_6$  (**6**). In the LSI FAB MS of **6** peaks at  $m/z$  650.21, 674.24, 697.99 and 722.20 also correspond to heterofullerene species  $^{12}C_{53}^{14}N^+$ ,  $^{12}C_{55}^{14}N^+$ ,  $^{12}C_{57}^{14}N^+$  and  $^{12}C_{59}^{14}N^+$ , respectively, and this could imply the presence of at least a group of two NR addends bonded to four carbons of the same hexagon of fullerene, as shown in Fig. 1 (**VI**), or mixed 5–6/6–6 trisadducts [2b,c]. However, the presence of groups of two NR addends bonded to three carbons of the same pentagon of fullerene cannot be

excluded in **6**. These bisazafulleroids (Fig. 1, **IV**) show four signals of  $C_{60}$  carbons in the range 134–130 ppm and the  $C_{60}$  carbons bonded to nitrogen appear toward 138 and 160 ppm [2a]. A signal at 133 ppm is clearly observed in the solid-state  $^{13}C$ -NMR spectrum of **6** and shoulders at the higher  $\delta$  side in the signals at 136.21 and 154.65 could correspond to the  $C_{60}$  carbons bonded to nitrogen as shown in Fig. 1 (**IV**). The presence of six addends with strong signals, as the phenyl and  $t$ butyl groups, makes it impossible to obtain  $^{13}C$ -NMR spectra of high resolution, in the solid-state and in solution, in the region of the fullerene carbons.

## 2.2. Deprotection attempts

Deprotection attempts were performed on derivatives **4** and **6** derivatives in order to obtain more coordinating species by elimination of the  $COOCH_2Ph$  groups. Treatment of **4** in EtOH with cyclohexene and Pd–C (10%) as catalyst at the reflux temperature for 24 h was inefficient and the starting product, probably contaminated with Pd (lower C and N contents), was recovered. The application of the same treatment to **6** for 48 h results in the formation of a deprotected product **7** (absence of aromatic signals in the  $^1H$ -NMR spectrum), isolated after filtration and evaporation of solvent as a brown, greasy solid. This product after treatment with  $[RhCl(CO)_2]_2$  in  $CH_2Cl_2$  yields a new product with very low carbon (40.63%) and Rh (2.36%) contents and with only weak  $\nu(CO)$  IR bands. This leads to the conclusion that this product could contain principally Pd(II) coordinated to the pyrrolidine and amide N atoms, hindering the coordination to Rh. The Pd(0) of the catalyst could be retained in **7** by  $\eta^2$ -coordination to fullerene carbons as in  $C_{60}Pd_n$  [5], capable of reaction with phosphines and phosphites to yield the well-known fullerene complexes  $C_{60}[\eta^2-Pd(PR_3)_2]_n$ . In the attempted reaction of **7** with  $[RhCl(CO)_2]$  in  $CH_2Cl_2$  a previous oxidation by the solvent of Pd(0) to  $PdCl_2$  could occur, followed by coordination to the deprotected  $C_{60}(NR)_6$  species. This may account for the low contents in carbon and rhodium found for this product.

Only a residual amount of Rh seems to be retained in this product. Additional  $NH_2R'$  ligands, potentially formed in the reduction process, could coordinate also to  $Rh^I$  or  $Pd^{II}$  and contribute to the relatively high N content (8.3%).

## 2.3. Formation of rhodium complexes

Reactions of the **2**, **4** and **6** derivatives with  $[RhCl(CO)_2]_2$  lead to the formation of complexes of general formula  $C_{60}(N-R)_n[RhCl(CO)_2]_n$  ( $n = 1$  (**8**),  $n = 4$  (**9**) and  $n = 6$  (**10**)), in which the NR groups could be coordinated to rhodium through its amide nitrogen and carbonyl oxygen atoms of the  $R^1$  and  $R^2$  substituents at the pyrrolidine ring. The IR spectra of these complexes show all the bands of the starting compounds, some of them shifted, and one strong  $\nu(CO)$  band at  $2023\text{ cm}^{-1}$ , which can correspond to a square-planar Rh–monocarbonyl– or *trans*-Rh–dicarbonyl species or to a bipyramidal trigonal *trans*-Rh–dicarbonyl species. Only scarce examples have been previously described for  $Rh^I$  complexes with only one carbonyl IR band towards  $2020\text{ cm}^{-1}$  and these correspond to cationic square-planar or bipyramidal trigonal dicarbonyl species containing  $PPh_3$  as additional ligands or to cationic monocarbonyl square-planar species containing  $PMePh_2$  as additional ligands [6]. It is to be noted that the most modified IR frequencies of the complexes with respect to the corresponding starting compounds are those of the carboxylate and amide carbonyl groups, which give rise to only a broad carbonyl band toward  $1685\text{ cm}^{-1}$ . This implies a coordination to  $Rh^I$  through both groups of this potentially bidentate *N,O*-R ligand and the complexes are probably bipyramidal trigonal species, in which the  $Rh^I$  is coordinated to two axial CO ligands and to the equatorial Cl, and the N and O atoms of the potentially bidentate *N,O*-donor R ligands, as shown in Fig. 4(A). Only this bipyramidal pentacoordinated configuration is compatible with a *trans*-dicarbonyl species with a bidentate *N,O*-donor R ligand. The alternative possibility of a square-planar monocarbonyl species (Fig. 4(B)) does not fit well with

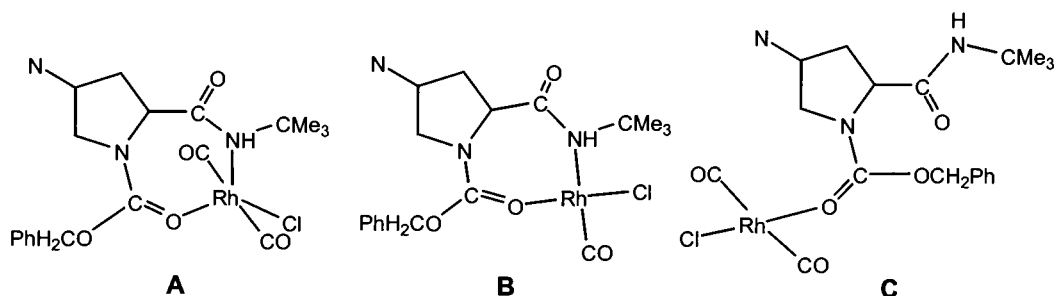


Fig. 4. Possible coordination mode of Rh in complexes with N–R addends attached to  $C_{60}$  (complexes **2**, **4** and **6**). (A) Bipyramidal trigonal for a *trans*-dicarbonyl species and *N,O*-bidentate coordination to R. (B) Square-planar for a monocarbonyl species and *N,O*-bidentate coordination to R. (C) Square-planar for a *trans*-dicarbonyl species and monodentate *O*-coordination to R.

the analytical and MS results. The presence of a peak at  $m/z = 1233.4$  in the ESI(AP) MS of **8**, corresponding to  $M^+$  for the formula  $C_{60}(NR)[RhCl(CO)_2]$  (FW = 1234.04), confirms the composition assigned to this complex, so as the presence of a fragmentation peak at  $m/z = 476.4$ , assignable to the  $[Rh(NH_2R)(CO)_2]^+$  species. Indeed, in the FAB spectrum of this same complex a series of peaks in the range  $m/z = 281–342$  appear, which are not found in the FAB spectra of  $C_{60}(NR)_n$  species and can be assigned to  $Rh(CO)_2$  units bonded to fragments of R. Another possible square-planar configuration for a *trans*-dicarbonyl species is the coordination only through the carbonyl oxygen of the ester group of R, being R in this case a monodentate *O*-donor ligand, as shown in Fig. 4(C). On the other hand, sterical requirements exclude the *trans* coordination of  $Rh^I$  to a bidentate *N,O*-donor R ligand, and the subsequent *trans* coordination of two carbonyls, in a hypothetical cationic, square-planar dicarbonyl complex, previous displacement of  $Cl^-$ .

The  $^1H$ -NMR spectra of complexes **8**, **9**, and **10** are similar to those of the corresponding starting ligands. Solid-state  $^{13}C$ -NMR spectrum of **10** shows almost all signals shifted to downfield with respect to those of the corresponding spectrum of **6**, as an effect of the coordination to rhodium, the greater shift corresponding to the  $CH_2Ph$  signal. Signals at 126.4, 122.5, 118.2, 114.2 and 106.8 ppm are observed in this case, some of which could correspond to fullerene carbons bonded to N. No signals appear in this region in the solid-state  $^{13}C$ -NMR spectrum of **8**.

#### 2.4. Catalytic experiments

The catalytic properties of  $C_{60}(N-R)_6[Rh(CO)_2Cl]_6$  (**10**) were examined under usual conditions for test reactions in the asymmetric hydrogenation of tiglic acid ( $MeCH=CMeCO_2H$ ). The reaction proceeded in 2 h with 12.3% ee.  $C_{60}(N-R)_6[Rh(CO)_2Cl]_6$  behaves as an efficient hydrogenation catalyst, but with a moderate enantiomeric excess.

### 3. Experimental

$C_{60}$  was separated from refined mixed fullerene (MER, about 80%  $C_{60}$ ) by flash chromatography as previously described [7]. All reactions were carried out under an atmosphere of dry  $N_2$  free of oxygen. Solvents were purified by standard methods. Azide **1** [8] and  $[RhCl(CO)_2]_2$  [9] were prepared by literature methods. Elemental analyses were performed at the ICMM (CSIC), using the atomic absorption technique for analysis of Rh. IR spectra were recorded with a Nicolet 20 SXC FTIR spectrophotometer using KBr disks. NMR spectra in solution were recorded on a Varian Gemini

200, Bruker AM 200, Varian XL 300 or Varian XL 400 spectrometers. High-resolution  $^{13}C$  MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence (in order to eliminate the spinning side bands) were performed at the ICMM. These spectra were recorded at 100.63 MHz, 6  $\mu s$  90° pulse width, 2 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 4 kHz. Mass spectra were performed at the UAM (SIDI), using the fast cesium ion bombardment (liquid secondary ion mass spectrometry, LSI MS) technique, and 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 MeCN +  $CHCl_3$  as solvent.

#### 3.1. Reactions in a molar ratio 1:1 $C_{60}$ -azide **1**

##### 3.1.1. Reaction at a concentration of $1.11 \times 10^{-3} M$

$C_{60}$  (60 mg, 0.083 mmol) and azide **1** (28.8 mg, 0.083 mmol) were sonicated in chlorobenzene (75 ml) for 30 min in an  $N_2$  atmosphere and refluxed (130°C) for 4 days to yield a reddish–brown solution. After evaporation of solvent, the dark-brown residue was washed with diethyl ether, dried and chromatographed using 1:1 hexane–EtOAc to separate different fractions of the reaction mixture. A 22 mg sample of unreacted  $C_{60}$  was recovered as the first fraction, after which was eluted the monoazafulleroid species **2** as the major fraction (32 mg, 34%), followed by another fraction containing the species **3** (28 mg, 23%). Finally, 9 mg of a more polar fraction containing the higher substitution derivative **4** (5%) was eluted with ethyl acetate.

##### 3.1.2. Reaction at a concentration of $3.32 \times 10^{-3} M$

$C_{60}$  (60 mg, 0.083 mmol) and azide **1** (28.8 mg, 0.083 mmol) were sonicated in chlorobenzene (25 ml) for 30 min in an  $N_2$  atmosphere and refluxed (130°C) for 4 days to yield a reddish–brown solution. After evaporation of solvent, the dark-brown residue was washed with diethyl ether, dried (110 mg) and chromatographed using hexane as first eluent to remove the unreacted  $C_{60}$ , 2:1 hexane–EtOAc to separate the lower substitution derivatives as a brown powder (**2** +  $C_{60}$ , 35.5 mg) and pure EtOAc to separate the higher substitution derivatives as a caramel–brown powder (**3** + **4** +  $C_{60}$ , 55.6 mg) after evaporation of solvent. Both products were again chromatographed to eliminate residual  $C_{60}$ , to yield the products **2** (25.0 mg, 26%) and **3** (42.6 mg, 35%), from the fractions eluted with 2:1 hexane–EtOAc and 10.5 mg (6%) of **4** from the second product eluted with EtOAc, after previous elution with hexane and 2:1 hexane–EtOAc.

### 3.1.3. Reaction at a higher concentration ( $5.55 \times 10^{-3}$ M)

The reaction was performed as described earlier, but using a higher concentration of reactants (100 mg (0.139 mmol) of  $C_{60}$  and 48 mg (0.139 mmol) of azide **1** in 25 ml of ClPh). After evaporation of solvent, the dark-brown residue was washed with diethyl ether, dried and chromatographed using 1:1 hexane–EtOAc to separate different fractions of the reaction mixture. A 55 mg sample of unreacted  $C_{60}$  was recovered as the first fraction, after which was eluted the monoaza-fulleroid species **2** as a minor fraction (16.0 mg, 10%), followed by another fraction containing the species **3** (26.5 mg, 13%). Finally, an orange–brown powder of the more polar substitution derivative **4** (46.8 mg, 16%) was isolated from the fraction eluted with ethyl acetate.

### 3.1.4. Reaction at a lower temperature

$C_{60}$  (60 mg, 0.083 mmol) and azide **1** (33.8 mg, 0.098 mmol) were sonicated in chlorobenzene (25 ml) for 30 min in an  $N_2$  atmosphere and heated at 100°C for 3 days. After evaporation of solvent, the reddish–brown solution yields a dark-brown powder, which was washed with diethyl ether and dried in vacuum. The crude product was chromatographed using hexane as the first eluent to remove 32.3 mg (54%) of unreacted  $C_{60}$ , and 2:3 hexane–EtOAc to separate three fractions containing the monosubstituted species **2** (11.5 mg, 12%), the disubstituted species **3** (21.93 mg, 18%) and an intermediate species of composition  $C_{60}(NR)(N_3R)_2$  (**5**, 17.2 mg, 12%), respectively. The subsequent elution with ethyl acetate leads to isolate the more polar polyazafulleroid species **4**, (7 mg, 4%).

### 3.2. Reaction in a 1:6 molar ratio of $C_{60}$ –azide **1**

$C_{60}$  (100 mg, 0.139 mmol) and azide **1** (287.7 mg, 0.833 mmol, six equivalents) were sonicated in chlorobenzene (25 ml) for 30 min in an  $N_2$  atmosphere and refluxed (b.p. 130°C) for 4 days to yield a brown solution. After evaporation of solvent, the residue was washed with  $Et_2O$  and dried. The crude product was chromatographed using hexane as the first eluent to remove residual  $C_{60}$  and EtOAc to recover the highly substituted fullerene **6** as a brownish–red solid (281.3 mg, 74%).

### 3.3. Characterisation of products **2–6**

All these products were isolated by evaporation of solvents from the corresponding chromatographic fractions and the solid residues were evacuated for 24 h.

**2**. Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)_2 \cdot \frac{1}{2}ClPh$  ( $\frac{1}{2}C_{160}H_{51}ClN_6O_6$ ): C, 87.81; H, 2.35; N, 3.84. Found: C, 87.75; H, 2.30; N, 3.90%. (KBr,  $cm^{-1}$ ) 3400sh br, 3322m, 2950m, 2914m, 2850mw, 1740mw, 1702s, 1686s, 1534m,

1450m, 1412ms, 1356s, 1213m, 1178mw, 1157mw, 1096s br, 1018s, 800m, 765w, 732w, 690w, 573w, 520m.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.48–7.30 (m, 5H, *Ph*), 5.20–5.10 (m, 2H,  $OCH_2Ph$ ), 4.20–4.10 (m, 1H, *CH–N*), 3.70–3.60 (m, 1H, *CH–CON*), 3.60–3.20 (m, 2H,  $CH_2–N$ ), 2.30–2.20 (m br, 2H,  $CH_2–CH–N$ ), 1.30 (s, 9H,  $CONHCOMe_3$ ).  $^{13}C$ -NMR (100 MHz,  $CDCl_3$ , 36 h)  $\delta$  172.20 (s br, *CONHR*), 157.20 (s br,  $COOCH_2Ph$ ), 147.98, 147.70, 147.10, 146.30, 145.95, 145.70, 145.40, 145.10, 144.60, 144.30, 143.75, 143.30, 142.75, 142.30, 141.80, 141.30, 140.80, 140.40, 139.90, 139.20, 138.70, 137.80, 137.25, 136.80, 136.60, 136.30 (28  $C_{60}$   $sp^2$ -carbons), 135.93 (s,  $C_{ipso}$  Ph), 135.80, 134.82, 133.73, 133.41 (4 $C_{60}$   $sp^2$ -carbons), 128.42, 128.03 (*o*-, *m*-, *p*-*Ph*), 67.57 (s,  $OCH_2Ph$ ), 61.15 (s br,  $NC^*HCO$ ), 57.20 (m,  $CH_2N$ ), 52.90 (m,  $CH–N–C_{60}$ ), 50.97 (s,  $CMe_3$ ), 34.40 (m br,  $CH_2$ ), 28.54 (s,  $CH_3$ ). Signals at 137.80, 139.20, 142.75 and 146.30 show lower intensities and probably each of them correspond to a single carbon. FAB MS (LSI MS, positive ion, peaks of *m*-nba matrix omitted), *m/z* (relative high of peak in brackets, %): 57.05 (100), 67.04 (32.35), 69.06 (60.00), 77.03 (37.43), 79.05 (20), 81.07 (31.4), 83.08 (26.16), 91.06 (89.90), 95.09 (25.67), 107.07 (20.92), 136.07 (23.06), 149.05 (10.09), 154.08 (14.56), 242.2 (0.25), 251.09 (0.15), 266.10 (0.10), 289.13 (0.10), 320.24 (0.08,  $NH_3–R^+$ ), 415.26 (0.41), 647.45 (1.14), 662.48 (0.60), 663.49 (1.11), 720.07 (5.23,  $C_{60}$ ), 721.08 (4.70).

API ES positive MS (*m/z*, relative intensity (%)) and assignment in brackets, time: 2.18 min): 1079.3 [1.4,  $C_{60}(NR) + MeCN$ ], 834.3 [5.0,  $C_{60}(NAH_5CHO)$ ,  $A = C_4H_2N$ ], 477.2 (8.6), 458.3 (12.8), 442.2 (25.7), 416.1 (50.0), 365.2 (100.0), 337.1 (54.3), 262.3 (11.0), 249.3 (8.2), 143.2 (9.1).

**3**. Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)_2 \cdot ClPh$  ( $C_{100}H_{51}ClN_6O_6$ ): C, 81.82; H, 3.50; N, 5.72. Found: C, 81.68; H, 3.67; N, 5.80%. IR (KBr,  $cm^{-1}$ ) 3320m, 2955m, 2918m, 2840sh, 1702s, 1686s, 1535m, 1446m, 1405m, 1344m, 1214s, 1157m, 1108m, 765w, 734w, 692w, 572w, 501mw.  $^1H$ -NMR ( $CDCl_3$ , 200 MHz)  $\delta$  7.55–7.15 (m, 5H, *Ph*), 5.43–5.02 (m, 2H,  $PhCH_2CO$ ), 4.48 (s br, 1H, *CH*), 4.40–3.40 (m, 3H,  $CH + CH_2$ ), 3.15–1.95 (m, 2H,  $CH_2$ ), 1.61 (s, br, 2H,  $H_2O$ ), 1.37–1.12 (broad signal with several peaks, the most prominent of them at  $\delta$  1.25, 9H,  $CONHCOMe_3$ ). In the spectrum in  $CDCl_3–S_2C$  at 40°C several signals of  $CMe_3$  groups also appear in the same region, but with more similar intensities, at 1.45, 1.37, 1.29 and 1.25 ppm, in increasing order of intensity. Solid-state  $^{13}C$ -NMR CP/MAS/TOSS spectrum:  $\delta$  169.81 (s br, *CONHR*), 154.77 (s br,  $COOCH_2Ph$ ), 149–130 (m br, with observable maxima at 144.54, 141.02, 138.25, 136.57 and 132.56,  $C_{60}$   $sp^2$ -carbons +  $C_{ipso}$  Ph), 127.96 (*o*-, *m*-, *p*-*Ph*), 119.46, 113.40 ( $C_{60}$   $sp^2$ -carbons), 66.56 (s,  $CH_2Ph$ ), 61.35 ( $NCHCO$ ), 58.20–52.50 (m,

$NCH_2 + C_{60}-NCH$ ), 50.79 ( $CMe_3$ ), 37.5–32.00 (m,  $CH_2$ ), 28.83 (s,  $CH_3$ ).

4. Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)_4 \cdot ClPh$ , ( $C_{134}H_{97}ClN_{12}O_{12}$ ): C, 76.54; H, 4.65; N, 7.90. Found: C, 76.89; H, 4.43; N, 7.95%. IR (KBr,  $cm^{-1}$ ): 3436w, 3323m, 2952m, 2914ms, 2840m, 1716vs, 1688sh, 1528m, 1446m, 1402ms, 1343m, 1212w, 1168w, 1110m, 748w, 710w, 690m.  $^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.48–7.20 (m, 5H, *Ph*), 5.42–5.00 (m, 2H,  $PhCH_2CO$ ), 4.65–3.40 (m br, 4H,  $2CH + CH_2$ ), 3.40–1.95 (m br, 2H,  $CH_2$ ), 1.45–1.10 (broad signal with the most prominent highs at 1.29 and 1.25 ppm, 9H,  $CONHCMe_3$ ).

FAB MS (LSI MS, positive ion, peaks of *m*-nba matrix omitted)  $m/z$  (relative height of peak in brackets, %): 55.00 (23.0), 57.02 (30.0), 67.02 (10.0), 68.01 (9.0), 69.03 (14.0), 71.05 (7.0), 77.01 (15.0), 83.05 (10.0), 89.02 (10.0), 91.03 (100.0), 92.04 (10.0), 107.04 (13.0), 136.04 (23.0), 137.04 (19.0), 138.05 (12.0), 154.05 (30.0), 158.09 (5.0), 167.20 (4.0), 179.16 (5.0), 181.17 (4.0), 189.17 (2.0), 207.13 (2.0), 221.18 (2.0), 259.15 (1.75), 272.13 (1.01), 273.10 (1.10), 274.17 (1.93), 289.08 (3.31), 290 (0.92), 320.19 (3.22), 529.43 (1.20), 545.43 (0.92), 671.99 (0.47), 695.99 (0.92), 696.99 (0.74), 697.99 (0.55), 719.99 (8.93), 720.99 (9.18), 722.00 (6.44), 723.00 (3.40), 724.00 (1.66), 725.00 (0.74), 734.01 (0.64),  $C_{60}N$ ; 735.01 (0.92), 736.00 (2.13), 737.00 (2.03), 738.01 (1.38), 739.01 (0.74), 751.02 (0.46), 744.01 (0.32), 745.01 (0.36), 746.01 (0.45), 747.01 (0.36), 748.02 (0.36), 752.02 (0.56), 753.01 (0.52), 754.03 (0.36), 768.02 (0.46), 769.02 (0.42), 770.02 (0.38), 771.02 (0.28), 772.03 (0.26), 773.02 (0.25), 774.03 (0.32), 775.04 (0.27), 776.04 (0.23), 789.04 (0.24), 792.04 (0.30), 793.04 (0.25), 797.04 (0.25), 798.04 (0.26), 799.05 (0.25), 800.05 (0.24), 801.05 (0.29), 802.05 (0.29), 803.06 (0.36), 804.06 (0.29), 805.06 (0.23), 810.05 (0.28), 811.05 (0.36), 812.05 (0.31), 813.05 (0.27), 814.05 (0.25), 815.05 (0.24), 816 (0.34), 817.05 (0.33), 818.05 (0.32), 819.06 (0.28), 825.05 (0.28), 826.05 (0.34), 827.05 (0.48), 828.06 (0.47), 829.06 (0.37), 830.06 (0.29), 831.06 (0.24), 840.05 (0.27), 842.06 (0.37), 843.06 (0.39), 844.05 (0.32), 845.06 (0.24), 859.07 (0.23), 876.07 (0.24), 893.08 (0.24), 1038.12 [0.42,  $C_{60}(NR)$ ], 1355.42 [0.43,  $C_{60}(NR)_2$ ], 1673.62 [0.39,  $C_{60}(NR)_3$ ], 1990.90 [0.16,  $C_{60}(NR)_4$ ] [4].

5. Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)(C_{17}H_{23}N_5O_3)_2 \cdot 2ClPh \cdot 2.5H_2O$  ( $1/2C_{246}H_{168}Cl_4N_{26}O_{23}$ ): C, 73.90; H, 4.24; N, 9.11. Found: C, 73.86; H, 4.41; N, 9.16%. Anal. Calc. (for the same sample after evacuation (24 h, 25°C)) for  $C_{60}(C_{17}H_{23}N_3O_3)(C_{17}H_{23}N_5O_3)_2$  ( $C_{111}H_{69}N_{13}O_9$ ): C, 77.12; H, 4.02; N, 10.53. Found: C, 76.98; H, 4.11; N, 10.44%. IR (KBr,  $cm^{-1}$ ) 3411sh, 3314m, 2950m, 2914m, 2880sh, 2094mw (free azide), 1704s, 1686sh, 1537m, 1448m, 1412ms, 1352ms, 1260m, 1212m, 1166m, 1110m, 765w, 732w, 692w, 572w.

6. Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)_6 \cdot ClPh$  ( $C_{168}H_{143}ClN_{18}O_{18}$ ): C, 73.71; H, 5.27; N, 9.21. Found: C, 73.70; H, 4.71; N, 9.38%. IR (KBr,  $cm^{-1}$ ): 3406w, 3332m, 2958ms, 2914m, 2840sh, 1720vs, 1688sh,

1520m, 1450m, 1408s, 1350s, 1262mw, 1214m, 1168w, 1110m, 978w, 766w, 738w, 693m, 604w.  $^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.52–7.20 (m, 5H, *Ph*), 5.44–4.96 (m, 2H,  $PhCH_2CO$ ), 4.86–3.26 (m br, 4H,  $2CH + CH_2$ ), 3.24–1.96 (m br, 2H,  $CH_2$ ), 1.27 (s br, 9H,  $CONHCMe_3$ ).  $^{13}C$ -NMR (100 MHz,  $CDCl_3 + Cr(acac)_3$ , 36 h)  $\delta$  169.80 ( $CONHR$ ), 156.25sh, 155.68, 155.00sh ( $COOCH_2Ph$ ), 150–135.00 (m br, with observable maxima at 147.3, 146.8, 146.1, 145.9, 145.5, 145.4, 144.9, 144.8, 144.0, 143.8, 143.4, 143.3, 142.7, 142.5, 140.2, 140.1, 139.9, 139.8, 139.6, 139.5, 138.9, 137.9, 137.7, 136.3, 136.1  $C_{60}$   $sp^2$ -carbons), 135.95 ( $C_{ipso}Ph$ ), 135–129 (m br, with observable maxima at 134.5, 133.9, 133.6, 131.2, 130.9 and 129.3 ppm,  $C_{60}$   $sp^2$ -carbons), 128.4, 128.00 (*o*-, *m*-, *p*-*Ph*), 67.48 (s,  $OCH_2Ph$ ), 61.18 ( $NC^*HCO$ ), 57.41 (m,  $CH_2N$ ), 53.21 (m,  $CH-N-C_{60}$ ), 50.79 (s,  $CMe_3$ ), 37.2–31.5 (m, with maxima centred at 34.8 and 33.5,  $CH_2$ ), 28.45 (s,  $CH_3$ ). Solid-state  $^{13}C$ -NMR CP/MAS spectrum:  $\delta$  170.06 ( $CONHR$ ), 154.65, 152.71 ( $COOCH_2Ph$ ), 150–135 (m br with a maximum at 136.21,  $C_{60}$   $sp^2$ -carbons +  $C_{ipso}Ph$ ), 133.45 (s,  $C_{60}$   $sp^2$ -carbons), 128.20 (s br, *o*-, *m*-, *p*-*Ph*), 121.04, ( $C_{60}$   $sp^2$ -carbon), 67.53 (s,  $OCH_2Ph$ ), 60.38 ( $NC^*HCO$ ), 58.31 (m,  $CH_2N$ ), 50.79 (m,  $CH-N-C_{60} + CMe_3$ ), 36.84 (m,  $CH_2$ ), 28.59 (s,  $CH_3$ ).

FAB MS (LSI MS, positive ion, peaks of *m*-nba matrix omitted),  $m/z$  (relative height of peak in brackets, %): 55.00 (7), 57.01 (18), 58.05 (15), 67.12 (7), 69.13 (6), 77.07 (4), 83.09 (4), 91.09 (100), 105.10 (3.0), 107.09 (3.5), 109.14 (1.5), 115.10 (1.1), 119.12 (1.9), 123.14 (1.3), 133.11 (1.3), 136.11 (4.9), 147.14 (1.6), 154.12 (5.0), 158.16 (3.2), 165.14 (0.72), 166.15 (0.49), 167.15 (0.50), 169.15 (0.32), 171.17 (0.41), 173.18 (1.47), 178.15 (0.31), 179.16 (0.31), 181.17 (0.39), 183.19 (0.33), 189.17 (0.31), 207.13 (0.35), 217.19 (0.24), 221.18 (0.24), 259.28 (0.32), 320.30 (0.23), 647.62 (0.10), 662.61 (0.10), 663.62 (0.14), 672.16 (0.05), 672.33 (0.15), 673.48 (0.10), 674.24 (0.10), 696.63 (0.08), 720.18 (1.00), 721.19 (1.00), 722.20 (0.90), 723.20 (0.49), 724.20 (0.30), 725.21 (0.12), 734.09 (0.10), 735.17 (0.21), 736.21 (0.37), 737.21 (0.32), 738.21 (0.23), 739.22 (0.11), 748.14 (0.10), 749.18 (0.11), 750.19 (0.12), 751.22 (0.14), 752.23 (0.14), 753.18 (0.10), 816.19 (0.10), 818.12 (0.12), 832.70 (0.10), 845.79 (0.08), 847.80 (0.08), 857.80 (0.06), 861.83 (0.06), 864.83 (0.06), 873.84 (0.05), 891.81 (0.04), 938.09 (0.03), 1038.12 (0.007).

### 3.4. Preparation of rhodium complexes 2, 4 and 6

#### 3.4.1. Reaction of 2 with $[RhCl(CO)_2]_2$

A 30 mg sample of monoazafulleroid 2 (0.0289 mmol) and 6 mg of  $[RhCl(CO)_2]_2$  (0.0154 mmol) were refluxed in  $CH_2Cl_2$  for 24 h. After filtration of a brown impurity, the solution was partially evaporated and a brown precipitate of 8 was obtained by addition of diethyl ether, which was filtered off and washed with the same solvent (22 mg, 68%).



Anal. Calc. for  $\{C_{60}(C_{17}H_{23}N_3O_3)[RhCl(CO)_2]\} \cdot 0.8CH_2Cl_2 \cdot 0.2H_2O$ : C, 73.50; H, 1.93; N, 3.22. Found: C, 73.50; H, 2.03; N, 3.16%. IR (KBr,  $cm^{-1}$ ) 3406m br, 3315sh, 2958m, 2914m, 2850sh, 2060sh, 2022v vs, 1682s br, 1526m, 1446m, 1406ms, 1344m, 1264w, 1210mw, 1174w, 1104m br, 814w, 778mw, 760mw, 742mw, 690mw, 516mw.  $^1H$ -NMR (300 MHz,  $CDCl_3$ ):  $\delta$  7.40–7.00 (m, 5H, *Ph*), 5.20–5.00 (m, 2H,  $OCH_2Ph$ ), 4.20 (m, 1H, *CH-N*), 3.90–3.80 (m, 1H, *CH-CON*), 3.70–3.40 (m, 2H,  $CH_2-N$ ), 2.30–2.10 (m br, 2H,  $CH_2-CH-N$ ), 1.30 (s, 9H,  $CONHMe_3$ ).

Solid-state  $^{13}C$ -NMR CP/MAS spectrum:  $\delta$  210.39 (Rh–CO), 171.32 (CONHR), 155.43 ( $COOCH_2Ph$ ), 149–135 (m br, with maxima at 148.57, 144.87, 142.85, 139.05, 135.90,  $C_{60}$   $sp^2$ -carbons +  $C_{ipso}$  Ph), 132.95 (s br,  $C_{60}$   $sp^2$ -carbons), 128.26 (*o*-, *m*-, *p*-*Ph*), 65.71 (s,  $OCH_2Ph$ ), 61.90 (s,  $NC^*HCO$ ), 56.79 (s,  $CH_2N$ ), 51.69 (s, *CH-N-C*<sub>60</sub>), 50.02 (s,  $CMe_3$ ), 36.57 (m,  $CH_2$ ), 28.15 (s,  $CH_3$ ).

FAB MS (LSI MS, positive ion, peaks of *m*-nba matrix omitted), *m/z* (relative high of peak (%)) and some assignments in brackets): 57.05 (25), 77.05 (22), 91.10 (100), 107.10 (12), 136.07 (26), 137.08 (13), 154.10 (21), 226.08 (0.26), 242.22 (0.48), 267.04 (0.54), 281.09 {0.57, [(AHCONHMe)Rh(CO)<sub>2</sub>]<sup>+</sup>}, 289.13 (0.71), 307.15 (0.87), 320.24 (4,  $NH_3R^+$ ), 325.15 {0.58, [(AH<sub>2</sub>R<sup>1</sup>)RhH(CO)<sub>2</sub>]<sup>+</sup>}, 327.03 [0.56, [(AH<sub>4</sub>R<sup>1</sup>)RhH(CO)<sub>2</sub>]<sup>+</sup>}, 329.10 (0.60), 342.20 {0.50, [(N-AH<sub>5</sub>R<sup>1</sup>)-RhH(CO)<sub>2</sub>]<sup>+</sup>}, 720.098 (1.13,  $C_{60}$ ), 721.106 (0.92), 722.105 (0.67), 736.02 (0.06), 966.10 (0.08).

API ES positive MS (*m/z*, relative intensity (%)) and assignment in brackets, time: 6.20 min): 1233.4 [1.9,  $C_{60}(NR)[RhCl(CO)_2]$ ], 1061.1 [5.0,  $C_{60}(NR)[RhCl(CO)_2]-(CH_2Ph + Cl)$ ], 475.3 [74.1, [(NR)Rh(CO)<sub>2</sub>]], 630.2 (5.6), 415.3 (16.7), 365.2 (100.0), 265.4 (11.1), 261.1 (11.1), 157.2 (10.1), 147.0 (8.1), 103.1 (5.6, Rh).

### 3.4.2. Reaction of **4** with $[Rh(CO)_2Cl]_2$

A mixture of **4** (13 mg, 0.011 mmol) and  $[Rh(CO)_2Cl]_2$  (15 mg) in  $CH_2Cl_2$  (10 ml) was sonicated for 5 min and heated at the reflux temperature for 6 h. After partial evaporation of solvent a brown solid (**9**) was separated by addition of diethyl ether, and was filtered off, washed three times with the same solvent (22 mg, 74%) and dried in vacuum. Anal. Calc. (after evacuation at 25°C for 24 h) for  $C_{60}(C_{17}H_{23}N_3O_3)_4[Rh(CO)_2Cl]_4 \cdot CH_2Cl_2$  ( $C_{137}H_{94}Cl_6N_{12}O_{20}Rh_4$ ): C, 57.68; H, 3.32; N, 5.89. Found: C, 57.59; H, 3.33; N, 5.85%. IR (KBr,  $cm^{-1}$ ): 3398w, 3318w, 2952m, 2914m, 2840sh, 2060sh, 2024vs, 1685vs, 1528m, 1448m, 1408ms, 1350m, 1266w, 1212m, 1170mw, 1112m, 748w, 710w, 692m, 517w, 468w.  $^1H$ -NMR ( $CDCl_3$ , 400 MHz)  $\delta$  7.50–7.20 (m, 5H, *Ph*), 6.75–6.05 (s br, 1H, *NH*), 5.48–4.73 (m, 2H,  $PhCH_2CO$ ), 4.65–3.38 (m br, 4H,

$2CH + CH_2$ ), 3.40–1.95 (m br, 2H,  $CH_2$ ), 1.45–1.10 (broad signal, with the only a prominent high at 1.27 ppm, 9H,  $CONHMe_3$ ).

### 3.4.3. Reaction of **6** with $[Rh(CO)_2Cl]_2$

A 50 mg (0.018 mmol) sample of **6** and 28.10 mg of  $[Rh(CO)_2Cl]_2$  (0.072 mmol) were sonicated for 5 min in  $CH_2Cl_2$  (10 ml) and heated for 2 h at the reflux temperature. After partial evaporation of solvent, a brown precipitate appears by addition of diethylether, which was filtered off, washed three times with the same solvent and dried to vacuum to yield 60 mg of a brown powder (**10**, 79%). Anal. Calc. for  $C_{60}(C_{17}H_{23}N_3O_3)_6[Rh(CO)_2Cl]_6 \cdot 2CH_2Cl_2$  ( $C_{176}H_{142}Cl_{10}N_{18}O_{30}Rh_6$ ): C, 53.37; H, 3.61; N, 6.39; Rh, 15.59. Found: C, 53.27; H, 3.67; N, 6.33; Rh, 15.38%. IR (KBr,  $cm^{-1}$ ): 3406mw, 3316m, 2952ms, 2914m, 2840sh, 2060sh, 2022vs, 1686vs, 1522m, 1446m, 1405s, 1344s, 1254w, 1206m, 1168w, 1107m, 766w, 732w, 690m, 604vw, 490m.  $^1H$ -NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.52–7.20 (m, 5H, *Ph*), 6.75–6.05 (s br, 1H, *NH*), 5.42–4.88 (m, 2H,  $PhCH_2CO$ ), 4.78–3.38 (m br, 4H,  $2CH + CH_2$ ), 3.36–1.95 (m br, 2H,  $CH_2$ ), 1.46–1.1 (broad signal, with the most prominent highs at 1.29, 1.27 and 1.23 ppm, 9H,  $CONHMe_3$ ). Solid-state  $^{13}C$ -NMR CP/MAS spectrum:  $\delta$  207.25 (Rh–CO), 172.43 (CONHR), 153.13 ( $COOCH_2Ph$ ), 150–135 (m br, with a maximum at 137.60,  $C_{60}$   $sp^2$ -carbons +  $C_{ipso}$  Ph), 133.60 (s,  $C_{60}$   $sp^2$ -carbons), 128.26 (*o*-, *m*-, *p*-*Ph*), 126.42sh, 122.52sh, 118.20, 114.20, 106.78 ( $C_{60}$   $sp^2$ -carbons probably bonded to N), 63.35 (s,  $OC^*H_2Ph$ ), 59.81 (s,  $NC^*HCO$ ), 56.51 (s,  $CH_2N$ ), 51.58 (s,  $CMe_3 + CH-N-C_{60}$ ), 36.29 (m,  $CH_2$ ), 28.65 (s,  $CH_3$ ).

### 3.5. Deprotection attempt of **6** and subsequent reaction with $[Rh(CO)_2Cl]_2$

A 50 mg sample of **6** was heated in ethanol (15 ml) and treated with cyclohexene and Pd–C (10%) as catalyst at the reflux temperature for 48 h. After filtration of solution and evaporation of solvent, a brown greasy solid (**7**) was isolated (25 mg, 44% for a possible composition  $C_{60}(N-R')_6(NH_2-NR')_2Pd \cdot 19H_2O$  (3171.49), the  $^1H$ -NMR of which does not show aromatic signals. This product was used without previous purification for reaction with  $[Rh(CO)_2Cl]_2$ . IR (KBr,  $cm^{-1}$ ): 3400s, 3244sh, 3095sh, 2966m, 2922m, 2840sh, 1665vs br, 1620s, 1560w, 1540w, 1465m, 1405m, 1372m, 1295w, 1260w, 1218m, 1170w, 1110s br, 1010w, 845s, 795sh, 740m, 710sh, 692m, 565w.

A 15 mg (0.0060 mmol) sample of **7** was treated with  $[Rh(CO)_2Cl]_2$  (10 mg) in  $CH_2Cl_2$  for 3 days at room temperature to give a brown powder, which was filtered off and washed with diethyl ether (18 mg, 63%). IR (KBr,  $cm^{-1}$ ): 3400vs br, 3210sh, 3097sh, 2978m,

2914m, 2840sh, 2060sh, 2022w br, 2008sh, 1796w, 1670sh, 1625s, 1553sh, 1536sh, 1404m br, 1258w, 1188mw, 1100m, 740w, 616w, 480w. Anal. Calc. for  $C_{60}(C_9H_{17}N_3O)_6(PdCl_2)_6 \cdot [PdCl_2(C_9H_{19}N_3O)_2]_{1/2}[RhCl(CO)_2]_2 \cdot 19H_2O$  ( $C_{134}H_{178}Cl_{15}N_{24}O_{29}Pd_7Rh$ ): C, 40.55; H, 4.52; N, 8.47; Rh, 2.59. Found: C, 40.63; H, 6.05; N, 8.30; Rh, 2.36%.

### 3.6. Catalytic experiments

The catalytic properties of  $C_{60}(NR)_6[Rh(CO)_2Cl]_6$  (**10**) were examined under usual conditions for test reactions.

Tiglic acid ( $MeCH=CMeCO_2H$ ) was hydrogenated in a batch reactor (Autoclave Engineers) of 100 ml capacity, at 323 K and 5 atm of dihydrogen pressure. The molar ratio of catalyst–substrate was 1:1000. The olefin was added to a suspension of the catalyst in ethanol (45 ml). The reaction products were analysed by GC.

The hydrogenation with  $C_{60}(N-R)_6[Rh(CO)_2Cl]_6$  as catalyst proceeded in 2 h with 12.3% ee.

## 4. Supplementary material

Copies of Table 2 [4] can be obtained from the authors.

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