Fullerenes

Deutsche Ausgabe: DOI: 10.1002/ange.201510872
Internationale Ausgabe: DOI: 10.1002/anie.201510872

Selective Multiamination of C_{70} Leading to Curved π Systems with 60, 58, 56, and 50 π Electrons

*Yanbang Li, Dan Xu, and Liangbing Gan**

Abstract: *Secondary aliphatic amines add to a pole pentagon of [70]fullerene in the presence of N-fluorobenzenesulfonimide to form cyclopentadienyl-type adducts, $C_{70}(NSO_2Ph)(NR^1R^2)_4$ (**1**), which can be converted into analogous C_{70} derivatives such as $C_{70}(NHSO_2Ph)(NHTol)_5$ (**2**). Further addition reactions of either **1** or **2** take place selectively at the opposite pole pentagon of the C_{70} cage, thus forming curved π systems with a reduced number of π electrons, and the products include a dodecakis-adduct with a Vögtle belt motif.*

Compared to the well-developed chemistry of [60]fullerene, the next most abundant fullerene, C_{70}, has received much less attention. Unlike the I_h symmetric C_{60} with 60 equivalent carbon atoms, the D_{5h} symmetric C_{70} has five different types of carbon atoms. As a result the selective preparation of C_{70} derivatives is more challenging, in particular for the multiadducts. In spite of the difficulty, remarkable progress has been achieved.[1] A series of isomerically/optically pure multiadducts of C_{70} has been prepared by controlled multiaddition.[2] Several octa- and deca-adducts, such as $C_{70}X_{10}$ (X = H,[3] Cl,[4] Br,[5] Me,[6] Ph,[7] OO*t*Bu[8]), have been reported with all the addends located along the equatorial belt region of C_{70}. Multi-perfluoroalkyl C_{70} adducts have been studied extensively.[9]

The addends in all the known multiadducts of C_{70} are preferentially attached to the side of the ellipsoid cage. Selective addition around the pentagon on the end poles is an attractive target since novel aromatic systems could be created through such an addition pattern. For example the 50π electron belt ($n = 0$) in Figure 1, called a Vögtle belt,[10] is an attractive target molecule. It corresponds to the belt region of C_{70}. Related molecular structures have been actively pursued by synthetic chemists.[10b,11] One possible strategy to make such a curved π system is by detracting the two pole π systems through double cyclopentadienyl-type addition reactions around the two pole pentagons of C_{70}. An analogous strategy has been elegantly applied, by Nakamura et al., to C_{60} to form the 40π electron belt using organocopper reagents.[12] Under similar reaction conditions organocopper reagents added to C_{70} on the side-top region to form the trisadducts $C_{70}R_3H$.[13] So far cyclopentadienyl-type addition reaction on the pole pentagon of C_{70} was confirmed only for multiadducts in which the belt region is fully occupied by other addends, such as $C_{70}Cl_{16}$[14] and $C_{70}(CF_3)_{20}$.[15] The π system of these C_{70} multiadducts is completely lost in the equator because of multiadditions on the carbon atoms in the belt region. In the chemistry of higher fullerenes, a highly unstable D_{5h}-C_{100} fullerene was captured through formation of $C_{100}Cl_{12}$, in which all 12 chlorine atoms are attached on the two pole pentagons of the nanotubular carbon cage.[16]

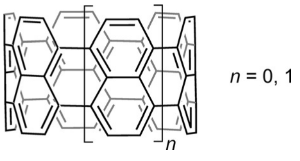


Figure 1. Structure of cyclic aromatic belts or Vögtle belts.

Secondary amines are among the most effective reagents for selective multiaddition reactions around the same pentagon in C_{60}.[17] A number of isomerically pure multiamino C_{60} derivatives have been reported under various reaction conditions, some of which showed active biological activities.[18] But complex mixtures were usually obtained in the amination reactions of C_{70}. There is no isomerically pure multiamino adduct for C_{70} known in the literature. Only the diamino oxahomo derivative $C_{70}(O)(NR^1R^2)_2$, having an ether moiety, was isolated by treating C_{70} with secondary amines under photochemical conditions.[19] Recently we reported that *N*-fluorobenzenesulfonimide (NFSI) directed addition of secondary amines to C_{60} resulted in the formation of multiadducts, $C_{60}(NSO_2Ph)(NR^1R^2)_4$, with all the addends around the same pentagon.[17e] Further exploration of the NFSI-mediated amination method resulted in selective multiamination around the pole pentagon of C_{70}. Herein we report the controlled detraction of the C_{70} π system to form various curved π systems, including the 50π electron system having a Vögtle belt motif.

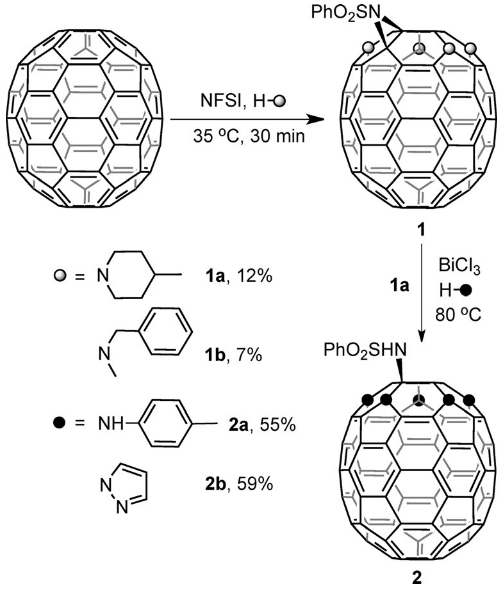
The amination reaction of C_{70} was carried out under essentially the same reaction conditions as those used for C_{60}.[17e] The amount of NFSI is important to obtain good yield, and a large excess of secondary amines is used to accelerate the reaction. Cyclic secondary amines other than the two shown in Scheme 1, such as pyrrolidine and thiomorpholine, also reacted with C_{70} under NFSI conditions. The mechanism for the formation of **1a**,**b** should be the same as that for the

---

[*] Y. B. Li, D. Xu, Prof. Dr. L. B. Gan
Beijing National Laboratory for Molecular Sciences
Key Laboratory of Bioorganic Chemistry and Molecular Engineering of the Ministry of Education
College of Chemistry and Molecular Engineering
Peking University, Beijing 100871 (China)
E-mail: gan@pku.edu.cn

Prof. Dr. L. B. Gan
State Key Laboratory of Organometallic Chemistry
Shanghai Institute of Organic Chemistry, Shanghai 200032 (China)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201510872.



Scheme 1. Selective multiamination of C_{70}.

reaction with C_{60}. The presence of the aziridinium moiety in the intermediates probably plays a key role in the present addition pathway.[17e]

In the preparation of **1b** another slightly more polar product **1b′** was observed with lower yield than that of **1b**, and it was not stable enough for NMR measurement. Its ESI-HRMS spectrum showed that it is an isomer of **1b**. In agreement with the observed instability of **1b′**, an intense fragment-ion signal (with intensity at 67% of the molecular ion base signal) corresponding to the loss of one *N*-methylbenzylaminyl group was present in the ESI-HRMS spectrum of **1b′**, whereas the same fragment signal is much weaker (with intensity at 8% of the molecular ion base signal) in the ESI-HRMS spectrum of **1b** under the same conditions. The isomer **1b′** probably has a structure with the addends around a pentagon on the side.

Multichlorinated fullerenes such as $C_{70}Cl_{10}$[6,7] have been used as precursors for other derivatives by selective nucleophilic replacement reaction. The compound **1** could also be converted into other analogues in the presence of a Lewis acid. *p*-Toluidine reacted with **1a** in the presence of $BiCl_3$ to form **2a**. Besides opening of the aziridine ring, the four 4-methylpiperidinyl groups in **1a** were replaced by *p*-toluidine in the formation of **2a**. Similarly pyrazole reacted with **1a** to form **2b**. Under similar reaction conditions other arylamines such as aniline could react with **1a** to form products analogous to **2a**, but imidazole, pyrrole, and 4-methylpiperidine did not give characterizable products. The compound **1b** could also be used as the precursor for **2a**, but with lower yield. Other Lewis acids such as $FeCl_3$, $CuCl_2$, and $LaCl_3$ gave poor selectivity compared to $BiCl_3$. The mechanism for the replacement reactions to form **2a**,**b** should be S_N1 in which the cation intermediate is stabilized by the lone pair electrons on the adjacent nitrogen atoms mainly through interaction similar to the transition state in the S_N2'-type reaction mechanism.

The compounds **1a**,**b** and **2a**,**b** exhibit the typical C_s symmetric NMR spectra. The ^{13}C NMR spectrum of **1a** shows four signals for sp^3-carbon atoms of the fullerene: $\delta = 63.5, 64.7, 71.3$ and 72.3 ppm in a 2:2:1:1 intensity ratio. There are 29 well-resolved signals for sp^2-carbon atoms for the fullerene cage and the phenyl group, a few of which are broad as a result of steric hindrance. The ^{13}C NMR spectrum of **1b** shows two signals at $\delta = 38.5$ and 38.8 ppm for methyl groups and two signals at $\delta = 59.2$ and 59.9 ppm for methylene groups, both in a 1:1 intensity ratio. The ^1H NMR spectra of **1a** and **1b** also showed a few broad signals indicating steric hindrance. Similarly **2b** showed a few broad signals in the ^1H and ^{13}C NMR spectra. For **2a**, sharp signals appeared in the ^1H and ^{13}C NMR spectra, thus indicating reduced steric hindrance. ESI-HRMS spectra showed molecular ion signals for **1a**,**b** and **2a**,**b**.

The above NMR data clearly established the C_s symmetry for **1a**,**b** and **2a**,**b**. But there are at least two possible structures with C_s symmetry wherein the addends are either around a pole pentagon or around a side pentagon. Single-crystal X-ray structures of **1a** and **1b** verified the structure as shown in Scheme 1 with the addends located at the top pentagon (Figure 2). Unlike the C_s symmetric structures determined by NMR data at room temperature, both crystals of **1a** and **1b** showed C_1 symmetry resulting from the existence of the rigid aziridino group at low temperature (180 K).

A pair of enantiomers is present in the unit cell for both compounds. In the crystal of **1a** the two enantiomers exist as a head to tail dimeric structure with weak interactions between the fullerene cage and hydrogen and oxygen atoms on a neighboring molecule. There is no close contact between the fullerene cages. The packing pattern of the crystal of **1b** has a more complicated polymeric network. Each molecule is in close contact with three enantiomeric molecules, one in

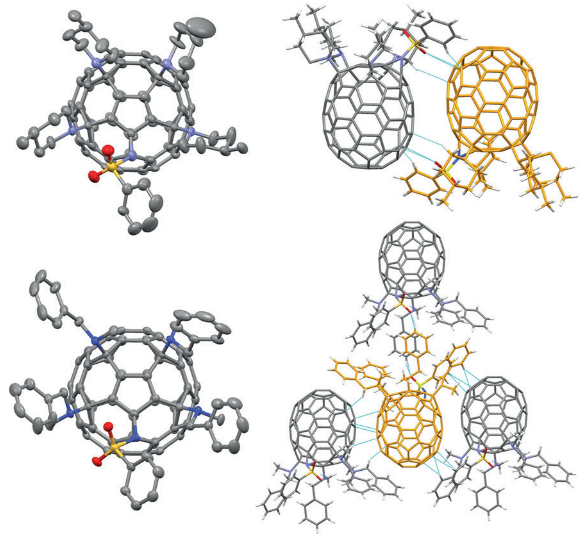
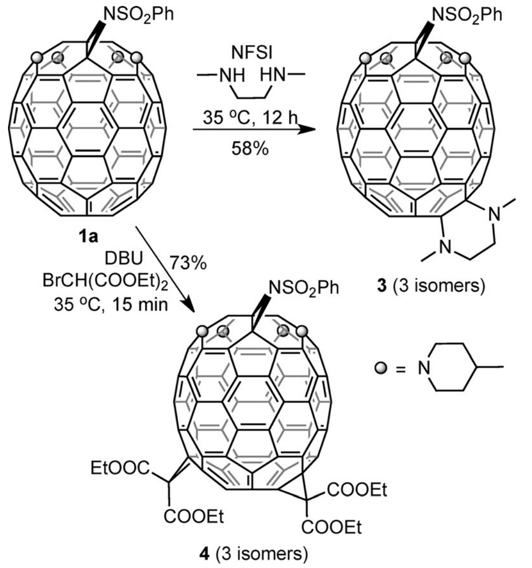


Figure 2. Single-crystal X-ray structure of compounds *rac*-**1a** (above) and *rac*-**1b** (below). Ellipsoids are shown at 50% probability. One enantiomer is shown for the ellipsoid model and their hydrogen atoms are omitted for clarity. C grey, N blue, O red, S yellow, H white. Close contacts are shown in light blue.

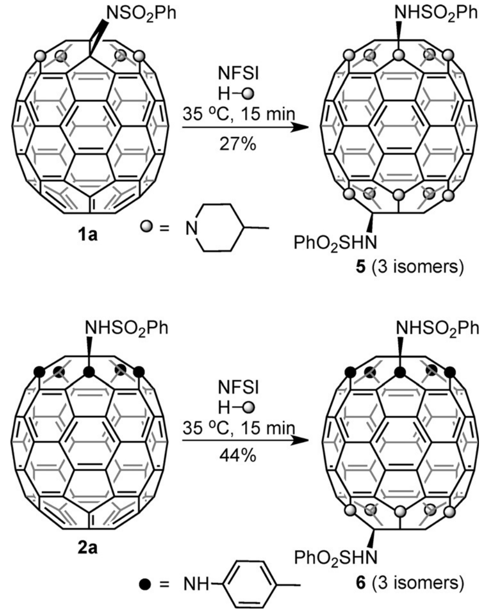
head to head style and two in head to tail style. In the head to head dimeric interaction one benzyl group on each molecule is located inside the "shuttlecock" pocket of the other molecule. The two head to tail interactions are different in that one has both fullerene/fullerene and fullerene/H–C interactions whereas the other has just multiple fullerene/H–C interactions.

The presence of the addends on the top pentagon has a significant effect on the chemical reactivity of the remaining double bonds on the C_{70} cage, particularly on the regioselectivity. Treating **1a** with NFSI and *N*,*N*-dimethylethylenediamine afforded **3** as a mixture of three constitutional isomers, one of which is C_s symmetric and the other two are pairs of enantiomers resulting from the chirality of the addition pattern (Scheme 2). The reaction readily stopped at the monopiperazine adduct even with a large excess of *N*,*N*-dimethylethylenediamine. We also prepared the *N*,*N*-dimethylethylenediamine monoadduct of C_{70}, and then treated it with NFSI and 4-methylpiperidine under the same reaction conditions for the formation of **1a**. The reaction resulted in neither **3**, nor any other characterizable product. Treating **1a** under either Bingel or Bingel–Hirsch condition resulted in the formation of the bis(ethylmalonate) adduct **4** as mixture of three constitutional isomers. Relative locations of the two cyclopropane moieties are assumed to be exactly the same as those in the tetrakis-ethylmalonate adduct of C_{70} reported by Diederich et al., and they were determined through comprehensive spectroscopic data, tether-directed synthesis, and theoretical calculations.[2a–c] Such a biscyclopropanation addition pattern has been well established for C_{60}.[20]



Scheme 2. Preparation of curved π systems having 58 and 56 π electrons.

The above reactions resulted in selective formation of curved π systems with 60 (**1**/**2**), 58 (**3**), and 56 π electrons (**4**). In an effort to prepare the π system with a Vögtle belt motif, we treated **1a** with a large excess of NFSI and 4-methylpiperidine. As expected multiple additions took place around the bottom pentagon to form **5** with a 50 π system (Scheme 3). The aziridine ring in **1a** was opened because of the presence of a large excess of 4-methylpiperidine. The yield of **5** from **1a** (27%) is much better than that from C_{70} to **1a** (12%). The compound **5** showed the molecular-ion signal on the ESI-HRMS spectrum, but its ^{1}H and ^{13}C NMR spectra were quite complex because of the existence of three constitutional isomers. Just like its precursor **1a**, the *p*-toluidine derivative **2a** reacted with NFSI and 4-methylpiperidine to form the adduct **6**. The adduct **6** was produced in higher yield than that of **5**, is much more stable than **5**, and can be stored for weeks with little decomposition.



Scheme 3. Preparation of curved π systems having 50 π electrons.

ESI-HRMS spectra of **3** and **4** showed the molecular-ion signal as the base peak, whereas **5** and **6** showed a weak molecular ion signal, resulting from the loss of two consecutive 4-methylpiperidinyl groups, as the base peak. The NMR spectra of these compounds are complex because of the existence of three constitutional isomers, including two pairs of enantiomers, which were not separable. The ratio of the isomers for **3** can be clearly determined as 2:1:2 from the integrals of the methyl groups on the piperazine moiety at $\delta = 2.91$, 2.88, 2.87 ppm (Figure 3). The other three piperazine methyl groups appear at $\delta = 3.47$ and 3.46 ppm in a 2:3 ratio because of overlapping signals. In the case of **4** the isomer ratio could be determined from the 2,6-phenyl proton signals, on the phenylsulfonyl group, which appear at $\delta = 8.27$, 8.22, 8.15 ppm as three doublets in a 1:2:2 ratio. The 2:1:2 and 1:2:2 ratio for the three constitutional isomers in both **3** and **4**, respectively, suggests that further additions take place around the other pole pentagon. Such an addition pattern would generate three constitutional isomers, two of which are pairs of enantiomers (Figure 3), thus their NMR spectra appear in either a 2:1:2 or 1:2:2 ratio. These results indicate that **5** and **6** should have the double pole pentagon addition pattern as shown in Scheme 3. It is not possible to determine the isomer ratio for **5** because of peak overlapping. The isomer ratio for **6**

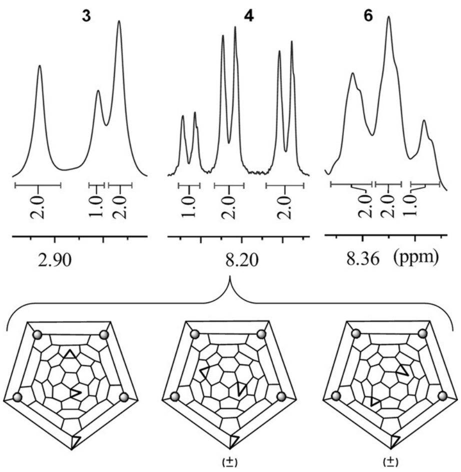


Figure 3. Top: Partial ^{1}H NMR spectra of **3**, **4**, and **6** in $CDCl_3$. Bottom: Schlegel diagrams of the three constitutional isomers of **4**. Dot = 4-methylpiperidinyl group, triangle = aziridine or cyclopropane.

is around 2:2:1 judging from the integrals of broad signals at $\delta = 8.36$, 8.35 and 8.34 ppm (Figure 3), which can be assigned to the 2,6-phenyl proton signals on the two phenylsulfonyl groups, as compared to the ^{1}H NMR spectra of **1a**,**b**, **2a**, and **4**.

The π conjugation systems in **1**–**6** are different because of the different addition patterns and number of addends. The differences are reflected in their UV/Vis spectra as shown in Figure 4. Clear absorption bands were observed for all compounds, including **3**–**6**, thus indicating that the three constitutional isomers for **3**–**6** have similar π conjugation systems. The compounds **1**–**4** showed two strong absorptions in the $\lambda = 400$–500 nm range with different shapes. As expected, **1a** and **1b** showed essentially the same absorptions bands at $\lambda = 383$, 418, and 458 nm. The compounds **2a** and **2b** showed similar absorption bands but with slightly shifted wavelengths compared to those of **1a**,**b** as a result of the opening of the aziridine ring. Weak *peri*-conjugation between the aromatic addends and the C_{70} cage may be responsible for the minor differences between the spectra of **2a** and **2b**. Surprisingly the absorption bands of **4** also look similar to those of **1a**,**b** and **2a**,**b**.[21]

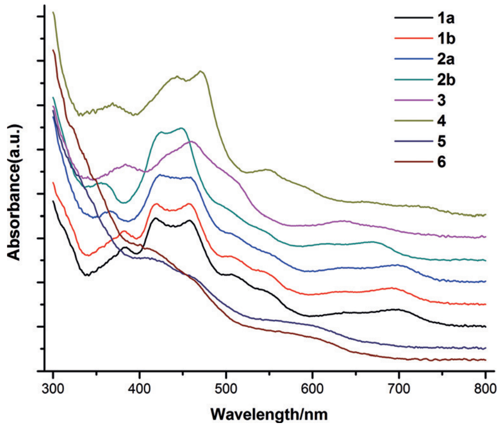


Figure 4. UV/Vis spectra of [70]fullerene derivatives in $CHCl_3$.

In conclusion cyclopentadienyl-type adducts, at the pole pentagon of C_{70}, have been prepared and fully characterized for the first time by using NFSI-mediated multiamination reactions. Intermediates with an aziridium moiety are believed to play a key role in the observed regioselectivity. Because of the strong directing effect of the already attached addends, further functionalization of the present cyclopentadienyl-type adducts follow mainly two pathways: either *ipso* substitution or addition to the other pole pentagon. Double cyclopentadienyl-type adducts around the two pole pentagons afforded a 50π electron Vögtle belt. In light of this result selective opening of the two poles of C_{70} to form a nanotube-like molecule appears to be a reasonable target.

Acknowledgments

This work is supported by NNSFC (Grants 21272013 and 21132007) and MOST (2015CB856600).

Keywords: amination · conjugation · fullerenes · nucleophilic addition · X-ray diffraction

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 2483–2487
Angew. Chem. **2016**, *128*, 2529–2533

---

[1] a) A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, **2005**; b) C. Thilgen, F. Diederich, *Chem. Rev.* **2006**, *106*, 5049.

[2] a) A. Herrmann, M. Rüttimann, T. Gibtner, C. Thilgen, F. Diederich, T. Mordasini, W. Thiel, *Helv. Chim. Acta* **1999**, *82*, 261; b) M. J. van Eis, P. Seiler, L. A. Muslinkina, M. Badertscher, E. Pretsch, F. Diederich, R. J. Alvarado, L. Echegoyen, I. P. Núñez, *Helv. Chim. Acta* **2002**, *85*, 2009; c) W. W. H. Wong, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 3463; d) V. S. P. K. Neti, M. R. Cerón, A. Duarte-Ruiz, M. M. Olmstead, A. L. Balch, L. Echegoyen, *Chem. Commun.* **2014**, *50*, 10584; e) W. W. H. Wong, J. Subbiah, J. M. White, H. Seyler, B. Zhang, D. J. Jones, A. B. Holmes, *Chem. Mater.* **2014**, *26*, 1686; f) H.-L. Hou, Z.-J. Li, Y. Wang, X. Gao, *J. Org. Chem.* **2014**, *79*, 8865; g) S.-H. Li, Z.-J. Li, T. Nakagawa, J. W. Ryan, Y. Matsuo, X. Gao, *Chem. Eur. J.* **2015**, *21*, 1894; h) M. R. Cerón, M. Izquierdo, A. Aghabali, J. A. Valdez, K. B. Ghiassi, M. M. Olmstead, A. L. Balch, F. Wudl, L. Echegoyen, *J. Am. Chem. Soc.* **2015**, *137*, 7502.

[3] H. P. Spielmann, B. R. Weedon, M. S. Meier, *J. Org. Chem.* **2000**, *65*, 2755.

[4] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1995**, 683.

[5] S. I. Troyanov, A. A. Popov, N. I. Denisenko, O. V. Boltalina, L. N. Sidorov, E. Kemnitz, *Angew. Chem. Int. Ed.* **2003**, *42*, 2395; *Angew. Chem.* **2003**, *115*, 2497.

[6] H. Al-Matar, A. K. A. Sada, A. G. Avent, R. Taylor, X.-W. Wei, *J. Chem. Soc. Perkin Trans. 2* **2002**, 1251.

[7] A. G. Avent, P. R. Birkett, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *Tetrahedron* **1996**, *52*, 5235.

[8] a) L. B. Gan, S. H. Huang, X. Zhang, A. X. Zhang, B. C. Cheng, H. Cheng, X. L. Li, G. Shang, *J. Am. Chem. Soc.* **2002**, *124*, 13384; b) Z. Xiao, F. D. Wang, S. H. Huang, L. B. Gan, J. Zhou, G. Yuan, M. J. Lu, J. Q. Pan, *J. Org. Chem.* **2005**, *70*, 2060.

[9] a) A. A. Popov, I. E. Kareev, N. B. Shustova, S. F. Lebedkin, S. H. Strauss, O. A. Boltalina, L. Dunsch, *Chem. Eur. J.* **2008**, *14*, 107; b) N. I. Gruzinskaya, A. I. Silin, A. S. Pimenova, P. A. Khavrel, V. Y. Markov, L. N. Sidorov, E. Kemnitz, S. I. Troyanov,

New J. Chem. **2010**, *34*, 243; c) O. V. Boltalina, A. A. Popov, I. V. Kuvychko, N. B. Shustova, S. H. Straus, *Chem. Rev.* **2015**, *115*, 1051.

[10] a) F. Vögtle, *Top. Curr. Chem.* **1983**, *115*, 157; b) G. J. Bodwell, D. O. Miller, R. J. Vermeij, *Org. Lett.* **2001**, *3*, 2093.

[11] For reviews: a) K. Tahara, Y. Tobe, *Chem. Rev.* **2006**, *106*, 5274; b) R. Gleiter, B. Esser, S. C. Kornmayer, *Acc. Chem. Res.* **2009**, *42*, 1108; c) S. E. Lewis, *Chem. Soc. Rev.* **2015**, *44*, 2221.

[12] Y. Matsuo, E. Nakamura, *Chem. Rev.* **2008**, *108*, 3016.

[13] a) M. Sawamura, H. Iikura, A. Hirai, E. Nakamura, *J. Am. Chem. Soc.* **1998**, *120*, 8285; b) Y. Matsuo, K. Tahara, T. Fujita, E. Nakamura, *Angew. Chem. Int. Ed.* **2009**, *48*, 6239; *Angew. Chem.* **2009**, *121*, 6357.

[14] S. I. Troyanov, A. A. Popov, *Angew. Chem. Int. Ed.* **2005**, *44*, 4215; *Angew. Chem.* **2005**, *117*, 4287.

[15] D. V. Ignat'eva, A. A. Goryunkov, N. B. Tamm, I. N. Ioffe, L. N. Sidorov, S. I. Troyanov, *New J. Chem.* **2013**, *37*, 299.

[16] M. A. Fritz, E. Kemnitz, S. I. Troyanov, *Chem. Commun.* **2014**, *50*, 14577.

[17] a) G. Schick, K.-D. Kampe, A. Hirsch, *J. Chem. Soc. Chem. Commun.* **1995**, 2023; b) H. Isobe, T. Tanaka, W. Nakanishi, L. Lemiègre, E. Nakamura, *J. Org. Chem.* **2005**, *70*, 4826; c) O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovski, R. N. Lyubovskaya, *Chem. Eur. J.* **2006**, *12*, 5569; d) Y. B. Li, L. B. Gan, *J. Org. Chem.* **2014**, *79*, 8912; e) Y. B. Li, N. Lou, L. B. Gan, *Org. Lett.* **2015**, *17*, 524.

[18] For example: a) R. Maeda-Mamiya, E. Noiri, H. Isobe, W. Nakanishi, K. Okamoto, K. Doi, T. Sugayad, T. Izumi, T. Homma, E. Nakamura, *Proc. Natl. Acad. Sci. USA* **2010**, *107*, 5339; b) A. B. Kornev, E. A. Khakina, S. I. Troyanov, A. A. Kushch, A. Peregudov, A. Vasilchenko, D. G. Deryabin, V. M. Martynenko, P. A. Troshin, *Chem. Commun.* **2012**, *48*, 5461.

[19] O. A. Troshina, P. A. Troshin, A. S. Peregudov, V. I. Kozlovski, R. N. Lyubovskaya, *Eur. J. Org. Chem.* **2006**, 5243.

[20] a) A. Hirsch, I. Lamparth, T. Grösser, *J. Am. Chem. Soc.* **1994**, *116*, 9385; b) F. Djojo, A. Herzog, I. Lamparth, F. Hampel, A. Hirsch, *Chem. Eur. J.* **1996**, *2*, 1537.

[21] The $C_{70}(OO\mathit{t}Bu)_6$ in Ref. [8b] and $C_{70}(O)(CF_3)_4$ in Ref. [9a] also showed absorptions bands similar to those of **1a**,**b** and **2a**,**b**.

Received: November 23, 2015