(**4**), 293 K (**5**), SADABS[8] for absorption correction, structure solution with direct methods (SHELXS-97[9]), refinement against F^2 (SHELXL-97[10]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2) on calculated positions. The PLATON[11] program was used for the geometric analysis of the structures. Data collection for **4**: crystal dimensions $0.42 \times 0.30 \times 0.24$ mm, orthorhombic, space group $Pbca$, $a = 25.2916(7)$, $b = 16.8904(5)$, $c = 10.9754(3)$ Å, $V = 4688.5(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.503 \times 10^3$ kg m^{-3}, $\mu = 0.720$ mm^{-1}, $F(000) = 2192$, $3.2° \leq 2\theta \leq 52.0°$, $-31 \leq h \leq 29$, $-20 \leq k \leq 12$, $-13 \leq l \leq 13$, 29774 data collected, 4597 unique data ($R_{int} = 0.0996$), 3439 data with $I > 2\sigma(I)$, 271 refined parameters, GOF(F^2) = 1.110, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1 = 0.0483$, $wR_2 = 0.0949$, max./min. residual electron density $0.842/-0.829$ e Å^{-3}. Data collection for **5**: crystal dimensions $0.76 \times 0.58 \times 0.42$ mm, monoclinic, space group $P2_1/c$, $a = 9.1647(1)$, $b = 22.9299(6)$, $c = 9.3960(2)$ Å, $\beta = 111.067(1)°$, $V = 1842.55(7)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.076 \times 10^3$ kg m^{-3}, $\mu = 0.183$ mm^{-1}, $F(000) = 648$, $3.6° \leq 2 \leq 50.0°$, $-10 \leq h \leq 7$, $-27 \leq k \leq 26$, $-11 \leq l \leq 11$, 11114 data collected, 3206 unique data ($R_{int} = 0.1493$), 1833 data with $I > 2\sigma(I)$, 187 refined parameters, GOF(F^2) = 1.045, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1 = 0.0903$, $wR_2 = 0.2057$, max./min. residual electron density $0.519/-0.445$ e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-158204 (**4**) and CCDC-158205 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] G. M. Sheldrick, Empirical Absorption Correction Program, Universität Göttingen, **1996**.

[9] G. M. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen, **1990**.

[10] G. M. Sheldrick, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

[11] A. L. Spek, PLATON A Multipurpose Crystallographic Tool, University of Utrecht, **2000**.

[12] a) E. H. Licht, H. G. Alt, W. Milius, S. Abu-Orabi, *J. Organomet. Chem.* **1998**, *560*, 69–75; b) H. G. Alt, C. E. Denner, U. Thewalt, M. D. Rausch, *J. Organomet. Chem.* **1988**, *356*, C83–C85.

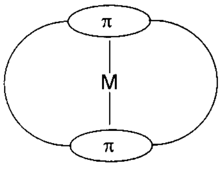
[13] J. Müller, C. Hirsch, K. Qiao, K. Ha, *Z. Anorg. Allg. Chem.* **1996**, *622*, 1441–1448.

A New Strategy for Synthesizing Endohedral Metallocenophanes**

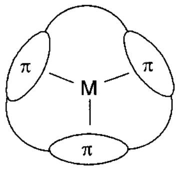
Gerald Scholz, Rolf Gleiter,* and Frank Rominger

Dedicated to Professor Edgar Heilbronner on the occasion of his 80th birthday

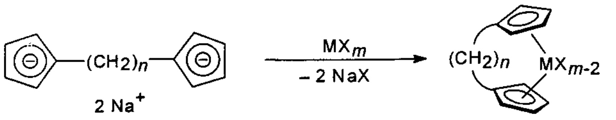
Cyclophanes are versatile ligands and are capable of including metals, as shown in **A** and **B**. Such endohedral metallocenophanes are known mostly for five- or six-membered-ring π systems, with transition metals or main group elements. Two methods have been described for the preparation of endohedral metallocenophanes:[1] the reaction of a cyclophane with metals or metal salts, or the stepwise assembly of the bridge from a metallocene. Examples for the first strategy are the preparation of bridged titanocenes, zirconocenes ($m = 4$), and ferrocenes ($m = 2$) [Eq. (1)][2, 3] as well as of chromocene derivatives ($n = 2, 3$) [Eq. (2)],[4] and complexes of Group III and IV metals with cyclophanes.[1, 5] In the second strategy [Eq. (3)], the tethers are built stepwise on the metallocene.[1, 6]



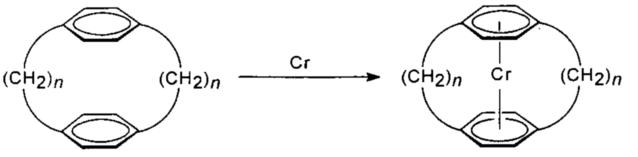
A



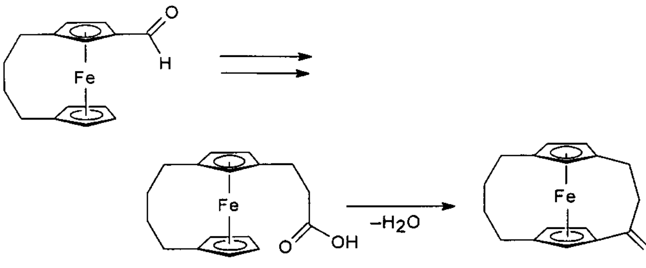
B



(1)



(2)



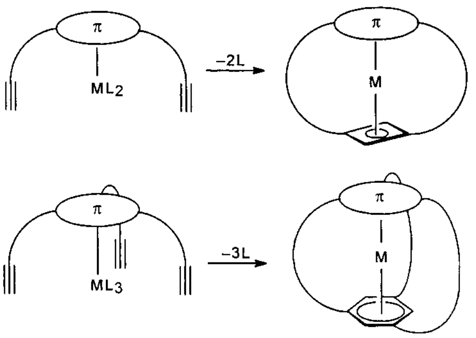
(3)

Our new protocol makes use of an intramolecular metal-catalyzed oligomerization of alkynes that are tethered to a π ligand (Scheme 1). This method is especially suited for constructing cyclobutadienes, cyclopentadienones, and benzene rings as π units, which are formed in a template reaction. We report herein the first synthesis of endohedral cobaltacyclophanes with cyclopentadienyl and cyclobutadiene rings as π units (Scheme 2 and 3). The key compounds in our protocol are the disubstituted dicarbonyl(η^5-cyclopentadienyl)cobalt derivatives **5a–c** in which two triple bonds are tethered to the Cp ring through an alkanediyl bridge. To synthesize the corresponding ligands **4a–c**, we treated 3-ethoxycyclopent-2-en-1-one (**2**)[7] with the Grignard reagents[8] derived from the ω-haloalkynes **1a–c**[9] and magnesium to yield the cyclopentenones **3a–c**. A second Grignard reaction gave the

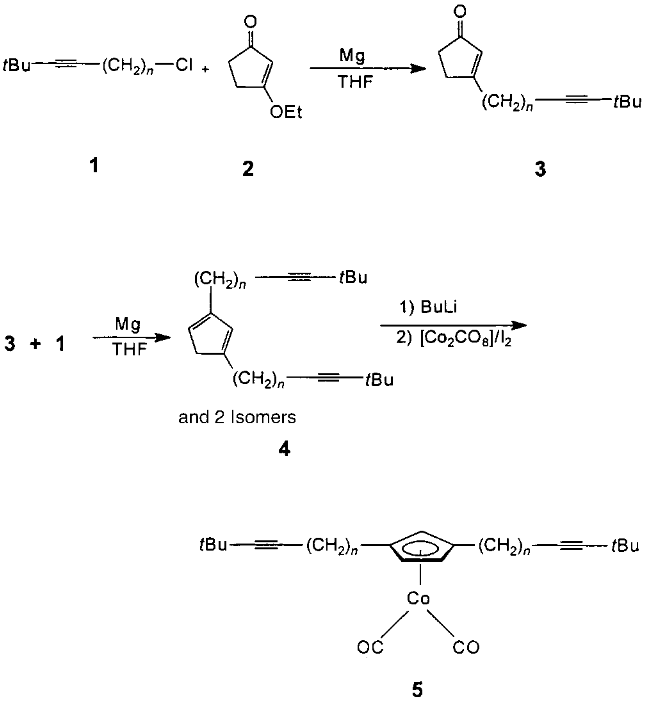
---

[*] Prof. Dr. R. Gleiter, Dipl.-Chem. G. Scholz, Dr. F. Rominger
Organisch-chemisches Institut der Universität
Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
Fax: (+49)6221-544205
E-mail: rolf.gleiter@urz.uni-heidelberg.de

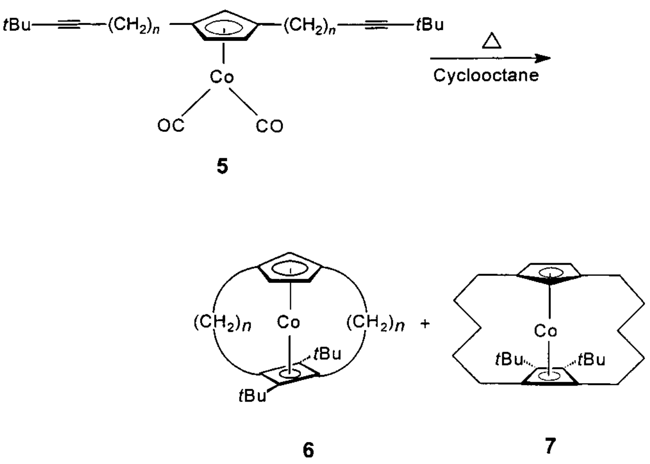
[**] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the BASF AG Ludwigshafen.



Scheme 1. General protocol for the synthesis of endohedral metallocenophanes by a template reaction.



Scheme 2. Synthesis of **5**. $n = 3$ (**a**), 4 (**b**), 5 (**c**).



Scheme 3. Thermolysis of **5**. $n = 3$ (**a**), 4 (**b**), 5 (**c**).

cyclopentadienes **4a–c** in 25% yield over two steps. This stepwise assembly facilitates the synthesis of cyclopentadienes with chains of different length. To obtain the metallocenes **5a–c**, we followed a protocol introduced by Rausch and coworkers[10] by treating the lithium salt of **4** with an equimolar mixture of [$Co_2(CO)_8$] and I_2 in THF (60–65% yield).[11]

The synthesis of the second π ligand was achieved by heating **5a–c** in cyclooctane at reflux (Scheme 3). Compounds **5a** and **5b** gave only one intramolecular reaction product, **6a** and **6b**, in yields of 35% and 39%, respectively. Treatment of **5c** under the same conditions gave a mixture of **6c** and **7** (1:1, 10% yield).[11] We ascribe this to the longer alkanediyl chains which allow the formation of two different metallacycles as intermediates. The composition of the **6c**/**7** mixture was determined by NMR spectroscopy. In the ^1H NMR spectrum we find three signals (1:4:1)[11] for the protons of the cyclopentadienyl rings. The *tert*-butyl groups give rise to three upfield signals (1:1:2).[11] From these observations we conclude that there is a 1:1 mixture of **6c** and **7**, which is corroborated by the ^{13}C NMR spectroscopic data of the mixture. Moreover, the data assigned to **6c** are close to those found for **6a** and **6b**.

In the case of **6a** and **6b**, we were able to isolate single crystals that allowed an X-ray diffraction study.[12] The molecular structure of **6a** in the solid state is shown in Figure 1. The planes of the two π ligands are not parallel but slightly inclined (6°) to each other. The atoms C7 and C10 of the propanediyl bridges are bent out of the C1-C6-C8-C12 and C3-C6-C11-C14 planes (see Figure 1), respectively, to avoid eclipsed conformations. The distances between the center of the Cp ring (Cp_c) and Co (1.604 Å) and the between the center of the cyclobutadiene (Cbd) ring (Cbd_c) and Co (1.645 Å) are slightly shorter than those reported for nontethered metallocenes (Cp_c–Co 1.660 Å, Co–Cbd_c 1.681 Å).[13] In the case of **6b**, in which both π ligands are tethered with two tetramethylene bridges, the distances between the cobalt atom and the centers of the Cp and Cbd

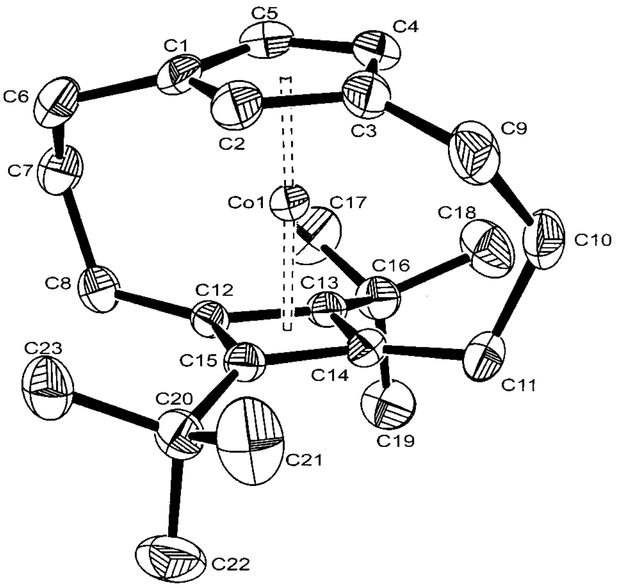


Figure 1. Structure of **6a** (ORTEP plot; thermal elipsoids at 50% probability level; H atoms have been omitted for clarity). Selected distances [Å]: C1-C2 1.441(3), C1-C5 1.424(3), C2-C3 1.443(3), C3-C4 1.420(3), C4-C5 1.420(3), C12-C13 1.482(2), C12-C15 1.463(3), C13-C14 1.476(3), C14-C15 1.469(2), Cp_c-Co 1.604(2), Co-Cbd_c 1.645(2).

ligands are larger than in **6a** (**6b**; Cp_c–Co 1.670 Å; Cbd_c–Co 1.692 Å) and close to those found for the parent system.[13] The new protocol reported herein for the synthesis of endohedral metallocenophanes has several advantages: it is not limited to stable cyclophanes as starting materials, and the length of the bridges and their substitution pattern on the first ligand are variable.

Received: February 9, 2001 [Z16591]

---

[1] Review: J. Schulz, F. Vögtle, *Top. Curr. Chem.* **1994**, *172*, 41.

[2] Reviews: R. L. Halterman in *Metallocenes: Synthesis, Reactivity, Applications, Vol. 1* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, p. 455; R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965.

[3] A. Lüttringhaus, W. Kullik, *Angew. Chem.* **1958**, *70*, 438; K. Hafner, C. Mink, H.-J. Lindner, *Angew. Chem.* **1994**, *106*, 1566; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1479; S. Miyake, L. M. Henling, J. E. Beslaw, *Organometallics* **1998**, *17*, 5328.

[4] C. Elschenbroich, R. Möckel, U. Zenneck, *Angew. Chem.* **1978**, *90*, 560; *Angew. Chem. Int. Ed. Engl.* **1978**, *17*, 531; A. R. Koray, M. L. Ziegler, N. E. Blank, M. W. Haenel, *Tetrahedron Lett.* **1979**, *26*, 2465.

[5] Review: H. Schmidbaur, *Angew. Chem.* **1985**, *97*, 893; *Angew. Chem. Int. Ed. Engl.* **1985**, *24*, 893; P. Jutzi, R. Krallmann, G. Wolf, B. Neumann, H. G. Stammler, *Chem. Ber.* **1991**, *124*, 2391.

[6] Review: M. Hisatome, *Rev. Heteroat. Chem.* **1992**, *6*, 142; M. Hisatome, J. Watanabe, K. Yamakawa, *Bull. Chem. Soc. Jpn.* **1994**, *67*, 280.

[7] C. Ruangstayanand, H.-J. Rimek, F. Zymalkowski, *Chem. Ber.* **1970**, *103*, 2403.

[8] K. Ishii, T. Nakano, T. Zenko, M. Kotera, M. Sakamoto, *J. Chem. Soc. Perkin Trans. 1* **1991**, 2057.

[9] The chloroalkynes were prepared analogously to those reported by J. White, C. G. Whiteley, *Synthesis* **1993**, 1141.

[10] W. P. Hart, D. W. Macomber, M. D. Rausch, *J. Am. Chem. Soc.* **1980**, *102*, 1196.

[11] Most relevant analytical data of **5**–**7**: **5a** ^{1}H NMR (500 MHz, C_6D_6): $\delta = 1.24$ (s, 18H), 1.46–1.52 (q, 4H), 2.01–2.08 (m, 8H), 4.48 (s, 2H), 4.61 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 18.7$ (CH_2), 27.4 (CH_2), 27.6 (C), 30.3 (CH_2), 31.6 (CH_3), 78.1 (C), 83,6 (CH), 85.6 (CH), 90.0 (C), 105.4 (C). **5b**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.22$ (s, 18H), 1.29–1.43 (m, 8H), 1.85–1.90 (m, 4H), 1.99–2.04 (m, 6H), 4.49 (2H), 4.61 (1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 18.8$ (CH_2), 27.6 (C), 27.9 (CH_2), 29.1 (CH_2), 30.0 (CH_2), 31.6 (CH_3), 78.4 (C), 83.4 (CH), 85.4 (CH), 89.4 (C), 105.9 (C). **5c**: ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.12$–1.91 (m, 28H), 2.06 (m, 4H), 2.08 (m, 6H), 4.50 (s, 2H), 4.60 (s, 1H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 18.7$ (CH_2), 27.3 (C), 28.1 (CH_2), 28.5 (CH_2), 28.9 (CH_2), 30.3 (CH_2), 31.4 (CH_3), 78.5 (C), 83.2 (CH), 85.3 (CH), 89.0 (C), 105.8 (C). **6a**: yellow solid, m.p. 95 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.13$ (s, 9H), 1.22 (s, 9H), 1.58–1.75 (m, 8H), 1.94–1.98 (m, 2H), 2.29–2.35 (m, 2H), 4.63 (s, 2H), 5.33 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 22.7$ (CH_2), 24.3 (CH_2), 31.3 (CH_3), 32.5 (CH_3), 32.6 (C), 33.4 (C), 41.6 (CH_2), 66.4 (C), 82.2 (CH), 85.7 (CH), 91.9 (C), 94.9 (C), 100.7 (C); HR-MS (positive ions) calcd for $C_{23}H_{33}Co$: 368.1914; found: 368.1904. **6b**: yellow solid, m.p. 135 °C; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 1.25$ (s, 9H), 1.30 (s, 9H), 1.51–1.72 (m, 8H), 2.13–2.17 (m, 4H), 2.25–2.33 (m, 2H), 2.62–2.69 (m, 2H), 4.84 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 28.3$ (CH_2), 28.5 (CH_2), 29.9 (CH_2), 31.7 (CH_2), 31.9 (CH_3), 32.0 (C), 32.9 (C), 33.1 (CH_3), 70.3 (C), 79.1 (CH), 81.4 (CH), 90.5 (C), 90.8 (C), 95.1 (C); HRMS (positive EI) calcd for $C_{25}H_{37}Co$: 396.2227; found: 396.2229. **6c** + **7**: yellow solid; ^{1}H NMR (300 MHz, C_7D_8): $\delta = 1.16$ (s, 9H), 1.17 (s, 9H), 1.26 (s, 18H), 1.73–1.30 (br, 18H), 2.03–1.75 (br, 10H), 2.73–2.21 (br, 12H), 4.48 (s, 1H), 4.72 (s, 4H), 4.89 (s, 1H); ^{13}C NMR (125 MHz, C_6D_6): $\delta = 22.5$ (CH_2), 23.6 (CH_2), 23.9 (CH_2), 24.2 (CH_2), 24.3 (CH_2), 24.9 (CH_2), 24.9 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 30.2 (CH_2), 30.8 (CH_3), 31.5 (C), 31.6 (CH_3), 31.8 (C), 32.4 (C), 32.9 (CH_3), 74.0 (C), 77.0 (C), 77.2 (CH), 77.3 (CH), 79.4 (CH), 83.5 (CH), 85.7 (C), 85.8 (C), 88.3 (C), 94.6 (C), 96.7 (C); HR-MS (positive ions) calcd for $C_{27}H_{41}Co$: 424.2540; found: 424.2537.

[12] X-ray analysis of **6a**: $C_{23}H_{33}Co$, $M_r = 368.42$, monoclinic, space group $P2_1/c$, crystal dimensions: $0.36 \times 0.20 \times 0.08$ mm^3, $a = 14.0457(1)$, $b = 9.9803(1)$, $c = 14.3919(2)$ Å, $\beta = 103.97(1)°$, $V = 1957.72(4)$ Å^3, $Z = 4$, $T = 200(2)$ K, $\rho_{calcd} = 1.25$ g cm^{-3}, Bruker Smart CCD, $Mo_{K\alpha}$ radiation, 19646 reflections collected, 4474 unique reflections ($R_{int} = 0.0446$), 3451 observed reflections with $I > 2\sigma(I)$, an empirical absorption correction was applied by using SADABS,[14] based on the Laue symmetry of the reciprocal space, $\mu = 0.88$ mm^{-1}, $T_{min} = 0.74$, $T_{max} = 0.94$. The structure was solved by the Patterson method and refined against F^2 with a full-matrix least-squares algorithm by using the SHELXTL (5.1) software package,[15] 223 parameters refined, $R1 = 0.034$, $wR2 = 0.073$ ($I > 2\sigma(I)$), GOF = 1.04. The maximum and minimum residual electron density is 0.28 and −0.35 e Å^{-3}, respectively. X-ray analysis of **6b**: $C_{25}H_{37}Co$, $M_r = 396.48$, orthorhombic, space group $Pna2_1$, crystal dimensions: $0.58 \times 0.42 \times 0.24$ mm^3, $a = 10.3000(1)$, $b = 13.5018(1)$, $c = 15.0996(1)$ Å, $V = 2099.88(3)$ Å^3, $Z = 4$, $T = 200(2)$ K, $\rho_{calcd} = 1.25$ g cm^{-3}, Bruker Smart CCD, $Mo_{K\alpha}$ radiation, 15308 reflections collected, 3098 unique reflections ($R_{int} = 0.0812$), 2306 observed reflections with $I > 2\sigma(I)$, an empirical absorption correction was applied by using SADABS,[14] based on the Laue symmetry of the reciprocal space, $\mu = 0.82$ mm^{-1}, $T_{min} = 0.65$, $T_{max} = 0.86$. The structure was solved by direct methods and refined against F^2 with a full-matrix least-squares algorithm by using the SHELXTL (5.1) software package,[15] 241 parameters refined, $R1 = 0.037$, $wR2 = 0.068$ ($I > 2\sigma(I)$), GOF = 0.96. The maximum and minimum residual electron density is 0.72 and −0.29 e Å^{-3}, respectively. The crystallographic data (excluding structure factors) for the structures reported herein have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161078 (**6a**) and CCDC-161079 (**6b**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] P. E. Riley, R. E. Davis, *J. Organomet. Chem.* **1976**, *113*, 157.

[14] G. M. Sheldrick, 1996, unpublished work based on the method described in R. H. Blessing, *Acta Crystallogr. Sect. A* **1995**, S1, S33.

[15] G. M. Sheldrick, Bruker Analytical X-ray-Division, Madison, WI, **1997**.

Low-Temperature Selective Catalytic Reduction (SCR) of NO with NH_3 by Using Mn, Cr, and Cu Oxides Supported on Hombikat TiO_2**

Panagiotis G. Smirniotis,* Donovan A. Peña, and Balu S. Uphade

Nitrogen oxides are man-made pollutants, emitted from mobile and stationary sources, that greatly contribute to the formation of smog, acid rain, and ozone. Automobiles are the primary mobile sources of NO_x emissions, while the stationary sources consist of oil and coal-fired power stations and nitric acid production plants. The direct health hazards related to NO_x are bronchitis, pneumonia, viral infections, and hay fever. Selective catalytic reduction (SCR) of NO with ammonia in the presence of oxygen [Eq. (1)] is the proven technology for

$$4\,NO + 4\,NH_3 + O_2 \longrightarrow 4\,N_2 + 6\,H_2O \tag{1}$$

---

[*] Prof. P. G. Smirniotis, D. A. Peña, B. S. Uphade
Chemical Engineering Department
University of Cincinnati
Cincinnati, OH 45221-0171 (USA)
Fax: (+1) 513-556-3473
E-mail: Panagiotis.Smirniotis@UC.EDU

[**] We are grateful to the Ohio Coal Development Office (OCDO), Columbus, Ohio, for financial support and for allowing us to publish the findings.

1433-7851/01/4013-2479 $ 17.50+.50/0