sealed in evacuated silica tubes to shield them from moisture and air. $La_3B_3N_6$ was obtained as colorless, transparent single crystals, and $Ce_3B_3N_6$ as black single crystals with defined faces but irregular shape.

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[1] H. Womelsdorf, H.-J. Meyer, *Z. Anorg. Allg. Chem.* **1994**, *620*, 262–265; M. Wörle, H. Meyer zu Altenschildesche, R. Nesper, *J. Alloys Compd.* **1998**, *264*, 107–114; F. E. Rohrer, Dissertation, ETH Zürich, **1997**; O. Reckeweg, Dissertation, Universität Tübingen, **1998**.

[2] T. Sato, T. Endo, S. Kashima, O. Fukunaga, M. Iwata, *J. Mater. Sci.* **1983**, *18*, 3054–3062.

[3] J. Gaude, P. L'Haridon, J. Guyader, J. Lang, *J. Solid State Chem.* **1985**, *59*, 143–148.

[4] P. Rogl, H. Klesnar, *J. Am. Ceram. Soc.* **1990**, *73*, 2634–2639.

[5] O. Reckeweg, H.-J. Meyer, *Z. Anorg. Allg. Chem.*, in press.

[6] Crystal structure analysis data for $La_3B_3N_6$: colorless, transparent crystal, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 661.3(1)$, $b = 687.0(1)$, $c = 779.8(1)$ pm, $\alpha = 106.06(1)$, $\beta = 90.55(1)^\circ$, $\gamma = 115.63(1)^\circ$; $V = 303.5 \times 10^6$ pm^3, $2\theta_{max.} = 62^\circ$, $Mo_{K\alpha}$ ($\lambda = 71.073$ pm), graphite monochromator, CAD4 (ω scan), $T = 293$ K, 2361 measured reflections, LP correction, 7 Ψ scans, SHELX-97, 64 parameters (B and N refined isotropically), residual electron density 5.1 e Å^{-3}, $R1 = 0.030$ for 1657 $F_o > 4\sigma(F_o)$ and 0.041 for all 1915 data, $wR2 = 0.069$, GOF = 1.09. $Ce_3B_3N_6$: black crystal, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 658.3(4)$, $b = 677.5(5)$, $c = 773.0(5)$ pm, $\alpha = 106.05(8)$, $\beta = 90.73(8)^\circ$, $\gamma = 115.52(8)^\circ$, $V = 295.5 \times 10^6$ pm^3, $2\theta_{max.} = 66^\circ$, $Mo_{K\alpha}$ ($\lambda = 71.073$ pm), graphite monochromator, Stoe IPDS (φ scan), $T = 293$ K, 3864 measured reflections, LP correction, X shape, SHELX-97, 110 parameters, all atoms refined anisotropically, residual electron density 3.6 e Å^{-3}, $R1 = 0.033$ for 1830 $F_o > 4\sigma$ (F_o) and 0.036 for all 1966 data, $wR2 = 0.086$, GOF = 1.07. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository numbers CSD- 410417 ($Ce_3B_3N_6$) and CSD-410598 ($La_3B_3N_6$)).

[7] P. Rogl, H. Klesnar, *J. Solid State Chem.* **1992**, *98*, 99–104.

[8] Extended Hückel method: program package BICON-CEDiT by M. Brändle, R. Rytz, G. Calzaferri, Universität Bern, **1997**.

[9] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

[10] With respect to the molar volume of lanthanide compounds that crystallize in the $Ln_3B_2N_4$ structure type an anomalous behavior has been assumed for Ln = Ce, which has been explained with the presence of Ce^{4+} (see reference [4]).

[11] Alternatively, defects in the crystal structure of $Ce_3B_3N_6$ could be a reason for the black appearance of the crystals. For the mixed valence of Sm_3S_4, see H. Heim, H. Bärnighausen, *Acta Crystallogr. Sect. B* **1978**, *34*, 2084–2092.

[12] R. Boese, A. H. Maulitz, P. Stellberg, *Chem. Ber.* **1994**, *127*, 1887–1889.

[13] H. Hess, B. Reiser, *Z. Anorg. Allg. Chem.* **1971**, *381*, 91–102.

[14] P. P. Power, *J. Organomet. Chem.* **1990**, *400*, 49–69.

[15] Program package CACAO: C. Mealli, D. M. Proserpio, *J. Chem. Educ.* **1990**, *67*, 399–402.

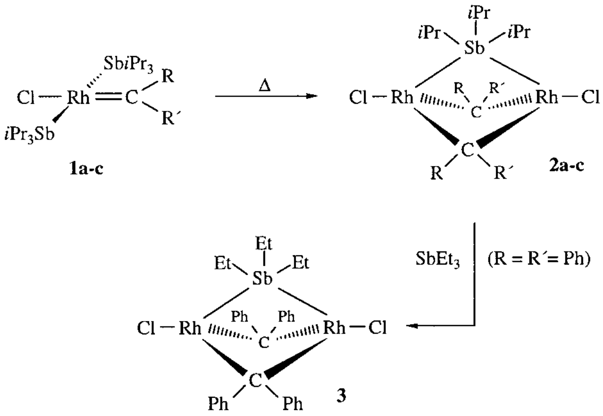
[16] The $B_3N_3H_6$ molecule has D_{3h} symmetry at its calculated global minimum: F. Ramondo, L. Bencivenni, G. Portalone, *J. Mol. Struct. (Theochem.)* **1991**, *236*, 29–39.

Formation of Novel Dinuclear Mixed-Valence Rhodium Complexes by Intramolecular Migration of a Chelating Ligand[**]

Ulrich Herber, Birgit Weberndörfer, and Helmut Werner*

Dedicated to Professor Nils Wiberg on the occasion of his 65th birthday

One of the most surprising results of recent work from our laboratory was that trialkylstibanes can function as bridging ligands in dinuclear transition metal complexes. In the course of investigations concerned with the reactivity of square-planar carbenerhodium(I) compounds **1**, which were obtained from *trans*-$[RhCl(C_2H_4)(SbiPr_3)_2]$ and diazoalkanes $RR'CN_2$ in excellent yields,[1] we discovered that these compounds are thermally quite labile and react upon heating in benzene at 80°C by partial elimination of $SbiPr_3$ to afford the Rh_2 complexes **2** (Scheme 1).[2] The notable feature is that the coordination geometry around the two metal centers of **2**, which are formally in the oxidation state +I, is distorted tetrahedral and that this geometry is preserved in the reactions with $SbMe_3$ or $SbEt_3$ (formation of **3**).[2] In textbooks and standard references it was generally considered as highly improbable[3] that trialkylstibanes as well as their phosphorus and arsenic counterparts can undergo a bridging coordination mode, and this expectation seemed to be confirmed by numerous studies on the chemistry of ligands of the general type ER_3 (E = P, As, Sb).[4]



Scheme 1. **a**: R = R′ = Ph; **b**: R = R′ = *p*-Tol; **c**: R = Ph, R′ = *p*-Tol).

Following our initial studies on the reactivity of **2** toward CO, CN*t*Bu, SbR_3, $PiPr_3$ etc.[2, 5] we were interested to know whether the dinuclear structure with the core molecular fragment $Rh(\mu\text{-}SbiPr_3)(\mu\text{-}CPh_2)_2Rh$ would be maintained if the axial chloro ligands are replaced by chelating anions. The outcome of this substitution would be of course an increase in

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the coordination number of rhodium. We knew already that the reaction of **2a** with NaC_5H_5 leads to the formation of the dinuclear complex $[(C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2]$, which does not contain a bridging stibane unit.[2] A different process takes place, however, if acetylacetonate (acac) is used as substrate. The dirhodium compound **4** (Scheme 2) is formed from **2a** and an equimolar amount of [Tl(acac)]. The structure of **4** (which is thermally stable up to 144 °C) is shown in Figure 1.[6] Owing to the increase of the coordination number at Rh1, the stibane as well as one of the diphenylcarbene ligands are linked to the two metal centers in an unsymmetrical fashion. The bond lengths Sb–Rh1 and Sb–Rh2 differ by about 0.35 Å and those between the carbene carbon atom C2 and Rh1 and Rh2, respectively, by approximately the same value. Compared to the distances in the starting material **2a**, the distance Sb–Rh1 is about 0.19 Å shorter and the distance Sb–Rh2 about 0.18 Å longer, which is probably due to the different types of anionic ligands. Quite unexpectedly, also the acetylacetonate is coordinated in an unsymmetrical mode [Rh1–O1 2.064(3) Å, Rh1–O2 2.274(4) Å] thereby the shorter bond Rh1–O1 being opposite to the shorter bond Rh1–C1. The Rh–Rh distance in **4** is about 0.15 Å longer than in compound **2a** but still lies in the range of other rhodium(I) complexes with a metal–metal bond.[7]

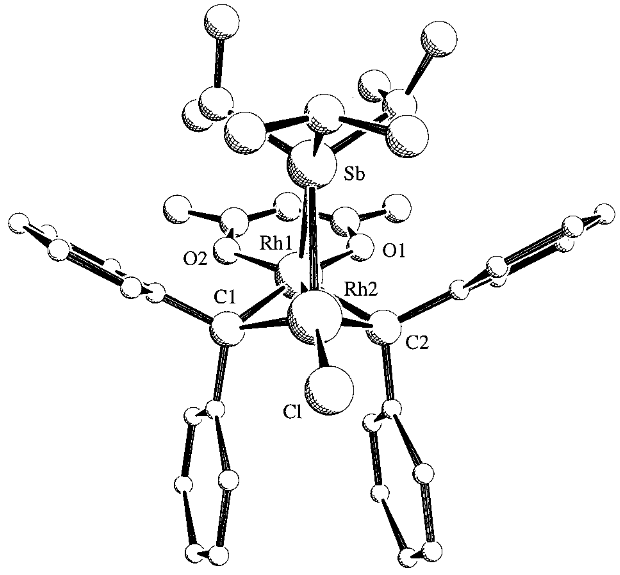
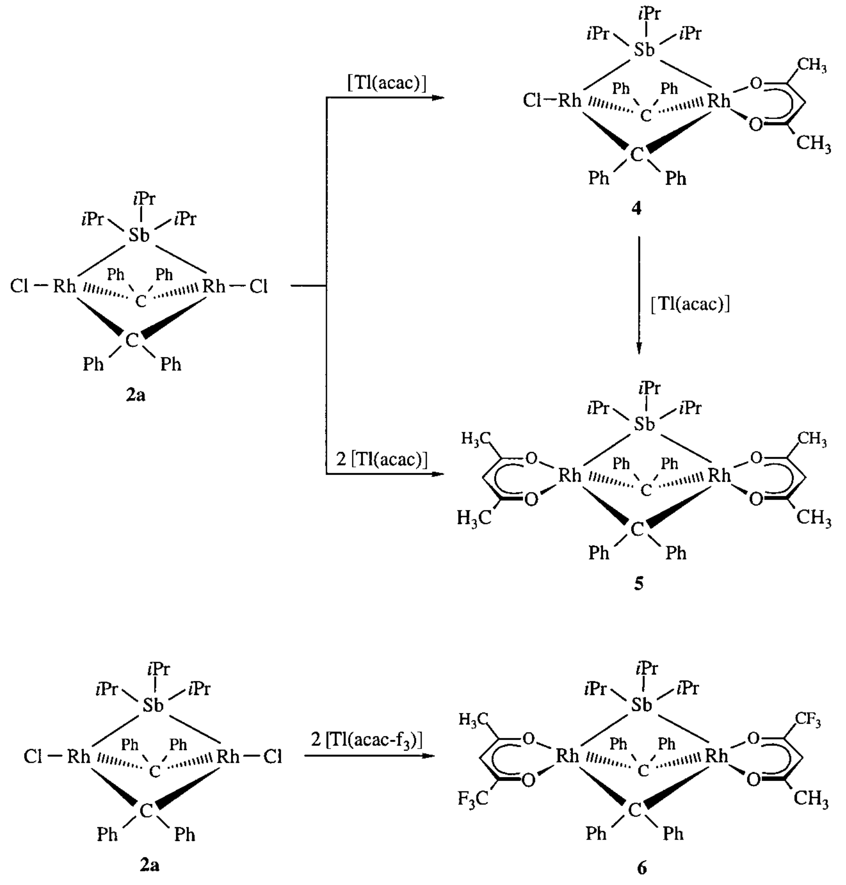


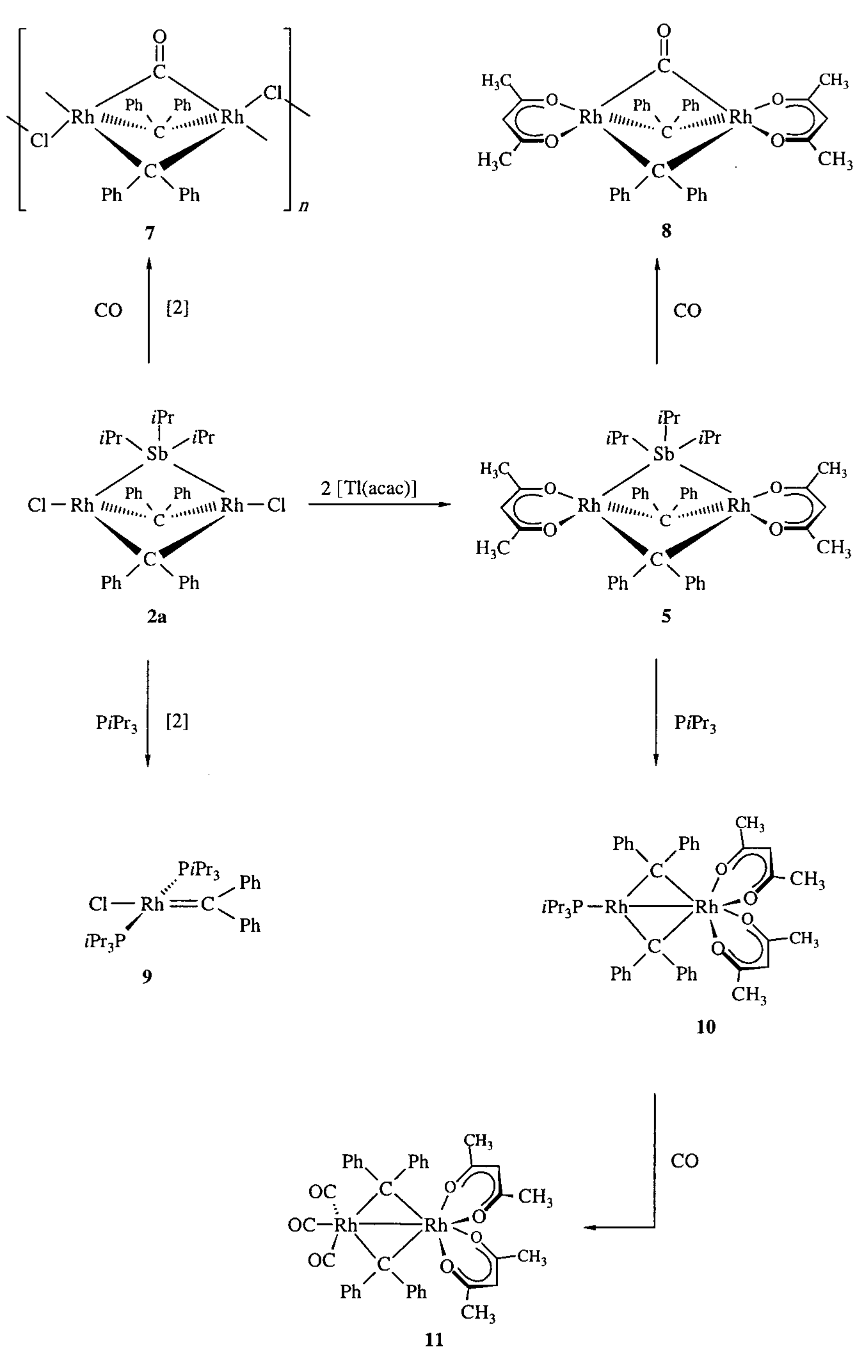
Figure 1. Molecular structure of **4** in the crystal (the carbon atoms of the phenyl groups were reduced in size for clarity). Selected bond lengths [Å] and angles [°]: Rh1–Rh2 2.6796(6), Rh1–C1 2.030(4), Rh1–C2 2.187(4), Rh1–O1 2.064(3), Rh1–O2 2.274(4), Rh1–Sb 2.498(1), Rh2–Sb 2.846(1), Rh2–C1 2.053(4), Rh2–C2 1.825(4), Rh–Cl 2.483(1); Rh1-Sb-Rh2 59.77(2), Sb-Rh1-Rh2 66.57(2), Sb-Rh2-Rh1 53.66(2), Rh1-Rh2-Cl 171.55(3), Rh1-C1-Rh2 82.0(2), Rh1-C2-Rh2 83.3(2), C1-Rh1-O1 167.0(1), C2-Rh1-O2 165.9(1), O1-Rh1-O2 78.5(1), C1-Rh1-C2 83.2(2), C1-Rh2-C2 92.3(2).

The reaction of **2a** with [Tl(acac)] in the molar ratio of 1:2.4 affords the symmetrical dinuclear compound **5** (Scheme 2), which after recrystallization from pentane is isolated as a brown, slightly air-sensitive solid in 86% yield. The related complex **6** with two trifluorinated acetylacetonate ligands is obtained in a similar way. A remarkable feature is the different reactivity of **2a** and **5** toward CO (Scheme 3). While the dichloro compound **2a** reacts with carbon monoxide to give the presumably polymeric complex **7**,[8] upon treatment of **5** with CO in benzene the triply bridged dinuclear compound **8** is cleanly formed. The exchange of one bridging ligand takes place without any further rearrangement of the molecular skeleton. Characteristic data of **8**[9] are the CO stretching frequency at 1842 cm^{-1} in the IR spectrum and the signal for the μ-CO carbon atom at $\delta = 182.8$ in the ^{13}C NMR spectrum.



Scheme 2.

The difference in the behavior of **2a** and **5** toward triisopropylphosphane is even more striking than toward CO. Recently, we reported that treatment of **2a** with $PiPr_3$ leads by substitution of the stibane and cleavage of the bridging bonds to the stable mononuclear complex **9**.[2] The bis(acetylacetonate) compound **5** reacts much more slowly than **2a** with an excess of $PiPr_3$ and affords after 4 h at 60 °C in benzene the dinuclear compound **10** in about 70% yield. Compound **10** is a brown, thermally stable solid which is modestly air-sensitive and soluble in most common organic solvents. Both the ^1H and the ^{13}C NMR spectra of **10** display two sets of signals for the protons and carbon atoms of the $OC(CH_3)$ moieties of the acetylacetonate ligands, which points



Scheme 3.

to an unsymmetrical structure of the dinuclear complex. This proposal has been confirmed by the X-ray crystal structure analysis (Figure 2).[6] One of the chelating ligands has migrated from one metal center to the other and its position is occupied by the triisopropylphosphane. The stibane ligand has been replaced while the bridging diphenylcarbene units are maintained. The distances between the less coordinated metal center Rh1 and the carbene atoms C1 and C2 are 0.17 Å shorter than those between Rh2 and C1 and C2, and they differ only slightly to the Rh–C bond lengths of **2a** (2.003(1) and 2.007(3) Å). The distance Rh1–Rh2 of **10** is nearly the same as in compound **4**. Similarly to **4**, also in compound **10** the acetylactonate ligands are not coordinated in a symmetrical fashion and, therefore, in both six-membered chelate rings the Rh–O bond lengths differ by 0.08–0.10 Å. The bond axis Rh2-Rh1-P is not exactly linear which is probably a consequence of the steric repulsion between the phenyl and the isopropyl groups.

The unsymmetrical dinuclear complex **10**, in which one of the rhodium centers (Rh1) formally has the oxidation state zero and the other (Rh2) the oxidation state +II, reacts with Lewis acids as well as with Lewis bases. While the composition of the products from **10** and HCl or CF_3SO_3Me, respectively, is not yet established, upon treatment of **10** with CO in pentane the tricarbonyl complex **11** is formed in excellent yield. We note that despite the use of a considerable excess of CO no cleavage of the carbene bridges occurs. Typical features for **11** are the three CO stretching vibrations at 2056, 2016, and 1965 cm^{-1} in the IR spectrum which support the proposed structure shown in Scheme 3.

To the best of our knowledge, compounds **10** and **11** are the first representatives of a novel type of mixed-valence dinuclear Rh^0–Rh^{II} complexes with bridging carbene ligands.[10] Dinuclear complexes with $Rh(\mu\text{-}CR_2)_2Rh$ as a core building block were already known,[7, 8, 11] but in none of these compounds the metals have a different oxidation state. Current work is not only aimed to broaden the scope of unsymmetrical Rh^0–Rh^{II} complexes, but also to find out whether these compounds possess a related reactivity to the rhodium(II) complexes, discovered and intensively investigated by Maitlis et al.,[12] with CH_2 and CHR as bridging ligands.

Experimental Section

4: A solution of **2a** (78 mg, 0.09 mmol) in acetone (15 mL) was treated at 0 °C with [Tl(acac)][13] (27 mg, 0.09 mmol) and then allowed to warm to room temperature and stirred for 30 min. The solvent was removed in vacuo and the residue was extracted with pentane (3 × 10 mL). The combined extracts were concentrated to about 2 mL, and the concentrated solution was chromatographed on Al_2O_3 (neutral, avtivity grade V). A colorless fraction (which was thrown away) was eluted with pentane and then a red-brown fraction with benzene. The latter was concentrated to dryness in vacuo, and the residue was recrystallized from acetone/diethyl ether (1:1) to give brown crystals; yield 61 mg (73 %); m.p. 144 °C (decomp); ^1H NMR (400 MHz, C_6D_6):[14] $\delta = 5.57$ (s, 1 H, CH of acac), 1.99 (s, 6 H, CH_3 of acac), 1.63 (sept, 3 H, $^3J(H,H) = 7.4$ Hz, $SbCHCH_3$), 0.99 (d, 18 H, $^3J(H,H) = 7.4$ Hz, $SbCHCH_3$); $^{13}C\{^1H\}$ NMR (100.6 MHz, C_6D_6): $\delta = 188.7$ (s, CO of acac), 177.3 (m, CPh_2), 101.3 (s, CH of acac), 28.3 (s, CH_3 of acac), 24.8 (s, $SbCHCH_3$), 21.4 (s, $SbCHCH_3$).

5: A solution of **2a** (84 mg, 0.10 mmol) in acetone (15 mL) was treated with [Tl(acac)] (73 mg, 0.24 mmol) and stirred for 2 h at room temperature. The

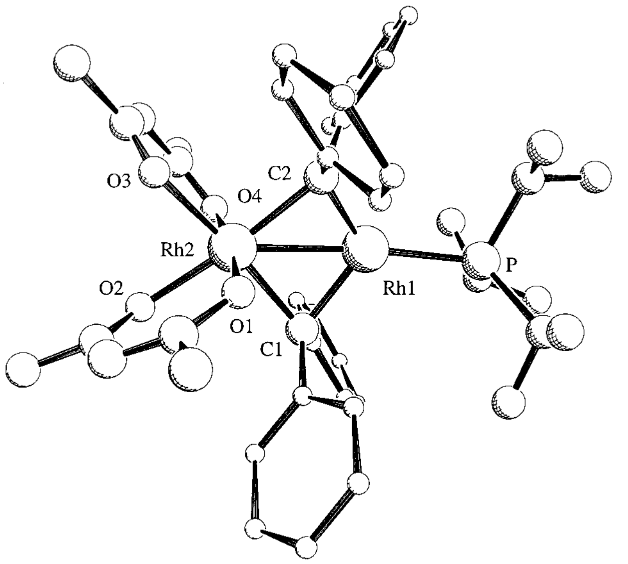


Figure 2. Molecular structure of **10** in the crystal (the carbon atoms of the phenyl groups were reduced in size for clarity). Selected bond lengths [Å] and angles [°]: Rh1−Rh2 2.6317(7), Rh1−P 2.332(2), Rh1−C1 1.982(6), Rh1−C2 1.982(5), Rh2−C1 2.158(5), Rh2−C2 2.153(6), Rh2−O1 2.008(4), Rh2−O2 2.114(4), Rh2−O3 2.115(4), Rh−O4 2.037(4); Rh2-Rh1-P 169.91(4), Rh1-C1-Rh2 78.8(2), Rh1-C2-Rh2 78.9(2), P-Rh1-C1 122.4(2), P-Rh1-C2 125.3(2), C1-Rh1-C2 103.7(2), C1-Rh2-C2 92.6(2), O1-Rh2-O2 92.2(2), O3-Rh2-O4 90.0(2), O1-Rh2-O4 170.0(2), O1-Rh2-O3 83.3(2), O2-Rh2-O4 82.6(2), O2-Rh2-O3 83.5(2), O2-Rh2-C2 173.1(2), O3-Rh2-C1 169.8(2).

work-up procedure was the same as described for **4**. Recrystallization from pentane (−78 °C) gave brown crystals; yield 85 mg (86 %), m.p. 55 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.58$ (s, 2H, CH of acac), 2.00 (s, 12H, CH_3 of acac), 1.91 (sept, 3H, ^3J(H,H) = 7.4 Hz, SbC*H*CH$_3$), 0.96 (d, 18H, ^3J(H,H) = 7.4 Hz, SbCHC*H*$_3$); ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6): $\delta =$ 188.4 (s, CO of acac), 176.8 (t, ^1J(Rh,C) = 20.8 Hz, *C*Ph$_2$), 100.6 (s, CH of acac), 28.6 (s, CH_3 of acac), 25.6 (s, Sb*C*HCH$_3$), 21.3 (s, SbCH*C*H$_3$). Compound **6** was prepared in a similar way; yield 77 %; ^{19}F NMR (188.3 MHz, C_6D_6): $\delta = -75.0$ (s).

8: A stream of CO was passed through a solution of **5** (85 mg, 0.09 mmol) in benzene (10 mL) for 15 s at room temperature. After the solution was stirred for 30 min, the solvent was removed in vacuo, and the residue was recrystallized from CH_2Cl_2/pentane (5 °C) to give red crystals; yield 59 mg (89 %); m.p. 48 °C (decomp); IR (C_6H_6): $\tilde{\nu}$(CO) = 1842 cm^{-1}; ^{1}H NMR (400 MHz, C_6D_6): $\delta = 5.36$ (s, 2H, CH of acac), 1.76 (s, 12H, CH_3 of acac); ^{13}C{H} NMR (100.6 MHz, C_6D_6): $\delta = 189.5$ (s, CO of acac), 182.8 (m, μ-CO), 101.5 (s, CH of acac), 27.9 (s, CH_3 of acac).

10: A solution of **5** (105 mg, 0.11 mmol) in benzene (20 mL) was treated with P*i*Pr$_3$ (105 µL, 0.55 mmol) and stirred for 4 h at 60 °C. After the mixture was cooled to room temperature, the solvent was removed in vacuo, the residue was dissolved in pentane (3 mL) and the solution was chromatographed on Al_2O_3 (neutral, avtivity grade V). A colorless fraction (which was thrown away) was eluted with pentane and then a brown fraction with benzene. The latter was concentrated to dryness in vacuo, and the residue was recrystallized from pentane (5 °C) to give brown crystals; yield 67 mg (68 %); m.p. 75 °C (decomp); ^{1}H NMR (400 MHz, C_6D_6): $\delta =$ 4.86 (s, 2H, CH of acac), 1.90 (m, 3H, PC*H*CH$_3$), 1.84, 1.42 (both s, 12H, CH_3 of acac), 0.83 (m, 18H, PCHC*H*$_3$); ^{13}C{H} NMR (100.6 MHz, C_6D_6): $\delta = 186.4$, 183.8 (both s, CO of acac), 160.5 (m, *C*Ph$_2$), 98.7 (s, CH of acac), 27.7, 26.7 (both s, CH_3 of acac), 25.4 (m, P*C*HCH$_3$), 22.5 (m, PCH*C*H$_3$); ^{31}P NMR (162.0 MHz, C_6D_6): $\delta = 40.5$ (dd, ^1J(Rh,P) = 257.7, ^2J(Rh,P) = 5.9 Hz).

11: A stream of CO was passed through a solution of **10** (150 mg, 0.17 mmol) in pentane (15 mL) for 10 s at room temperature. After the solution was stirred for 15 min, the solvent was removed in vacuo, and the residue was recrystallized from diethyl ether/pentane (1:3) at 5 °C to give red crystals; yield 116 mg (83 %); m.p. 111 °C (decomp); IR (C_6H_6): $\tilde{\nu}$(CO) = 2056, 2016, 1965 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6): $\delta = 4.55$ (s, 2H, CH of acac), 1.71, 1.21 (both s, 12H, CH_3 of acac).

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[1] a) P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1993**, *105*, 1498 – 1500; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1480 – 1482; b) H. Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, *3*, 1375 – 1384.

[2] P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1994**, *106*, 82 – 84; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 97 – 99.

[3] F. A. Cotton, G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., Wiley, New York, **1980**, Chap. 3 – 10. The preparation of dinuclear complexes with bridging Sb, SbR, and SbR_2 ligands has been reported: U. Weber, L. Zsolnai, G. Huttner, *J. Organomet. Chem.* **1984**, *260*, 281 – 291; G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang, L. Zsolnai, *J. Organomet. Chem.* **1985**, *282*, 331 – 348.

[4] a) W. Levason, C. A. McAuliffe, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, **1977**; b) W. Levason, C. A. McAuliffe, *Acc. Chem. Res.* **1978**, *11*, 363 – 368; c) N. R. Champness, W. Levason, *Coord. Chem. Rev.* **1994**, *133*, 115 – 217.

[5] a) P. Schwab, Dissertation, Universität Würzburg, **1994**; b) H. Werner, *J. Organomet. Chem.* **1995**, *500*, 331 – 336.

[6] Data for the X-ray structure analyses: **4**: Crystals from acetone/diethyl ether (1:1), $C_{40}H_{48}ClO_2Rh_2Sb$ (923.80); crystal size 0.13 × 0.11 × 0.10 mm^3; monoclinic, space group $P2_1/c$ (no. 14), $a = 11.664(3)$, $b = 18.993(4)$, $c = 16.978(5)$ Å, $\beta = 89.57(3)°$, $Z = 4$, $V = 3761(2)$ Å^3, $\rho_{calcd} = 1.631$ g cm^{-3}; $T = 173(2)$ K; $2\theta = 61.04°$; 40486 reflections measured, 8126 were unique ($R_{int} = 0.0580$), and 5486 observed ($I > 2\sigma(I)$); IPDS (Stoe), Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated; Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0337$, $wR_2 = 0.0708$ (for 5486 reflections with $I > 2\sigma(I)$), $R_1 = 0.0596$, $wR_2 = 0.0763$ (for all 8126 data); data-to-parameter ratio 17.90; residual electron density +0.809/−1.169; two isopropyl groups consisting of the atoms C40, C43, C44 and C42, C47, C48 are disordered; the two alternative positions were refined anisotropically with restraints on the anisotropic displacement parameters and bond lengths with the occupation factors 56.7 % and 43.3 % or 67.3 % and 32.7 %, respectively. **10**: Crystals from pentane/diethyl ether (1:1), $C_{45}H_{55}O_4PRh_2$ (896.68); crystal size 0.11 × 0.10 × 0.08 mm^3; monoclinic, space group $P2_1/c$ (No. 14), $a = 10.5918(11)$, $b = 18.0901(16)$, $c = 21.567(2)$ Å, $\beta = 99.88(1)°$, $Z = 4$, $V = 4071.2(7)$ Å^3, $\rho_{calcd} = 1.463$ g cm^{-3}; $T = 173(2)$ K; $2\theta = 56.42°$; 42944 reflections measured, 9945 were unique ($R_{int} = 0.0783$) and 5632 observed ($I > 2\sigma(I)$); IPDS (Stoe), Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), graphite-monochromated; Lp correction. The structure was solved by direct methods and refined with the full-matrix, least-squares method; $R_1 = 0.0598$, $wR_2 = 0.01370$ (for 5632 reflections with $I > 2\sigma(I)$), $R_1 = 0.1080$, $wR_2 = 0.1624$ (for all 9945 data); data-to-parameter ratio 20.76; residual electron density +0.884/−2.087. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-114162 (**4**) and CCDC-114163 (**10**). 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).

[7] a) T. Yamamoto, A. R. Garber, J. R. Wilkinson, C. B. Boss, W. E. Streib, L. J. Todd, *J. Chem. Soc. Chem. Commun.* **1974**, 354 – 356; b) H. Ueda, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2250 – 2254; c) W. A. Herrmann, *Adv. Organomet. Chem.* **1982**, *20*, 159 – 263; d) M. J. Krause, R. G. Bergman, *Organometallics* **1986**, *5*, 2097 – 2108.

[8] P. Hong, N. Nishii, K. Sonogashira, N. Hagihara, *J. Chem. Soc. Chem. Commun.* **1972**, 993.

[9] The structure of **8** has been determined by X-ray crystallography: B. Weberndörfer, Dissertation, Universität Würzburg, in preparation.
[10] It was mentioned by a referee that the CPh_2 groups could be considered as dianionic ligands. The metal centers would then be Rh^{II} and Rh^{IV}. The total electron count would be unaltered due to this formalism.
[11] T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. Mills, G. N. Pain, F. G. A. Stone, P. Woodward, *ACS Symp. Ser.* **1981**, *155*, 299–313.
[12] Reviews: a) P. M. Maitlis, *J. Organomet. Chem.* **1995**, *500*, 239–249; b) P. M. Maitlis, H. C. Long, R. Quyoum, M. L . Turner, Z.-Q. Wang, *Chem. Commun.* **1996**, 1–8.
[13] J. Vicente, M. T. Chicote, *Inorg. Synth.* **1998**, *32*, 172–177.
[14] The ^1H and ^{13}C NMR data of the phenyl groups were omitted for simplicity.

Chemistry of C_{84}: Separation of Three Constitutional Isomers and Optical Resolution of D_2-C_{84} by Using the "Bingel–Retro-Bingel" Strategy[**]

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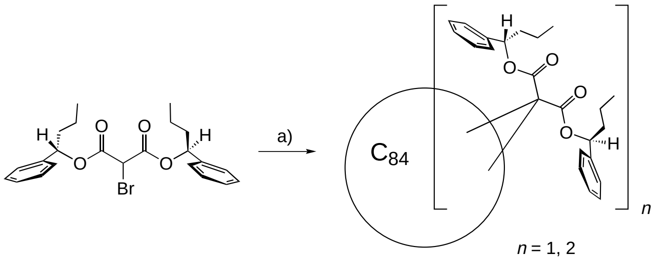
Although C_{84} is the third most abundant fullerene,[1] its chemistry remains remarkably unexplored. Computational studies revealed that this higher fullerene has 24 theoretically possible constitutional isomers that obey the isolated pentagon rule (IPR), with a D_2- and a D_{2d}-symmetrical isomer being the most stable ones.[2] These two isomers are indeed the most abundant ones in the C_{84} fraction of fullerene soot, with a ratio of D_2-C_{84}:D_{2d}-C_{84} of approximately 2:1, but their chromatographic separation is extremely difficult and, for several years, they had only been isolated and characterized as a mixture by ^{13}C NMR spectroscopy[3] and other methods. The successful separation by recycling high performance liquid chromatography (HPLC) and full characterization of these two isomers was only reported recently by Shinohara and coworkers.[4] The structure of the D_{2d} isomer was unambiguously proven by Balch et al. who prepared the $[(\eta^2\text{-}D_{2d}\text{-}C_{84})Ir(CO)Cl(PPh_3)_2]\cdot 4C_6H_6$ complex and solved its X-ray crystal structure.[5] This is the only characterized derivative of a C_{84} isomer reported thus far. Although four possible structures exist that fit the ^{13}C NMR data of the major D_2 isomer,[3, 4] the experience with the isomers of another higher fullerene, C_{78},[6] and preliminary 2D NMR (INADEQUATE) data of the C_{84} isomers[7a] suggest that the compound with the calculated lowest energy structure is the one isolated in all published work. Both ^{13}C NMR studies[3c, 7] and the analysis of endohedral ^3He complexes of the C_{84} fraction of the fullerene soot by ^3He NMR spectroscopy[8] have provided evidence for the presence of minor amounts of additional isomers, but none of them have been isolated to date. Here, we describe a powerful new protocol to isolate pure constitutional isomers of higher fullerenes by the intermediacy of defined covalent adducts,[9] by using the recently introduced Bingel–retro-Bingel reaction sequence.[10, 11] This protocol takes advantage of the fact that covalent adducts of isomeric higher fullerenes are much easier to separate than the parent unfunctionalized carbon spheroids. By this method we not only isolated the two known major constitutional isomers of C_{84} but also succeeded in the first isolation and spectroscopic characterization of a third minor isomer in pure form. Furthermore, we describe the application of this protocol to the optical resolution of D_2-C_{84}.[12] Also, contradictory reports in the literature concerning the electrochemistry of C_{84} isomers[13, 14] are clarified.

The C_{84} fraction (52 mg, 0.052 mmol)[15] of soot enriched in higher fullerenes, provided by Hoechst AG, was treated in *o*-dichlorobenzene (*o*-DCB) at 20 °C with bis[(*S*)-1-phenylbutyl]-2-bromomalonate[16] in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; Scheme 1). Subsequent purification by column chromatography (SiO_2, CH_2Cl_2/hexane (1/1) $\rightarrow$ CH_2Cl_2) yielded four fractions containing, according to matrix-assisted laser-desorption-ionization time-of-flight mass spectrometry (MALDI-TOF MS), pure C_{84}, mono-adducts, bis-adducts, and tris-adducts, respectively. The mono-adduct fraction was further separated by HPLC ((*S*,*S*)-Whelk-O, 250 × 10 mm, hexane/CH_2Cl_2 (7/3), flow rate 2 mL min^{-1}) to give four main products **Ia**–**Id** of which two (**Ia** (0.8 mg, 1 % and **Id** (2.5 mg, 3.5 %)) were isolated and characterized



Scheme 1. Formation of mono- and bis-adducts of various C_{84} isomers by Bingel cyclopropanation. a) C_{84}, DBU, *o*-DCB, Ar, 20 °C, 14 h.

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