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[9] Cyclic voltammetry has been performed with a conventional three-electrode set-up with a Pt-disk electrode and a Ag/AgCl pseudo-reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate/CH_2Cl_2. Internal standard: ferrocene (Fc/Fc$^+$); scan rate: 250 mV s^{-1}.

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[12] AM1-CI calculations were performed using the MOPAC 93 program package (Fujitsu). The geometry of $\mathbf{3}^{3+}$ (methoxy substituents were omitted for simplicity) was optimized at the UHF level as a quartet state; the geometry was restricted to D_3 symmetry. This geometry was used for an CI calculation involving three doubly and three singly occupied orbitals (parameters: C.I. = (6,3), open(3,3)).

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Hexahelicenophanes and Their Racemization[**]

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Dieter Schollmeyer

Dedicated to Professor Alan R. Katritzky
on the occasion of his 70th birthday

Helicenes represent a fascinating class of compounds that exhibit exceptional properties.[1–4] Since the first synthesis of [6]helicene by Newman and Lednicer,[5] this area has developed rapidly, with the parent systems at the center of interest. The number of substituted [6]helicenes described in the literature remains relatively small, and bridged [6]helicenes are almost unknown.[3, 6–8] We have now synthesized [6]helicenes whose terminal benzene rings are linked by polymethylenedioxy chains so that the influence of the cyclophane structure on the racemization can be studied.

We first prepared the dialdehydes **3a–c** from salicylaldehyde (**1**) and α,ω-dibromoalkanes (**2a–c**) and then reduced them to the diols **4a–c** (Scheme 1). The transformation to the bisphosphonium salts **5a–c** and the subsequent twofold Wittig olefination, carried out in highly diluted solution with 2,7-naphthalenedicarbaldehyde (**6**), generated the macrocycles **7a–c**.[9] The compounds **7a–c** were obtained as mixtures of *E,E* and *E,Z* isomers; however, the configuration does not play a role in the subsequent oxidative photocyclization. (The *E,Z* ratio from the cyclization process $\mathbf{5}+\mathbf{6}\rightarrow\mathbf{7}$ decreases with decreasing chain length from 33% for **7a**, to 20% for **7b**, and almost 0% for **7c**). The twofold photocyclization in the presence of methyloxirane with iodine as an oxidating agent[10] yielded the bridged [6]helicenes **8a** and **8b**.[11] In **7c** the short polymethylenedioxy chain did not permit the formation of the corresponding helicene.

Even in high dilution photodimerization of **7c** dominated completely and a totally different type of cyclophane **9c** was formed (Scheme 2). To enable a better investigation of the latter reaction, we improved the solubility of the cyclophane by the introduction of two dodecyloxy groups and optimized the reaction conditions for the photodimerization. Cyclophane **9d**[12] was then obtained from **7d** in high yields. The dimerization reaction was also observed in competition to the photocyclization of **7b**, but to a smaller extent, while the dimerization of **7a** did not occur.

It was possible to enrich the enantiomers of **8a** and **8b** by chromatography on silica gel doped with the Newman reagent (*R*)-(−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminoxy)propionic acid ((*R*)-(−)-TAPA).[13] The (*M*)-(−)-configuration forms weaker complexes with (*R*)-(−)-TAPA and was eluted first. The first-order kinetics for the racemization were determined by the measurement of the optical rotation $[\alpha]_D$ in 1,2,4-trichlorobenzene. Linear regression led to determination of the rate constant k_{rac} and the half-life $t_{1/2} = k_{rac}^{-1} \times$

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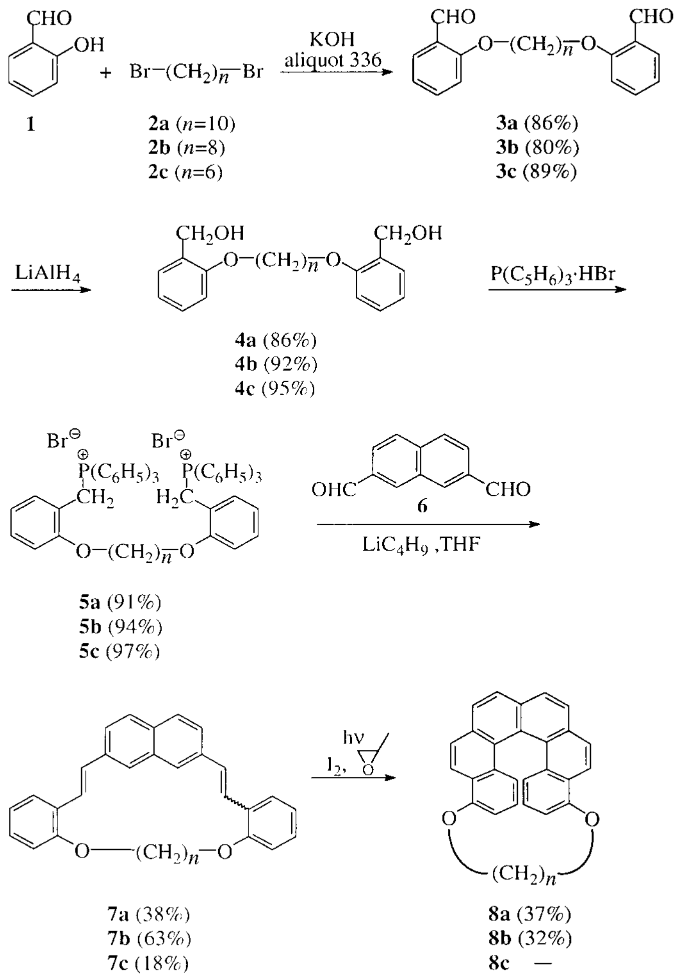
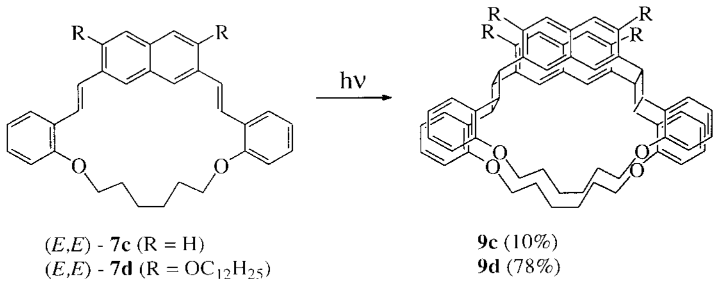
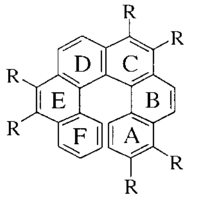


Scheme 1. Synthesis of the hexahelicenophanes **8a** and **8b**.



Scheme 2. Photodimerization of **7c** and **7d**.

ln2. The rate constants for the racemization reactions were determined at constant temperatures of 200, 180, 160, 150, 140, 130, and 120 °C, and by application of the Arrhenius equation, $\ln k_{rac} = f(1/T)$, the activation energy E_a could be calculated. In an analogous manner, application of the Eyring equation gave the $\Delta G^{\ddagger}$ values. Table 1 summarizes these parameters together with the results for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. For comparison the data for the racemization of the unsubstituted [6]helicene **8d** were determined under the same conditions.



8d (R = H)
8e (R = OC_6H_{13})

Table 1. Kinetic parameters for the racemization of the [6]helicenes **8a**, **8b**, and **8d** in 1,2,4 trichlorobenzene.[a]

Compd	E_a [kJ mol^{-1}]	ln$A$	$\Delta G^{\ddagger}$ [kJ mol^{-1}]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J K^{-1}mol^{-1}]	$t_{1/2}$ [min]
8d[14, 15]	148.1	27.9	156.3	144.2	– 25.6	106
8a	143.7	29.0	147.7	139.8	– 16.7	12
8b	116.7	24.7	137.3	112.8	– 51.8	0.8

[a] The values for $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $t_{1/2}$ refer to the reaction at 200 °C. The relative error in the determination of the parameters is ±6%, but for $\Delta S^{\ddagger}$ it can be somewhat higher.

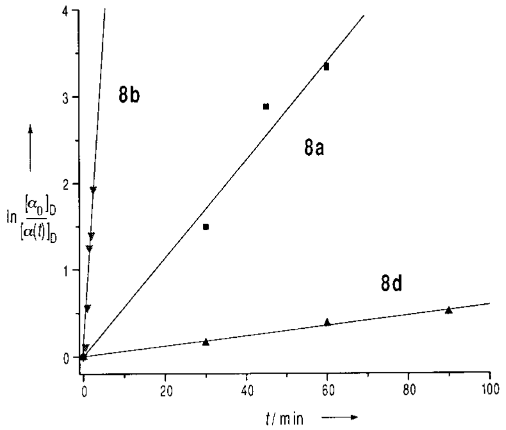


Figure 1. Rate of racemization of the helicenophanes **8a** and **8b** in 1,2,3-trichlorobenzene at 200 °C relative to that of [6]helicene **8d**.

Figure 1 demonstrates impressively the influence of the bridges on the rate of racemization; k_{rac} increases drastically with chain length. However, this effect is not representative for alkoxy-substituted [6]helicenes; compound **8e** has a half-life $t_{1/2}$ which is more than twice as long as that of the unsubstituted **8d** under the conditions mentioned above.[16] Normally, alkoxy substituents decelerate the racemization, and the acceleration for **8a** and **8b** is therefore a result of the cyclophane structure!

To interpret this unexpected effect, we performed an X-ray analysis of **8a** and **8b** (Figure 2). The helical structure of the compounds **8** becomes apparent from the increasing twist

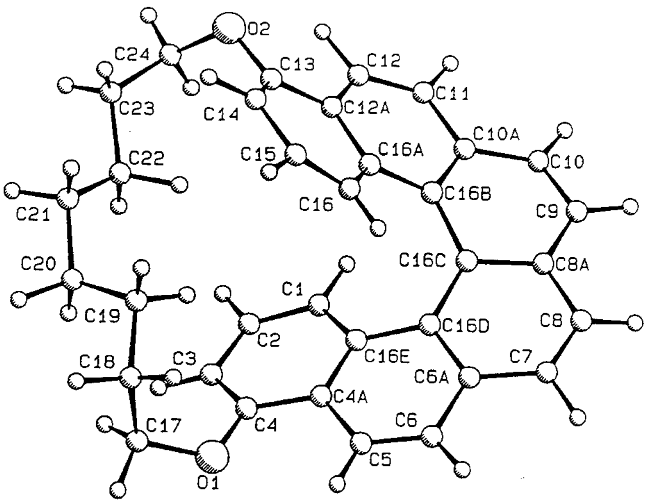


Figure 2. Molecular structure of (*M*)-(–)-**8b** in the solid state. The angles between neighboring planes of the benzene rings A–F (values for [6]helicene[18] are given in parentheses) are: AB: 12.9° (9.8); BC: 11.4° (15.2°); CD: 16.2° (14.4°); DE: 17.7° (15.2°); EF: 14.6° (11.5°).

angles along the (averaged) ring planes. The polymethylenedioxy chains clip the terminal benzene rings A and F together in such a way that the centers of the bridges lie on the (formal) C_2 axis. Due to crystal effects there are considerable deviations from C_2 symmetry. This statement is also valid for **8a**, whose crystal structure analysis gave very similar data.[16]

The symmetry of the helicenes changes during the racemization from C_2 in the ground state to C_s in the transition state. This mechanism is in agreement with recent semiempirical and ab initio quantum-mechanical calculations. The experimental $\Delta H^{\ddagger}$ values of [6]helicenes are reproduced best by the AM1 method.[19, 20] Figure 2 shows the strong steric interference of the polymethylenedioxy chains with the terminal rings A and F, especially in the range of the carbon atoms C-3 and C-14. This effect increases the energy of the C_2 ground states and is more pronounced for the shorter chain in **8b** than for the longer chain in **8a**. Figure 3 shows schematically that the bridge can turn aside into the C_s transition state,[21] thus decreasing the energy of the steric interaction.

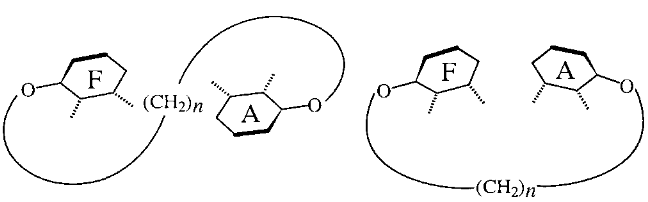


Figure 3. Schematic representation of the bridges between the terminal rings A and F in the C_2-symmetric ground state (left) and the C_s-symmetric transition state (right) of the racemization of **8a** and **8b**.

The drastic lowering of the racemization barrier in going from **8d** to **8a** to **8b** is due to the differences between the steric energies (included in the enthalpy term) of the ground and transition states of the cyclophanes. Moreover, the high negative activation entropy $\Delta S^{\ddagger}$ of **8b** should be noted. The shorter bridge is less flexible and has a lower probability for the turn.

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[9] **7a**: M.p. 211 °C; *E,E* configuration: ^{1}H NMR (CDCl$_3$): $\delta = 1.54$ (m, 8H, CH$_2$), 1.75 (m, 4H, CH$_2$), 1.88 (m, 4H, CH$_2$), 4.09 (t, 4H, OCH$_2$), 7.43 (AB, $^3J = 16.7$ Hz, 4H, olefinic H), 7.58 (AB, $^3J = 16.7$ Hz, 4H, olefinic H), 6.90 (d, 2H), 6.95 (t, 2H), 7.21 (t, 2H) 7.45 (d, 2H), 7.60 (d, 2H), 7,76 (d, 2H), 7.88 (s, 2 H) (aromatic H); ^{13}C NMR (CDCl$_3$): $\delta =$ 27.2, 29.8, 30.2, 30.2 (CH$_2$), 68.1 (OCH$_2$), 125.2, 128.8 (olefinic CH), 111.7, 120.5, 124.6, 125.4, 127.9, 128.5, 130.2 (aromatic CH), 126.0, 132.5, 134.0, 136.1, 156.9 (aromatic C$_q$). **7b**: M.p. 266 °C; *E,E* configuration: ^{1}H NMR (CDCl$_3$): $\delta = 1.61$ (m, 4H, CH$_2$), 1.87 (m, 4H, CH$_2$), 1.91 (m, 4H, CH$_2$), 4.03 (t, 4H, OCH$_2$), 7.33 (AB, $^3J = 16.6$ Hz, 2H, olefinic H), 7.74 (AB, $^3J = 16.6$ Hz, 2H, olefinic H), 6.86 (d, 2H), 6.96 (t, 2H), 7.22 (t, 2H), 7.45 (d, 2H), 7.64 (d, 2H), 7.75 (d, 2H), 8.08 (s, 2H) (aromatic H); the ^{13}C NMR data correspond largely to that of **7a**. **7c**: M.p. 260 °C, pure *E,E* configuration, ^{1}H NMR (CDCl$_3$): $\delta = 1.89$ (m, 4H, CH$_2$), 2.00 (m, 4H, CH$_2$), 4.04 (t, 4H, OCH$_2$), 7.14 (AB, $^3J =$ 16.5 Hz, 4H), 8.01 (AB, $^3J = 16.5$ Hz, 4H) (olefinic H), 6.91 (d, 2H) 6.99 (t, 2H), 7.24 (t, 2H), 7.37 (d, 2H), 7.70 (d, 2H), 7.74 (d, 2H), 8.29 (s, 2H) (aromatic H); the ^{13}C NMR data correspond largely to that of **7a.**

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[11] **8a**: M.p. 252 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.41$ (m, 12H, CH$_2$), 1.67 (m, 2H, CH$_2$), 1.99 (m, 2H, CH$_2$), 4.33 (m, 2H, OCH$_2$), 4.50 (m, 2H, OCH$_2$), 6.48 (t, 2H, 2-H), 6.64 (d, 2H, 3-H), 6.90 (d, 2H, 1-H), 7.85 (d, 2H, 6-H), 7.92 (d, 2H, 7-H), 7.97 (d, 2H, 8-H), 8.32 (d, 2H, 5-H); ^{13}C NMR (CDCl$_3$): $\delta = 25.0$, 28.9, 29.0, 29.1 (CH$_2$), 67.0 (OCH$_2$), 107.2 (C-3), 120.7 (C-1), 121.5 (C-5), 123.8 (C-4a), 123.9 (C-2), 124.5 (C-16c), 124.8 (C-6), 126.4 (C-8), 126.6 (C-7), 127.7 (C-16b), 130.8 (C-16a), 131.9 (C-6a), 132.6 (C-8a), 153.9 (C-4); FD-MS: m/z (%) = 498 (100) [M^+]. **8b**: M.p. 243 °C; ^{1}H NMR (CDCl$_3$): $\delta = 1.12$ (m, 4H, CH$_2$), 1.31 (m, 4H, CH$_2$), 1.70 (m, 2H, CH$_2$) 1.82 (m, 2H, CH$_2$), 4.23 (m, 2H, OCH$_2$), 4.56 (m, 2H, OCH$_2$), 6.48 (t, 2H, 2-H), 6.70 (m, 4H, 1-H, 3-H), 7.82 (d, 2H, 6-H), 7.90 (d, 2H, 7-H), 7.95 (d, 2H, 8-H), 8.20 (d, 2H, 5-H); the ^{13}C NMR data correspond largely to that of **8a**; FD-MS: m/z (%) = 470 (100) [M^+].

[12] **9d**: M.p. 225 °C; ^{1}H NMR (CDCl$_3$): $\delta = 0.89$ (t, 12H, CH$_3$), 1.29–2.16 (m, 96H, CH$_2$), 3.69 (t, 8H, OCH$_2$), 3.77 (t, 8H, OCH$_2$), 4.96(AA′BB′, 8H), 5.24 (AA′BB′, 8H) (CH, four-membered ring), 6.21 (s, 4H), 6.64 (d, 4H), 6.82 (t, 4H), 7.06 (t, 4H), 7.31 (d, 4H), 7.80 (s, 4H) (aromatic H); ^{13}C NMR (CDCl$_3$): $\delta = 14.2$–32.0 (CH$_2$), 68.1, 68.2 (OCH$_2$), 37.5, 41.5 (CH, four-membered ring), 103.6, 110.7, 119.5, 126.5, 128.0, 130.1 (aromatic CH), 124.4, 126.4, 130.7. 133.1, 155.7, 157.0 (aromatic C$_q$); FD-MS*:* m/z (%) = 1630 (33) [M^+], 815 (100) [M^{2+}]. The less soluble compound **9c** gives corresponding ^{1}H NMR and MS data.

[13] See F. Mikeš, G. Boshart, E. Gil-Av, *J. Chromatog.* **1997**, *122*, 205–221, and references therein.

[14] In naphthalene the parameters $\Delta G^{\ddagger} = 154.7\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger} = -28.0\,\mathrm{J\,mol^{-1}\,K^{-1}}$, and $\Delta H^{\ddagger} = 141.3\,\mathrm{kJ\,mol^{-1}}$ (T = 205 °C) were determined.[15]

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[17] Crystal structure of **8b**: Enraf-Nonius CAD4 diffractometer, Cu$_{K\alpha}$ radiation: $\lambda = 154$ pm, T = 22 °C, scan-type $\omega/2\theta$, scan range $1.5 \leq \theta \leq 75.0°$, $0 \leq h \leq 22$, $0 \leq k \leq 15$, $0 \leq l \leq 13$, reflections: measured 4962, unique 4962 ($R_{\mathrm{sigma}} = 0.0178$), observed 4855 ($|F|/\sigma(F) > 4.0$), Lorentz and polarization correction, structure solution: SIR-92, refinement: SHELXL-93, 348 refined parameters, weighting scheme: $W = 1/[\sigma^2F_o^2 + (0.0860\,P)^2 + 0.32\,P]$ with $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$, hydrogen atoms were located from difference Fourier maps and refined isotropically assuming riding motion, other atoms were refined anisotropically; $\omega R_2 = 0.1229$ ($R^1 = 0.0423$ for observed reflections, 0.0431 for all reflections), goodness of fit $S = 1.032$, extinction $g = 0.0050(4)$, largest peak in difference Fourier synthesis −0.18, 0.33 e Å^{-3}. C$_{34}$H$_{30}$O$_2$, $M_r = 470.58$, orthorombic, space group $Pna2_1$, $a = 18.1447(4)$, $b = 12.3799(3)$, $c = 10.8228(3)$ Å, $V = 2431.1(1)$ Å^3, $Z = 4$, $F(000) = 1000$, $\rho_{\mathrm{calcd}} = 1.286\,\mathrm{g\,cm^{-3}}$, crystal dimensions: 0.320 × 0.512 × 0.512 mm^3. Crystallographic data (without structure factors) for the structures reported in this publication have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-408279. 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).

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[21] Force field calculations (PC Model 4.0, Serena Software)[16] are in accordance with models.

Nonclassical Metal Carbonyls: Appropriate Definitions with a Theoretical Justification**

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There is a growing class of metal carbonyl compounds with unusually high $\tilde{\nu}$(CO) values.[1–5] Examples are (average values for $\tilde{\nu}$(CO) in parentheses; for free CO: $\tilde{\nu}(CO) = 2143\ cm^{-1}$) $[Cu(CO)_2][AsF_6]$ ($2171\ cm^{-1}$),[6] $[Ag(CO)_2][Nb(OTeF_5)_6]$ ($2208\ cm^{-1}$),[7] $[Au(CO)_2][Sb_2F_{11}]$ ($2236\ cm^{-1}$),[8] $[Hg(CO)_2][Sb_2F_{11}]_2$ ($2280\ cm^{-1}$),[9] and $[Ir(CO)_6][Sb_2F_{11}]_3$ ($2268\ cm^{-1}$).[10] There is a concensus that these and other high $\tilde{\nu}$(CO) values are due to greatly diminished π backbonding for late transition metal $[M(CO)_n]^{m+}$ species.[2-5, 11–20] For the vast majority of metal carbonyl complexes (i.e., *classical* metal carbonyl complexes), the effect of π backbonding to lower $\tilde{\nu}$(CO) below $2143\ cm^{-1}$ more than compensates for the factors that tend to raise $\tilde{\nu}$(CO) above $2143\ cm^{-1}$, such as σ bonding and/or the positive charge on the metal center.[2–5] Nevertheless, a $\tilde{\nu}$(CO) value greater than $2143\ cm^{-1}$ can occur for two distinguishable situations: 1) negligible or relatively minor M→CO π backbonding (i.e., *nonclassical* behavior) or 2) π backbonding that is *significant* (i.e., classical behavior) *but insufficient* to lower $\tilde{\nu}$(CO) below $2143\ cm^{-1}$.[2] The two situations are illustrated in Figure 1,[2] which was adapted from theoretical results in the literature.[19, 20]

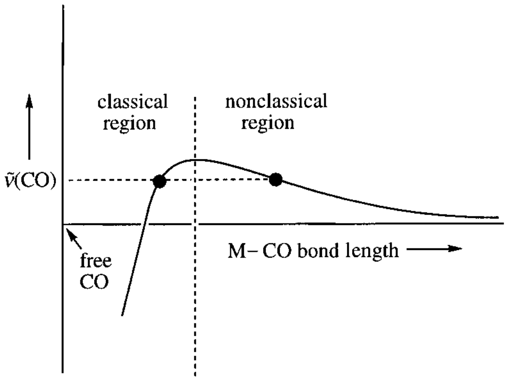

Figure 1. Separation of classical and nonclassical metal carbonyls based on their position relative to the $\tilde{\nu}$(CO) vs. M–C curve maximum. The circles represent equilibrium geometries for a hypothetical classical metal carbonyl (left circle, $\partial(\tilde{\nu}(CO))/\partial((M-C) > 0)$ and for a hypothetical nonclassical metal carbonyl (right circle, $\partial(\tilde{\nu}(CO))/\partial((M-C) < 0)$. Note that both complexes have the same $\tilde{\nu}$(CO) value, which is greater than $2143\ cm^{-1}$. The difference in M–C values for the two complexes is not to scale.

According to this model, two different complexes with different bonding characteristics can have the same unusually high $\tilde{\nu}$(CO) value. A related distinction between classical and nonclassical behavior, based on new theoretical results, will be discussed below. Nevertheless, it is often convenient to use a definition based on a simple experimental observable, so that the experimentalist can decide in "real time" whether to further modify a new metal complex for a particular application. Therefore, some workers have referred to *all* metal carbonyl complexes with $\tilde{\nu}(CO)_{av} > 2143\ cm^{-1}$ as nonclassical, a definition that can be simply applied once vibrational spectra of a new compound are recorded ($\tilde{\nu}(CO)_{av}$ is the average over all C–O stretching normal modes, weighted according to their degeneracies).

Aubke, Willner, and co-workers have recently argued that "as smooth correlations between the formal charge on the metal and the bonding characteristics in the CO ligands emerge, it becomes increasingly obvious that any arbitrary subdivision using vague terms like "classical" and "nonclassical (σ-only)" carbonyl complexes as proposed sometime ago for the thermally unstable $[Ag(CO)_n]^+$ ($n = 1$, 2) species is incorrect, inappropriate, and unnecessary. The first metal carbonyl derivative $[Pt(CO)_2Cl_2]$ reported in 1868 with an average $\tilde{\nu}_{CO}$ value of $2175\ cm^{-1}$ [well above that ($2143\ cm^{-1}$) for free CO] would be assigned "nonclassical," which is in our view absurd."[10] It is historically ironic, but hardly absurd, that the very first carbonyl complex has an average $\tilde{\nu}$(CO) value higher than that of free CO, while more than 95 % of the metal carbonyls which were subsequently studied have average $\tilde{\nu}$(CO) values less than $2143\ cm^{-1}$. Since the ordering of metal carbonyls as classical or nonclassical is not a historical classification, it is irrelevant if the first carbonyl complex ever synthesized belongs to one or the other category.

Herein we present computational evidence that the metal–carbon bonds in the d^{10} $D_{\infty h}$ dicarbonyl species $[Rh(CO)_2]^-$, $[Pd(CO)_2]$, $[Cu(CO)_2]^+$, and $[Au(CO)_2]^+$ are fundamentally different than the metal–carbon bonds in the isoelectronic, isoleptic, and isostructural species $[Ag(CO)_2]^+$, $[Zn(CO)_2]^{2+}$, $[Cd(CO)_2]^{2+}$, and $[Hg(CO)_2]^{2+}$. Based on this fundamental difference, two categories of metal carbonyls are clearly warranted (no matter what they are called). It is our hope that the distinction we now report will cause chemists to think in new ways and, most importantly, to discover new chemistry. Note that there is spectroscopic and/or structural data for four of the eight $D_{\infty h}$ dicarbonyl species we have studied: $[Cu(CO)_2]^+$,[6] $[Ag(CO)_2]^+$,[7] $[Au(CO)_2]^+$,[8] and $[Hg(CO)_2]^{2+}$.[9]

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