Le Bas, A. Navaza, C. de Rango, *Bull. Soc. Chim. Belg.* **1979**, *88*, 863–870.

[19] S. Grimme, S. D. Peyerimhoff, *Chem. Phys.* **1996**, *204*, 411–417.

[20] R. H. Janke, G. Haufe, E.-U. Würthwein, J. H. Borkent, *J. Am. Chem. Soc.* **1996**, *118*, 6031–6035.

[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**

Anthony J. Lupinetti, Gernot Frenking,* and Steven H. Strauss*

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 $M \rightarrow CO$ 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]

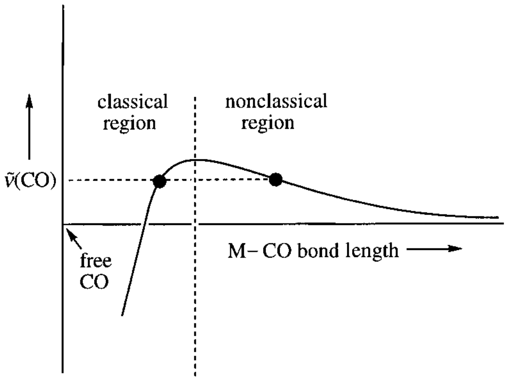


Figure 1. Separation of classical and nonclassical metal carbonyls based on their position relative to the $\tilde{\nu}(CO)$ vs. M–C curve maximum. The circles represent equilibrium geometries for a hypothetical classical metal carbonyl (left circle, $\partial(\tilde{\nu}(CO))/\partial((M-C) > 0)$ and 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]

---

[*] Prof. Dr. G. Frenking
Fachbereich Chemie der Universität
Hans-Meerwein-Strasse, D-35032 Marburg (Germany)
Fax: (+49) 6421-282-189
E-mail: Frenking@ps1515.chemie.uni-marburg.de

Prof. S. H. Strauss, A. J. Lupinetti
Department of Chemistry, Colorado State University
Fort Collins, CO 80523 (USA)
Fax: (+1) 970-491-1801
E-mail: Strauss@chem.colostate.edu

[**] This work was supported by the U.S. NSF (CHE-9628769), the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie. We acknowledge the excellent service and generous allotment of computer time of the HRZ Marburg.

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 1998 1433-7851/98/3715-2113 $ 17.50+.50/0

Our approach was to monitor the effect of two F^- ions placed 3 Å away from the metal centers of the dicarbonyl complexes listed above. The pair of F^- ions was added to each $D_{\infty h}$ $[M(CO)_2]^n$ complex so that the $M\cdots F^-$ vectors were orthogonal to the M–C vectors, and the entire $[M(CO)_2(F)_2]^{n-2}$ fragment was planar (D_{2h} symmetry; Figure 2). The hard base F^- was selected to model the weak $M\cdots F^-$ interactions that exist in crystals of $[Ag(CO)_2][B(OTeF_5)_4]$[7, 21] and $[Hg(CO)_2][Sb_2F_{11}]_2$[9] and that are presumed to exist in other late transition metal dicarbonyl species such as $[Cu(CO)_2][AsF_6]$ and $[Au(CO)_2][Sb_2F_{11}]$. Note that one of the three unique $[Ag(CO)_2]^+$ ions in $[Ag(CO)_2][B(OTeF_5)_4]$ interacts with two fluorine atoms from different $B(OTeF_5)_4^-$ ions such that the centrosymmetric $[Ag(CO)_2(F)_2]$ moiety is planar with an $Ag\cdots F$ distance of 3.02(1) Å and an F-Ag-C angle of 70.4(9)° (the sum of van der Waals radii for silver and fluorine is about 3.2 Å).[7, 21] It does not matter that some of the $[M(CO)_2(F)_2]$ moieties in this study are unknown species at the time of this writing; our objective was to create a set of homologous $[M(CO)_2]^n$ and $[M(CO)_2(F)_2]^{n-2}$ complexes and to study the effect of changing the metal on the M–C and C–O bond lengths.

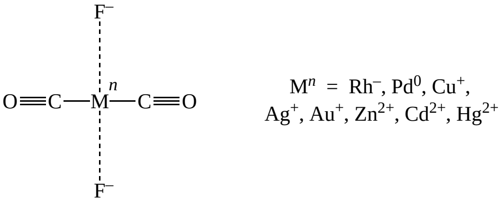


Figure 2. Calculated geometry for the D_{2h}-symmetric complexes $[M(CO)_2(F)_2]^{n-2}$.

Table 1. Calculated distances and symmetric carbon–oxygen stretching frequencies for D_{2h} $[M(CO)_2(F)_2]^{n-2}$ species.[a]

M	M–F [Å]	M–C [Å]	C–O [Å]	$\tilde{\nu}_{sym}$(CO) [cm^{-1}]
Rh^-	∞	1.901	1.182	2019
Rh^-	3	1.797	1.241	1817
Pd^0	∞	1.942	1.156	2112
Pd^0	3	1.924	1.167	2046
Cu^+	∞	1.884	1.142	2196
Cu^+	3	1.850	1.148	2164
Ag^+	∞	2.160	1.142	2184
Ag^+	3	2.196	1.147	2152
Au^+	∞	2.007	1.142	2201
Au^+	3	1.983	1.148	2164
Zn^{2+}	∞	2.011	1.140	2187
Zn^{2+}	3	2.046	1.142	2182
Cd^{2+}	∞	2.228	1.140	2185
Cd^{2+}	3	2.365	1.143	2176
Hg^{2+}	∞	2.126	1.139	2195
Hg^{2+}	3	2.725	1.148	2138

[a] Calculated values of the free CO molecule: $\tilde{\nu}_{sym}(CO) = 2118$ cm^{-1}, C–O = 1.151 Å.

Table 2. Summary of the results of the calculations on $[M(CO)_2]^n$ and $[M(CO)_2(F)_2]^{n-2}$.[a]

Group 9	Group 10	Group 11	Group 12
		Cu^+ Δ(C–O) = 0.006 Å Δ(M–C) = −0.034 Å	Zn^{2+} Δ(C–O) = 0.002 Å Δ(M–C) = 0.035 Å
Rh^- Δ(C–O) = 0.059 Å Δ(M–C) = −0.104 Å	Pd^0 Δ(C–O) = 0.011 Å Δ(M–C) = −0.018 Å	Ag^+ Δ(C–O) = 0.005 Å Δ(M–C) = 0.036 Å	Cd^{2+} Δ(C–O) = 0.003 Å Δ(M–C) = 0.136 Å
		Au^+ Δ(C–O) = 0.006 Å Δ(M–C) = −0.024 Å	Hg^{2+} Δ(C–O) = 0.009 Å Δ(M–C) = 0.599 Å

[a] Δ(C–O) and Δ(M–C) are the differences of the C–O and M–C bond lengths between $[M(CO)_2(F)_2]^{n-2}$ ($M\cdots F^- = 3$ Å) and $[M(CO)_2]^n$ ($M\cdots F^- = \infty$).

The geometry optimizations and frequency calculations were carried out in the gas phase at the MP2 level of theory. For each metal atom, the quasi-relativistic, small-core, effective-core potential (ECP) developed by Stoll and Preuss with a (311111/22111/411) valence shell basis set was used.[22, 23] A 6-31G(d) basis set was used for C, O, and F atoms. The calculations were carried out using the program package Gaussian 94.[24] All bond lengths were optimized except for the $M\cdots F^-$ distances, which were fixed at either 3 Å or ∞ (for infinite $M\cdots F^-$ distances the fluoride-free $[M(CO)_2]^n$ species were studied). The $M\cdots F^-$ distances were intentionally fixed at exactly 3 Å for all of the $[M(CO)_2(F)_2]^{n-2}$ species so that all of the $[M(CO)_2]^n$ species would be subject to the same perturbation by the two F^- ions. It was not our intention to calculate the equilibrium $M\cdots F^-$ distances for the different complexes.

The calculated bond lengths and wavenumbers are listed in Table 1, the changes in the C–O and M–C bond lengths in Table 2. The C–O bond length increased in all cases when the two F^- ions were added to the metal dicarbonyl complexes. However, the same ligand-field perturbation *decreased* the M–C bond length for $[Rh(CO)_2]^-$, $[Pd(CO)_2]$, $[Cu(CO)_2]^+$, and $[Au(CO)_2]^+$ but *increased* the M–C bond length for the other four complexes. The decreases in M–C bond lengths for the rhodium(−I), palladium(0), copper(I), and gold(I) complexes are indicative of metal carbonyl complexes with significant π backbonding. The presence of the F^- ions leads to a less positive (or more negative) effective charge on the metal centers, which should weaken the $M \leftarrow CO$ σ bonds (as well as decrease the $M\cdots CO$ electrostatic attraction[20]) but should strengthen the $M \rightarrow CO$ π bonds (i.e., the F^- ions induce a significant amount of *additional* π backbonding between the metal ion and the CO ligands). The decrease in the M–C distance strongly suggests that the M–CO bonds in the species $[Rh(CO)_2(F)_2]^{3-}$, $[Pd(CO)_2(F)_2]^{2-}$, $[Cu(CO)_2(F)_2]^-$, and $[Au(CO)_2(F)_2]^-$ are *stronger* than in the parent dicarbonyl complexes $[Rh(CO)_2]^-$, $[Pd(CO)_2]$, $[Cu(CO)_2]^+$, and $[Au(CO)_2]^+$, respectively. Therefore, for these four d^{10} metal dicarbonyl complexes, the fluoride-ion perturbation resulted in an increase in $M \rightarrow CO$ π backbonding that more than offset the decrease in $M \leftarrow CO$ σ bonding or the change in the $M\cdots CO$ electrostatic interaction.

In contrast, the M–C bond lengths for the silver(I), zinc(II), cadmium(II), and mercury(II) species *increased* as the $M\cdots F$ distance decreased from ∞ to 3 Å, indicating that the M–C bonds in these $[M(CO)_2(F)_2]^{n-2}$ species are probably *weaker* than in the corresponding parent dicarbonyl cations. As above, the presence of the F^- ions lowered the effective charge on the Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+} ions. However, for these metal ions the increase in π backbonding, if any, did not offset the weakening of the $M \leftarrow CO$ σ bonds. Therefore, the set of eight parent dicarbonyl complexes $[M(CO)_2]^n$ in Table 2 should be divided into two distinct categories depending on whether $\Delta(M-C)$ is negative (classical behavior; Rh^-, Pd^0, Cu^+, and Au^+) or positive (nonclassical behavior; Ag^+, Zn^{2+}, Cd^{2+}, and Hg^{2+}).

Let us compare the related complexes $[Cu(CO)_2]^+$ and $[Ag(CO)_2]^+$ with and without the pair of F^- ions at 3 Å. In the case of the copper(I) complex, $\Delta(C-O) = 1.148\ \text{Å} - 1.142\ \text{Å} = 0.006\ \text{Å}$ and $\Delta(M-C) = 1.850\ \text{Å} - 1.884\ \text{Å} = -0.034\ \text{Å}$; in the case of the silver(I) complex, $\Delta(C-O) = 1.147\ \text{Å} - 1.142\ \text{Å} = 0.005\ \text{Å}$ and $\Delta(M-C) = 2.196\ \text{Å} - 2.160\ \text{Å} = 0.036\ \text{Å}$. The virtual equivalence of the $\Delta(C-O)$ values for these two systems provides no clue that the metal–carbon bonds respond so differently to the same chemical perturbation. Based on the $\Delta(M-C)$ values, it certainly seems appropriate to place the parent complexes in different categories, classical for $[Cu(CO)_2]^+$ and nonclassical for $[Ag(CO)_2]^+$. Note that $[Cu(CO)_2]^+$ is classical by the $\Delta(M-C)$ definition even though the calculated value of $\tilde{\nu}_{sym}(CO)$, at $2195\ cm^{-1}$, is much higher than the calculated value for free CO, $2118\ cm^{-1}$ (the experimental values for $\tilde{\nu}_{sym}(CO)$ and $\tilde{\nu}_{asym}(CO)$ for $[Cu(CO)_2][AsF_6]$ are 2177 and $2164\ cm^{-1}$, respectively[6]). This observation provides additional justification for the concept shown graphically in Figure 1.

It is important to note that our results should only be used to interpret the magnitude of *changes* in the amounts of σ and π bonding for a given system, not the absolute amounts of σ and π bonding in a given complex. The fact that $\Delta(M-C)$ is negative for $[Cu(CO)_2]^+$ and positive for $[Ag(CO)_2]^+$ means that these two complexes should be categorized as classical and nonclassical metal carbonyl complexes, respectively. Our results do not indicate that there is zero π backbonding in $[Ag(CO)_2]^+$, only that charge and σ effects outweigh any π effects. The behavior of $[Cu(CO)_2]^+$ (classical) and $[Ag(CO)_2]^+$ (nonclassical), as probed by the fluoride-ion perturbation, is consistent with other theoretical[20] and experimental[25] results.

Finally, let us compare the four d^{10} complexes of the fifth period $[Rh(CO)_2]^-$, $[Pd(CO)_2]$, $[Ag(CO)_2]^+$, and $[Cd(CO)_2]^{2+}$. The monotonic trends in the C–O distances at $M \cdots F = \infty$ (1.182, 1.156, 1.142, and 1.140 Å, respectively), $\tilde{\nu}_{sym}(CO)$ at $M \cdots F = \infty$ (2019, 2112, 2184, and $2185\ cm^{-1}$, respectively), $\Delta(C-O)$ (0.059, 0.011, 0.005, and 0.003 Å, respectively), and $\Delta\tilde{\nu}_{sym}(CO)$ (-202, -66, -32, and $-9\ cm^{-1}$, respectively) mask the more significant result that $\Delta(M-C)$ is *negative* for $[Rh(CO)_2]^-$ and $[Pd(CO)_2]$ but *positive* for $[Ag(CO)_2]^+$ and $[Cd(CO)_2]^+$. The "smooth correlation" in the C–O bond lengths and $\tilde{\nu}(CO)$ values is smooth only because weakening the $M \leftarrow CO$ σ bond and strengthening the $M \rightarrow CO$ π bond *both* cause the C–O distance to increase and $\tilde{\nu}(CO)$ to decrease regardless of whether the complex is classical or nonclassical.

The distinction between classical and nonclassical metal carbonyls based on $\Delta(M-C)$ is unequivocal, nonarbitrary, and chemically relevant. In the former category, the change in $M \rightarrow CO$ π backbonding due to the fluoride-ion perturbation has a larger effect on the M–C bond than the offsetting but less significant change in $M \leftarrow CO$ σ bonding or the change in the ionic component of the M–CO bond. In the latter category, the opposite is true. However, this appropriate definition will be difficult (at least) for the experimentalist to apply routinely. For this very important practical reason, neither we nor other chemists should object to the continued use of the definition that nonclassical metal carbonyls exhibit $\tilde{\nu}(CO)_{av} > 2143\ cm^{-1}$. The $\tilde{\nu}(CO)$ definition, although arbitrary and equivocal, is appropriate in a very important way. A $\tilde{\nu}(CO)_{av}$ value $> 2143\ cm^{-1}$ should put the chemist on alert that the compound under study deserves very careful scrutiny; if nothing else, it is "in the range" where unusual (i.e., not usual = not classical = nonclassical) behavior such as $\Delta(M-C) > 0$ *can* occur.

Other definitions[2] of "nonclassical metal carbonyl" can and undoubtedly will be conceived and tested by other researchers. It is expected that further experimental and theoretical work will lead to new surprises, new insights, and new debates about the metal–carbon bonds in metal carbonyls with $\tilde{\nu}(CO)_{av}$ values $> 2143\ cm^{-1}$.

Received: November 3, 1997 [Z11114IE]
German version: *Angew. Chem.* **1998**, *110*, 2229–2232

Keywords: ab initio calculations · carbonyl complexes · pi interactions · transition metals

---

[1] F. Aubke, *Abstract INORG-205, 215th American Chemical Society National Meeting*, Dallas, TX, 1998.
[2] S. H. Strauss, *Chemtracts:Inorg. Chem.* **1997**, *10*, 77–103.
[3] J. E. Ellis, W. Beck, *Angew. Chem.* **1995**, *107*, 2695–2697; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2489–2491.
[4] L. Weber, *Angew. Chem.* **1994**, *106*, 1131–1133; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1077–1078.
[5] F. Aubke, C. Wang, *Coord. Chem. Rev.* **1994**, *137*, 483–524.
[6] J. J. Rack, J. D. Webb, S. H. Strauss, *Inorg. Chem.* **1996**, *35*, 277–278.
[7] P. K. Hurlburt, J. J. Rack, J. S. Luck, S. F. Dec, J. D. Webb, O. P. Anderson, S. H. Strauss, *J. Am. Chem. Soc.* **1994**, *116*, 10003–10014.
[8] H. Willner, J. Schaebs, G. Hwang, F. Mistry, R. Jones, J. Trotter, F. Aubke, *J. Am. Chem. Soc.* **1992**, *114*, 8972–8980.
[9] H. Willner, M. Bodenbinder, C. Wang, F. Aubke, *J. Chem. Soc. Chem. Commun.* **1994**, 1189–1190.
[10] C. Bach, H. Willner, C. Wang, S. J. Rettig, J. Trotter, F. Aubke, *Angew. Chem.* **1996**, *108*, 2104–2106; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1974–1976.
[11] C. D. Desjardins, D. B. Edwards, J. Passmore, *Can. J. Chem.* **1979**, *57*, 2714–2715.
[12] M. Pasquali, C. Floriani, A. Gaetani-Manfredotti, *Inorg. Chem.* **1981**, *20*, 3382–3388.
[13] F. Calderazzo, *J. Organomet. Chem.* **1990**, *400*, 303–320.
[14] L. A. Barnes, M. Rosi, C. W. Bauschlicher, *J. Chem. Phys.* **1990**, *93*, 609–624.
[15] A. Veldkamp, G. Frenking, *Organometallics* **1993**, *12*, 4613–4622.
[16] E. I. Solomon, P. M. Jones, J. A. May, *Chem. Rev.* **1993**, *93*, 2623–2644.
[17] M. A. Lynn, B. E. Bursten, *Inorg. Chim. Acta* **1995**, *229*, 437–443.
[18] A. S. Goldman, K. Krogh-Jespersen, *J. Am. Chem. Soc.* **1996**, *118*, 12159–12166.
[19] D. E. Sherwood, M. B. Hall, *Inorg. Chem.* **1983**, *22*, 93–100.
[20] A. J. Lupinetti, S. Fau, G. Frenking, and S. H. Strauss, *J. Phys. Chem.* **1997**, *101*, 9551.
[21] P. K. Hurlburt, J. J. Rack, S. F. Dec, O. P. Anderson, S. H. Strauss, *Inorg. Chem.* **1993**, *32*, 373–374.
[22] M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phys.* **1987**, *86*, 866–872.

[23] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123–141.

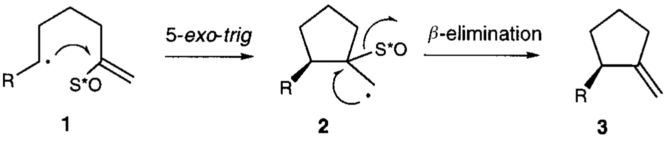
[24] Gaussian 94: M. J. Frish, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomberts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. DeFrees, I. Baker, J. J. P. Stewart, Head-Gordon, M., C. Gonzalez, Pople, J. A., Eds., Gaussian Inc.: Pittsburgh, PA, **1995**.

[25] J. J. Rack, S. H. Strauss, *Catal. Today* **1997**, *36*, 99.

Radical Cyclization/β-Elimination Tandem Reactions: Enantiopure Sulfoxides as Temporary Chiral Auxiliaries[**]

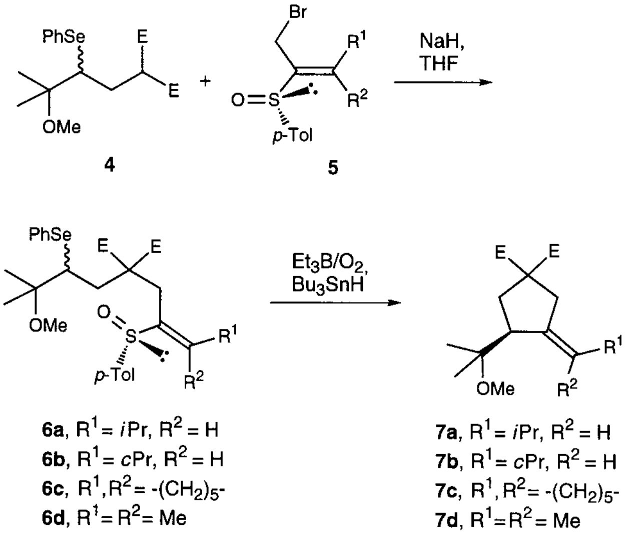
Emmanuel Lacôte, Bénédicte Delouvrié, Louis Fensterbank, and Max Malacria[*]

Owing to their compatibility with a large number of interesting functionalities and their occasionally high efficiency, diastereoselective radical cyclizations now represent a strategy of choice in the field of asymmetric synthesis.[1, 2] Notably, the addition of a carbon-centered (alkyl or vinyl) radical to an alkene moiety bearing a chiral auxiliary has been well studied, and generally higher diastereoselectivities are obtained when the addition occurs in the position α to the chiral auxiliary.[3] Nonetheless, good to excellent β-diastereoselectivities have also been observed,[4] the use of Lewis acids being critical in the case of chiral acrylates[5] and oxazolidinones amides.[6] Continuing our interest in chiral sulfur-based auxiliaries (sulfoxides[4c] and sulfinimines[7]), we have proposed the tandem reaction depicted in Scheme 1 as a new means for the preparation of enantiomerically enriched five-membered rings. We anticipated a highly diastereoselective radical cyclization (with an a priori quite favorable α-selectivity), followed by the well-documented elimination of β-sulfinyl radicals.[8]



Scheme 1. Proposed new tandem reaction. S*O = homochiral sulfoxide auxiliary

This approach, which relies on the easy introduction and the low cost of the homochiral sulfoxide unit, was first tested with **6a**, which is easily prepared by coupling of malonate **4**[9] and the known enantiopure *E* allylic bromide **5a** (Scheme 2).[10] Under low-temperature radical cyclization conditions (Et_3B/O_2),[11] **6a** underwent an exclusive *anti*-Michael 5-*exo-trig* radical cyclization to afford the cyclopentyl derivative **7a** in 60% yield (Table 1, entry 1). The substitution of the vinyl sulfoxide at the β-position is sufficient here to preclude the 6-*endo-trig* mode of cyclization. Moreover, no cyclopentyl derivative incorporating the sulfoxide moiety was observed, which confirmed the efficiency of the β-elimination of the sulfoxide auxiliary. The promising stereoselectivity of this sequence (54% *ee*) was equally interesting.[12]



Scheme 2. Synthesis of the precursors **6** and the subsequent radical tandem reactions. E = CO_2Me

Table 1. Results of the tandem reaction (yields and stereoselectivity)

Entry	Precursor	T [°C]	Lewis acid	Product, yield [%][a]	*ee* [%],[12] abs. config.[b]
1	**6a**	−78	–	**7a**, 60	54, *S*
2	**6b**	−78	–	**7b**, 52[c]	48, *S*
3	**6b**	0	–	**7b**, 90	42, *S*
4	**6b**	0	MAD	**7b**, 46	64, *R*
5	**6c**	−40	–	**7c**, 62	88, *S*
6	**6c**	0	–	**7c**, 77	86, *S*
7	**6d**	−78	–	**7d**, 72	>96, *S*
8	**6d**	−40	–	**7d**, 70	>96, *S*
9	**6d**	0	–	**7d**, 93	>96, *S*
10	**6d**	0	Et_2AlCl	**7d**, 63	60, *S*
11	**6d**	0	MAD	**7d**, 52	92, *R*

[a] See the Experimental section. [b] The absolute configuration of **7d** was determined by a CD measurement.[16] Ozonolysis of **7a–c** afforded ketone **9** with positive specific rotations as found for **7d**, which also suggests a mainly *S* configuration for **7a–c**. [c] Starting material (38%) was recovered.

---

[*] Prof. Dr. M. Malacria, E. Lacôte, B. Delouvrié, Dr. L. Fensterbank
Laboratoire de Chimie Organique de Synthèse, associé au CNRS
Université Pierre et Marie Curie
4, place Jussieu, Tour 44–54, Case 229
F-75252 Paris Cedex 05 (France)
Fax: (+33) 1-44-27-73-60
E-mail: malacria@ccr.jussieu.fr

[**] Acknowledgment is made to the Ministère de l'Education Nationale and the CNRS. The authors thank Professor Philippe Renaud (Université de Fribourg), Dr. Pierre Mangeney, and Professor Alexandre Alexakis (Université Pierre et Marie Curie) for helpful discussions, Dr. Karin Schein for experimental assistance, Dr. Serge Thorimbert (Université Pierre et Marie Curie) for assistance with chiral GC analysis, and Dr. René Thouvenot (Université Pierre et Marie Curie) for ^{31}P NMR measurements.