

Coordination of CO to the Alkaline Earth Metallocene $[(\text{Me}_5\text{C}_5)_2\text{Ca}]^{**}$

Peter Selg, Hans H. Brintzinger,*
Richard A. Andersen,* and István T. Horváth*

*Dedicated to Professor Richard R. Schmidt
on the occasion of his 60th birthday*

Compared to the countless transition metal carbonyl complexes, in which CO acts as a π acceptor for d electrons on the metal center, CO coordination to main group compounds has been observed in a few instances only. A gas-phase species HCO^+ has been found to have its $\nu(\text{CO})$ absorption at 2184 cm^{-1} .^[1] Diborane reacts with CO to give a volatile complex $[\text{H}_3\text{B-CO}]$ with $\nu(\text{CO}) = 2165\text{ cm}^{-1}$.^[2] Microwave spectroscopy yields a dipole moment of 1.8 D for this molecule,^[3] consistent with the charge distribution $[\text{H}_3\text{B}^- - \text{C}\equiv\text{O}^+]$.^[4] Me_3Al was found to form a complex $[\text{Me}_3\text{Al-CO}]$ with $\nu(\text{CO}) = 2185\text{ cm}^{-1}$ in a CO matrix at 15–35 K.^[5] The increase of $\nu(\text{CO})$ above that of free CO (2143 cm^{-1})^[6] in all of these complexes indicates that CO is acting solely as a σ -donor ligand here. In $[\text{Me}_2\text{Si-CO}]$ and $[(\text{Me}_5\text{C}_5)_2\text{Si-CO}]$,^[7, 8] on the other hand, $\nu(\text{CO})$ is decreased to 1962 and 2065 cm^{-1} , respectively, consistent with a π -donor action of these divalent silicon species. Apart from low-temperature matrix studies,^[9] CO coordination to alkaline earth compounds has not been reported so far. Here, we describe evidence

[*] Prof. Dr. H. H. Brintzinger, Dipl.-Chem. P. Selg
Fakultät für Chemie der Universität
D-78434 Konstanz (Germany)
Telefax: Int. code + (7531)883137

Prof. Dr. R. A. Andersen
Department of Chemistry and
Chemical Science Division of Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720 (USA)
Telefax: Int. code + (510)642-8369

Dr. I. T. Horváth
Corporate Research Science Laboratories
Exxon Research and Engineering Company
Annandale, NJ 08801 (USA)
Telefax: Int. code + (908)730-3042

[**] This work was supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemische Industrie, and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy, under contract DE-AC03-76SF00098. R. A. A. thanks the Alexander-von-Humboldt Foundation for a Senior Scientist Award.

for the formation of the first carbonyl complex of an organo alkaline earth molecular compound, $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$.

When a solution of $[(\text{Me}_5\text{C}_5)_2\text{Ca}]^{[11]}$ in toluene is exposed to CO pressures of 2.5–70 bar in an elevated-pressure IR cell,^[12] a new $\nu(\text{CO})$ absorption appears at 2158 cm^{-1} . The appearance of this band, as well as its loss in intensity upon release of CO pressure, is practically instantaneous; repeated measurements at any given pressure show that these changes are reversible. Figure 1 shows the IR spectrum as a function of CO pressure at 10°C . It is apparent that the change in absorbance at 2158 cm^{-1} , $\Delta E(2158)$, is a suitable measure for the extent of complex formation. A linear Hildebrand–Benesi plot^[13] of $\Delta E(2158)^{-1}$ against

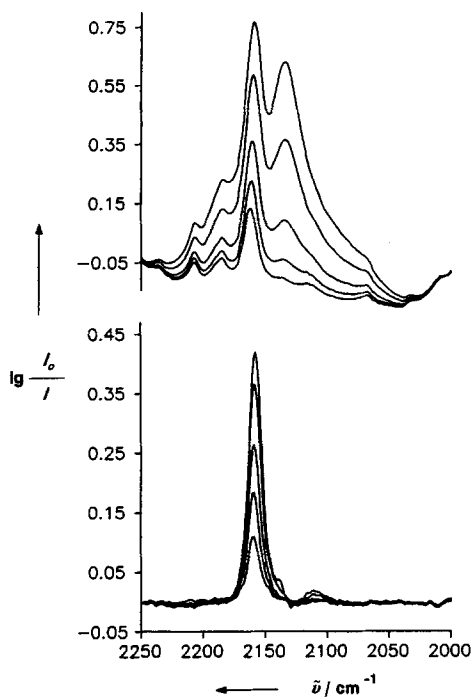
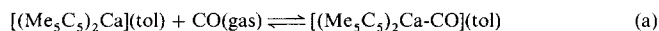
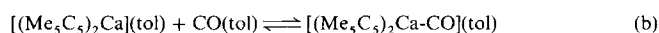


Fig. 1. IR spectra of a $4 \times 10^{-2}\text{ M}$ solution of $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ in toluene at 10°C at CO pressures of 5, 10, 20, 40, and 60 bar; top: Base-line corrected spectra; bottom: Spectra corrected for the absorption of solvent and free CO in solution.

$p(\text{CO})^{-1}$ indicates a stoichiometry $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]^{[14]}$ and an equilibrium constant $K = 0.036\text{ bar}^{-1}$ for the reaction between solvated decamethyl calocene and gaseous CO [Eq. (a)]. Since



the concentration of dissolved CO is proportional to CO pressure, $c(\text{CO}) = p(\text{CO}) \times 7.1 \times 10^{-3}\text{ M bar}^{-1}$, throughout the temperature and pressure range considered here,^[12] a value of $K = 5.1\text{ M}^{-1}$ is obtained for the corresponding reaction involving dissolved CO [Eq. (b)]. IR spectroscopic measurements in the



temperature range of -27 to 32°C give values for the equilibrium constants as summarized in Table 1;^[16] from these, thermodynamic values of $\Delta H_a^\circ = -25 \pm 5\text{ kJ mol}^{-1}$ and $\Delta S_a^\circ = -110 \pm 10\text{ J mol}^{-1}\text{ K}^{-1}$ are obtained for complex formation according to Equation (a), while values of $\Delta H_b^\circ = -25 \pm 5\text{ kJ mol}^{-1}$ and $\Delta S_b^\circ = -70 \pm 10\text{ J mol}^{-1}\text{ K}^{-1}$ are obtained for Equation (b).

Table 1. Temperature dependence of equilibrium constants K for reaction (a) and K for reaction (b) in toluene, as determined by IR spectroscopy (with e.s.d.).

$T/^\circ\text{C}$	+32	+10	+3	-9	-18	-27
K/kbar^{-1}	15(3)	36(8)	51(3)	71(3)	115(14)	127(11)
K/M^{-1}	2.1	5.1	7.2	10.0	16.1	17.9

These data are confirmed by a ^{13}C NMR study at elevated CO pressures.^[17] Solutions of $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ in $[\text{D}_8]\text{toluene}$ under CO pressures up to 80 bar give only one ^{13}C NMR signal each for their C_5 -ring, CH_3 , and CO carbon atoms in the temperature range between $+30$ and -70°C ,^[18] indicating that the exchange of CO is rapid on the NMR time scale. The chemical shifts of these signals change with increasing CO pressure as indicated in Table 2. As changes in chemical shifts, $\Delta\delta$, are a

Table 2. ^{13}C NMR data for $[(\text{Me}_5\text{C}_5)_2\text{Ca}] + \text{CO} \rightleftharpoons [(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$ in $[\text{D}_8]\text{toluene}$ at $T = 31.5^\circ\text{C}$ [a].

$p(\text{CO})/\text{bar}$	$\delta(\text{CH}_3)$	$\delta(\text{C}_5)$	$\delta(\text{CO})$
0	10.39	113.94	184.7 [b]
15	10.53	113.75	183.36
30	10.61	113.62	183.59
50	10.67	113.55	183.80
80	10.72	113.48	183.96
$[(\text{C}_5\text{Me}_5)_2\text{Ca}\cdot\text{CO}]$	10.90(1) [b]	113.19(4) [b]	180.4 [b]

[a] Measured with a JEOL JMN GX 400 spectrometer operated at 96.4 MHz. chemical shifts relative to $\delta(\text{C}_6\text{D}_6\text{CD}_3) = 20.4$. [b] Obtained by least-square analysis from the values observed at $p(\text{CO}) = 15\text{--}80$ bar.

linear function of the mole fractions of free and complexed species, the equilibrium constant K , as well as the limiting values of $\Delta\delta$ for complete complex formation, can be obtained by a least-squares analysis of the essentially linear plots of $\Delta\delta^{-1}$ against $p(\text{CO})^{-1}$. A value of $K = 0.024\text{ bar}^{-1}$ at 31.5°C , obtained in this manner, is in agreement with that derived from the IR data discussed above. A chemical shift of $\delta = 180.4$, determined for CO in $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$, places this CO resonance at higher fields than that of free CO in toluene solution ($\delta = 184.7$). $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$ differs in this regard from transition metal carbonyl complexes with partly filled nd subshells; in these, the CO ligands have their ^{13}C NMR signals at substantially lower fields than the signal of free CO.^[19,20]

With regard to both the ^{13}C chemical shift of its CO ligand to higher fields and the shift of $\nu(\text{CO})$ to higher frequencies, compared to the respective values of free CO, $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$ resembles a number of recently reported noble metal CO complexes, mostly with nd^{10} electron configuration.^[15] Our results show that d electrons are not essential for exothermic CO coordination. $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ appears to make up for its lack of d electrons by an unusual Lewis acidity, which is probably related to its bent structure.^[21,22] Metal–ligand bond formation can thus presumably occur with expenditures of reorganization energy much smaller than those required to bend typical transition metal sandwich compounds.^[22,23] In accord with this notion, no carbonyl complex formation is observed, up to CO pressures of 50 bar, in solutions of $[(\text{Me}_5\text{C}_5)_2\text{Mg}]$ in toluene, for which a strictly linear geometry has been established.^[11] Preliminary experiments with the bent alkaline earth metallocene $[(\text{Me}_5\text{C}_5)_2\text{Sr}]$ ^[22,24] indicate the formation of a carbonyl complex with $\nu(\text{CO}) = 2159\text{ cm}^{-1}$, similar to that observed for $[(\text{Me}_5\text{C}_5)_2\text{Ca}\cdot\text{CO}]$.

This is the first example of CO binding to a molecular alkaline earth metal compound. Previously described $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ complexes, such as $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{PEt}_3)]$,^[25] $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{Me}-\text{C}\equiv\text{C}-\text{Me})]$,^[26] $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3)]$,^[27] and $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{CN}-2,6\text{-xylyl})_2]$ ^[25] show that one or two ligands can be coordinated at the Ca center. In the case of the carbonyl complex reported here, only one CO ligand appears to be taken up in the pressure range studied. The binding of CO to the Ca center is weaker than that of the diethyl ether ligand in $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{OEt}_2)]$, as OEt_2 is not displaced by CO at pressures up to 120 bar. This observation and the similarity of $\nu(\text{CO})$ frequencies in $[\text{H}_3\text{B}-\text{CO}]$ and $[(\text{Me}_5\text{C}_5)_2\text{Ca}-\text{CO}]$ are consistent with the view that CO acts solely as a σ -donor ligand towards $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ and that dipolar interactions are important for the Ca-CO bond.

Keywords: alkaline earth metal compounds · carbonyl complexes · high-pressure chemistry · metallocenes

- [1] S. C. Foster, A. R. W. McKellar, T. J. Sears, *J. Chem. Phys.* **1984**, *81*, 578; P. B. Davies, P. A. Hamilton, W. J. Rothwell, *ibid.* **1984**, *81*, 1598.
- [2] A. B. Burg, H. I. Schlessinger, *J. Am. Chem. Soc.* **1937**, *59*, 780; A. B. Burg, *ibid.* **1952**, *74*, 3482; G. W. Bethke, M. K. Wilson, *J. Chem. Phys.* **1957**, *26*, 1118; R. C. Taylor, *ibid.* **1957**, *26*, 1131.
- [3] W. Gordy, H. Ring, A. B. Burg, *Phys. Rev.* **1950**, *78*, 512.
- [4] M. W. P. Strandberg, C. S. Pearsall, M. T. Weiss, *J. Chem. Phys.* **1949**, *17*, 429.
- [5] R. Sanchez, C. Arrington, C. A. Arrington, Jr., *J. Am. Chem. Soc.* **1989**, *111*, 9110. At room temperature no indication of coordination was obtained up to a CO pressure of 10 bar.
- [6] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd. edition, Wiley, New York, **1970**, p. 78.
- [7] C. A. Arrington, J. T. Petty, S. E. Payne, W. C. K. Haskins, *J. Am. Chem. Soc.* **1988**, *110*, 6240; M. Pearsall, R. West, *ibid.* **1988**, *110*, 7228.
- [8] M. Tacke, C. Klein, D. J. Stufkens, A. Oskam, P. Jutzi, E. A. Bunte, *Z. Anorg. Allg. Chem.* **1993**, *619*, 865.
- [9] Coordination of carbon monoxide to the alkaline earth fluorides MgF_2 , CaF_2 , SrF_2 , and BaF_2 as well as to CaCl_2 in CO matrices at temperatures of about 10 K was deduced from the observation of one or several infrared absorption bands between 2160 and 2205 cm^{-1} [10a] and from changes in the Ca-Cl stretching frequency [10b].
- [10] a) R. H. Hauge, S. E. Gransden, J. L. Margrave, *J. Chem. Soc. Dalton Trans.* **1979**, 745; b) I. R. Beattie, P. J. Jones, N. A. Young, *J. Am. Chem. Soc.* **1992**, *114*, 6146.
- [11] R. A. Andersen, J. M. Boncella, C. J. Burns, R. Blom, A. Haaland, H. V. Volden, *J. Organomet. Chem.* **1986**, *312*, C49; R. A. Andersen, R. Blom, J. M. Boncella, C. J. Burns, H. V. Volden, *Acta Chem. Scand. Ser. A* **1987**, *41*, 24.
- [12] E. U. van Raaij, C. D. Schmulbach, H. H. Brintzinger, *J. Organomet. Chem.* **1987**, *328*, 275. Blank experiments in the same cell without $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ give rise only to the absorption of free CO at 2134 cm^{-1} .
- [13] H. A. Benesi, J. H. Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703.
- [14] A stoichiometry of $[(\text{Me}_5\text{C}_5)_2\text{Ca}(\text{CO})_2]$ cannot be excluded on the basis of the observation of a single CO stretching absorption alone, since the symmetric and asymmetric stretching vibrations of such a dicarbonyl species could be unresolved (cf. ref. [15]); this stoichiometry is unlikely, however, since a plot of $\Delta E(2158)^{-1}$ vs. $\rho(\text{CO})^{-2}$ deviates significantly from linearity.
- [15] σ -Bonded carbonyl complexes of Pd^{2+} , Pt^{2+} , Ag^+ , Au^+ , Hg_2^{2+} , and Hg_2^{1+} : D. Belli Dell'Amico, F. Calderazzo, P. Robino, A. Segre, *J. Chem. Soc. Dalton Trans.* **1991**, 3017; J. J. Rack, B. Moasser, J. D. Gargulak, W. L. Gladfelder, H. D. Hochheimer, S. H. Strauss, *J. Chem. Soc. Chem. Commun.* **1994**, 685; H. Willner, M. Bodenbinder, C. Wang, F. Aubke, *ibid.*, **1994**, 1189; H. Willner, J. Schaeb, G. Hwang, F. Mistry, R. Jones, J. Trotter, F. Aubke, *J. Am. Chem. Soc.* **1992**, *114*, 8972; L. Weber, *Angew. Chem.* **1994**, *106*, 1131; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1077.
- [16] An essentially unchanged value of $\nu(\text{CO}) = 2159 \text{ cm}^{-1}$ and similar absorbance changes in dependence on pressure and temperature are observed in methylecyclohexane solution and indicate that solvent effects are of minor importance for this equilibrium reaction.
- [17] I. T. Horváth, J. M. Millar, *Chem. Rev.* **1991**, *91*, 1339.
- [18] At lower temperatures, the solubility of $[(\text{Me}_5\text{C}_5)_2\text{Ca}]$ is insufficient for ^{13}C NMR measurements.
- [19] B. E. Mann, B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*, Academic Press, New York **1981**.
- [20] A ^{13}C NMR signal at $\delta = 158$ is observed for $[\text{H}_3\text{B}-\text{CO}]$: L. W. Hall, D. W. Lowman, P. D. Ellis, J. D. Odom, *Inorg. Chem.* **1975**, *14*, 580.
- [21] R. A. Williams, T. P. Hanusa, J. C. Huffman, *Organometallics* **1990**, *9*, 1128.
- [22] The energy required to change the centroid-calcium-centroid angle in the range of 180 to 150° has been estimated to be very small: R. Blom, K. Faegri, Jr., H. V. Volden, *Organometallics* **1990**, *9*, 372; M. Kaupp, P. von R. Schleyer, M. Dolg, H. Stoll, *J. Am. Chem. Soc.* **1992**, *114*, 8202; T. K. Hollis, J. K. Burdett, B. Bosnich, *Organometallics* **1993**, *12*, 3385.
- [23] H. H. Brintzinger, L. L. Lohr, Jr., K. L. Tang Wong, *J. Am. Chem. Soc.* **1975**, *97*, 5146; K. M. Simpson, M. F. Rettig, R. M. Wing, *Organometallics* **1992**, *11*, 4363.
- [24] R. A. Andersen, R. Blom, C. J. Burns, H. V. Volden, *J. Chem. Soc. Chem. Commun.* **1987**, 768.
- [25] C. J. Burns, R. A. Andersen, *J. Organomet. Chem.* **1987**, *325*, 31.
- [26] C. J. Burns, PhD Thesis, University of California Berkeley, **1987**.
- [27] R. A. Williams, T. P. Hanusa, J. C. Huffman, *J. Am. Chem. Soc.* **1990**, *112*, 2454.