LBL-36671
UC-401
Preprint

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December 1994

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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Coordination of CO to the Alkaline-Earth Metallocene $[(Me_5C_5)_2Ca]$

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December 1994

This work was supported by DFG, by 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 No. DE-AC03-76SF00098. R.A.A. also was funded by the Alexander-von-Humboldt Foundation with a Senior Scientist Award.

Abstract

$[(Me_5C_5)_2Ca]$ reacts with CO gas in toluene solution to form a complex $[(Me_5C_5)_2Ca{-}CO]$ with $\underline{\nu}(CO) = 2158\ cm^{-1}$, i.e. with higher frequency than that of free CO in toluene ($\underline{\nu}(CO) = 2134\ cm^{-1}$). Changes of the complex formation constant between $-27°C$ ($\underline{K} = 0.13\ bar^{-1}$) and $+32°C$ ($\underline{K} = 0.015\ bar^{-1}$) yield a complex formation enthalpy of $\Delta\underline{H}° = -25\ kJ\ mol^{-1}$. Comparison with related complexes indicates that CO is bound to the Ca center by σ-bonding and/or dipolar interactions. No evidence for CO coordination is obtained with $[(Me_5C_5)_2Mg]$.

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 $\underline{\nu}$(CO) absorption at 2184 cm^{-1}.[1] Diborane reacts with CO to give a volatile complex [H_3B—CO] with $\underline{\nu}$(CO) = 2165 cm^{-1}.[2] Microwave spectroscopy yields a dipole moment of 1.8 D for this molecule,[3] consistent with the charge distribution [H_3B^-—C≡O^+].[4] Me_3Al was found to form a complex [Me_3Al—CO] with $\underline{\nu}$(CO) = 2185 cm^{-1} in a CO matrix at 15-35 K.[5] The increase of $\underline{\nu}$(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 [Me_2Si—CO] and [$(Me_5C_5)_2Si$—CO],[7,8] on the other hand, $\underline{\nu}$(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 for the formation of the first carbonyl complex of a molecular alkaline-earth organyl compound, [$(Me_5C_5)_2Ca$—CO].

When a solution of [$(Me_5C_5)_2Ca$] [11] in toluene is exposed to CO pressures of 2.5-70 atm in an elevated-pressure infrared cell,[12] a new $\underline{\nu}$(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}, $\Delta\underline{A}$(2158) is a suitable measure for the extent of complex formation. A linear Hildebrand-Benesi plot [13] of $\Delta\underline{A}(2158)^{-1}$ against $\underline{p}(CO)^{-1}$ indicates a stoichiometry [$(Me_5C_5)_2Ca$—CO] [14] and an equilibrium constant $\underline{K}$ = 0.036 bar^{-1}

for the reaction between solvated decamethyl calcocene and gaseous CO [eq. (a)]. With the concentration of dissolved CO being proportional to CO pressure, $\underline{c}(CO) = \underline{p}(CO) \cdot 7.1 \cdot 10^{-3}$ M bar^{-1}, throughout the temperature and pressure range considered here,[12] a value of $\underline{K}' = 5.1$ 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 $\Delta\underline{H}^\circ_a = -25 \pm 5$ kJ mol^{-1} and $\Delta\underline{S}^\circ_a = -110 \pm 10$ J mol^{-1} K^{-1} are obtained for complex formation according to equation (a), while values of $\Delta\underline{H}^\circ_b = -25 \pm 5$ kJ mol^{-1} and $\Delta\underline{S}^\circ_b = -70 \pm 10$ J mol^{-1} K^{-1} are obtained for equation (b).

$$[(Me_5C_5)_2Ca](sol) + CO(gas) \rightleftharpoons [(Me_5C_5)_2Ca{-}CO](sol) \qquad (a)$$

$$[(Me_5C_5)_2Ca](sol) + CO(sol) \rightleftharpoons [(Me_5C_5)_2Ca{-}CO](sol) \qquad (b)$$

These data are confirmed by a ^{13}C NMR study at elevated CO pressures.[17] Solutions of $[(Me_5C_5)_2Ca]$ in d_8-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, $\Delta\underline{\delta}$, are a linear function of the mole fractions of free and complexed species, the equilibrium constant $\underline{K}$, as well as the limiting values of $\Delta\underline{\delta}$ for complete complex formation, can be obtained by a least-squares analysis of the essentially linear plots of $\Delta\underline{\delta}^{-1}$ against $\underline{p}(CO)^{-1}$. A value of $\underline{K} = 0.024$ 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

180.4 ppm, determined for CO in $[(Me_5C_5)_2Ca-CO]$, places this CO resonance at higher fields than that of free CO in toluene solution (184.7 ppm). $[(Me_5C_5)_2Ca-CO]$ 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 free CO.[19,20]

With regard to both the ^{13}C chemical shift of its CO ligand to higher fields and the shift of ν(CO) to higher frequencies, compared to the respective values of free CO, $[(Me_5C_5)_2Ca-CO]$ 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. $[(Me_5C_5)_2Ca]$ 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 toluene solutions of $[(Me_5C_5)_2Mg]$,[10] for which a strictly linear geometry has been established.[11] Preliminary experiments with the bent alkaline earth metallocene $[(Me_5C_5)_2Sr]$ [22,24] indicate the formation of a carbonyl complex with ν(CO) = 2159 cm^{-1}, similar to that observed for $[(Me_5C_5)_2Ca-CO]$.

This is the first example of CO binding to a molecular alkaline-earth metal compound. Previously described $[(Me_5C_5)_2Ca]$ complexes, such as $[(Me_5C_5)_2Ca(PEt_3)]$,[25] $[(Me_5C_5)_2Ca(Me-C\equiv C-Me)]$,[26]

$[(Me_5C_5)_2Ca(Me_3Si{-}C{\equiv}C{-}C{\equiv}C{-}SiMe_3)]$ [27] and $[(Me_5C_5)_2Ca(CN{-}2,6{-}xylyl)_2]$ [26] 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 $[(Me_5C_5)_2Ca(OEt_2)]$, as OEt_2 is not displaced by CO at pressures up to 120 bar. This observation and the similarity of ν(CO) frequencies in $[H_3B{-}CO]$ and $[(Me_5C_5)_2Ca{-}CO]$ are consistent with the view that CO acts solely as a σ-donor ligand towards $[(Me_5C_5)_2Ca]$ and that dipolar interactions are important for the Ca-CO bond.

Footnotes and References

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

$\underline{T}$/°C	+32	+10	+3	-9	-18	-27
$\underline{K}$/kbar^{-1}	15(3)	36(8)	51(3)	71(3)	115(14)	127(11)
$\underline{K}'$/M^{-1}	2.1	5.1	7.2	10.0	16.1	17.9

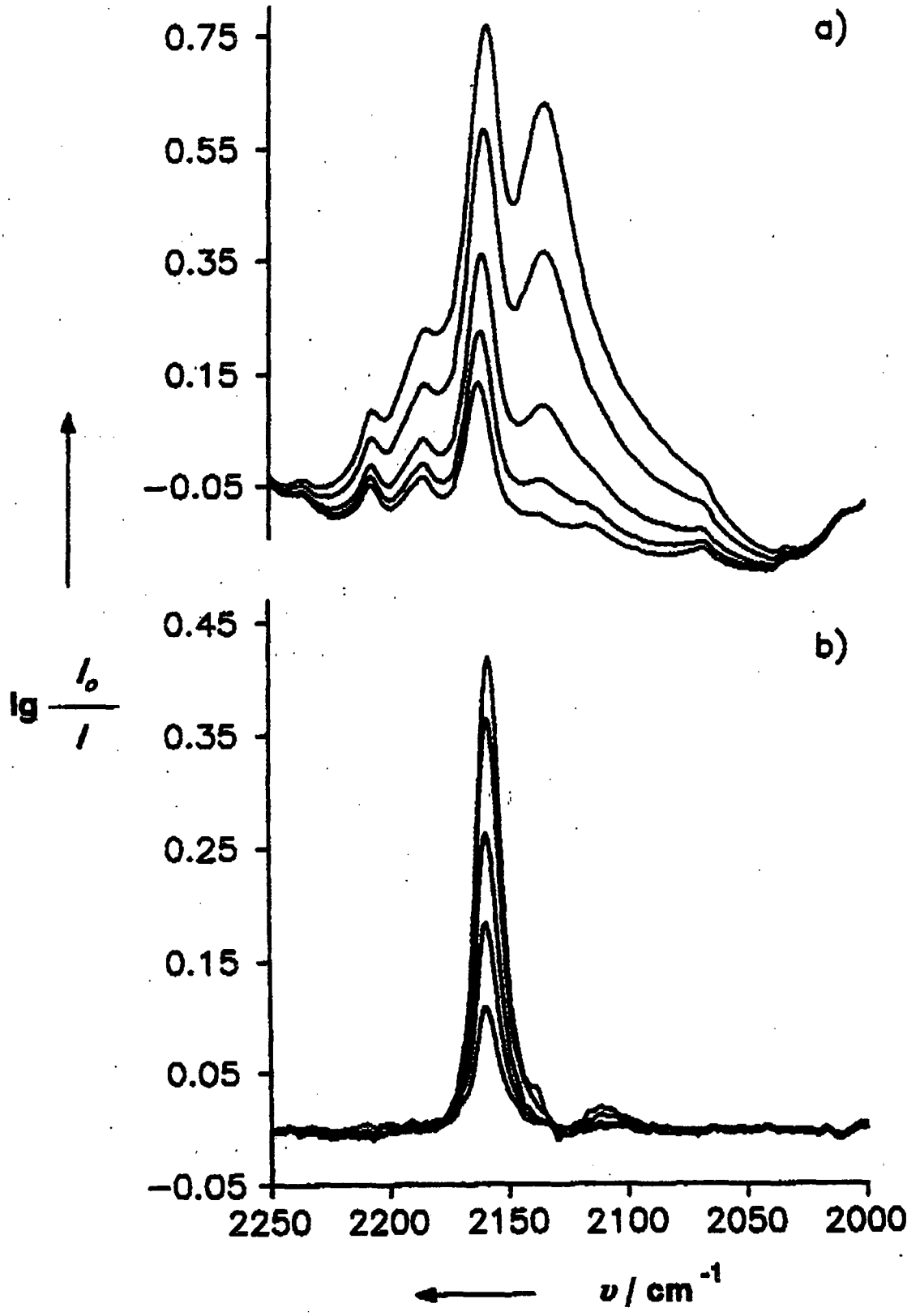
Table 2. ^{13}C NMR data for $[(Me_5C_5)_2Ca] + CO \rightleftharpoons [(Me_5C_5)_2Ca-CO]$ in d_8-toluene at $\underline{T}$ = 31.5°C. [a]

$\underline{p}$(CO)/bar	$\underline{\delta}$(CH$_3$)	$\underline{\delta}$(C$_5$)	$\underline{\delta}$(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
$[(Me_5C_5)_2Ca-CO]$	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 in ppm relative to $\underline{\delta}(C_6D_5CD_3)$ = 20.4 ppm; [b] obtained by least-square analysis from the values observed at $\underline{p}$(CO) = 15-80 bar.

Legend

Fig. 1. IR spectra of a $4 \cdot 10^{-2}$ M solution of $[(Me_5C_5)_2Ca]$ in toluene at 10°C at CO pressures of 5, 10, 20, 40 and 60 bar; a) base-line corrected spectra (top); b) spectra corrected for the absorption of solvent and free CO in solution (bottom).


a)
b)
0.75
0.55
0.35
0.15
−0.05
0.45
0.35
0.25
0.15
0.05
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lg $\frac{I_o}{I}$
2250
2200
2150
2100
2050
2000
ν / cm^{-1}

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