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Carbon Dioxide Activation. Deoxygenation and Disproportionation of Carbon Dioxide Promoted by Bis(cyclopentadienyl)titanium and -zirconium Derivatives. A Novel Bonding Mode of the Carbonato and a Trimer of the Zirconyl Unit

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Abstract: Carbon dioxide is quantitatively deoxygenated to carbon monoxide by [Cp₂TiCl]₂ [Cp = η⁵-C₅H₅] which is converted to [Cp₂TiCl]₂O, while Cp₂Ti(CO)₂ promotes the disproportionation of CO₂ to CO and carbonato. This reaction gives rise to a tetranuclear carbonato complex of titanium(III), [(Cp₂Ti)₂(CO₃)₂], in which the CO₃²⁻ ligand, engaged in a novel bonding mode, bridges three Cp₂Ti units. The ν_{CO} stretching frequencies for the coordinated CO₃²⁻ fall at 1475 m-s and 1425 v-s cm⁻¹, and, as confirmed by the isotopic labeling, the two bands in [(Cp₂Ti)(¹³CO₃)₂] are at 1432 and 1385 cm⁻¹. Carbon dioxide converts Cp₂Zr(CO)₂ to the cyclic trimer (Cp₂ZrO)₃, which is unprecedented both in cyclopentadienyl and zirconium chemistry. The X-ray structural analysis showed that (Cp₂ZrO)₃ contains a six-membered, nearly planar ring, formally derived from the trimerization of the zirconyl unit Zr=O. Noteworthy are both the Zr-O bond distances, which are not significantly different [average value of 1.959 (3) Å], and the Zr-O-Zr bond angles averaging to 142.5 (2)°. These values indicate the presence of a multiple Zr-O bond. Crystallographic details for [(Cp₂Ti)₂(CO₃)₂]: space group *Cmca* (orthorhombic), *a* = 11.282 (1) Å, *b* = 16.038 (1) Å, *c* = 19.729 (2) Å, and *Z* = 4. The final *R* factor is 5.8% for 1508 observed reflections. Crystallographic details for (Cp₂ZrO)₃·C₇H₈: space group *P2₁/c* (monoclinic), *a* = 10.230 (1) Å, *b* = 18.612 (2) Å, *c* = 17.406 (2) Å, β = 95.27 (1)°, and *Z* = 4. The final *R* factor is 4.3% for 4153 observed reflections.

Introduction

Recently much interest was focused on "model" complexes which could realize fixation and/or elementary transformations of carbon dioxide.^{2,3} At present, however, while there are several reports on the insertion reactions of CO₂,²⁻⁴ little is known concerning its fixation, or other metal-promoted transformations, such as disproportionation, dimerization, and

deoxygenation. This mainly results from lack of strategy to find complexes able to realize, at the least, CO₂ coordination. In several cases, CO₂ seems to require a bifunctional system, i.e., acid-base, for its fixation and activation,⁵ while inorganic chemists normally employ monofunctional complexes in molecular activation processes. The highly basic Ir(I),^{6,7} Rh(I),⁸ and Ni(0)⁹ complexes, which so far have been found to be

Table I. Summary of Crystal Data and Intensity Collection

	$[(Cp_2Ti)_2(CO_3)]_2$	$(Cp_2ZrO)_3 \cdot C_7H_8$
<i>a</i> , Å	11.282 (1)	10.230 (1)
<i>b</i> , Å	16.038 (1)	18.612 (2)
<i>c</i> , Å	19.729 (2)	17.406 (2)
α , deg	90.0	90.0
β , deg	90.0	95.27 (1)
γ , deg	90.0	90.0
<i>Z</i>	4	4
<i>M</i>	832.4	804.4
calcd density, g/cm ³	1.548	1.618
space group	<i>Cmca</i>	<i>P2₁/c</i>
radiation	nickel-filtered Cu K α (λ = 1.541 78)	niobium-filtered Mo K α (λ = 0.710 69)
μ , mm ⁻¹	7.81	0.94
scan type	θ - 2θ	θ - 2θ
scan range	$\pm 0.5^\circ$ from peak center	
scan speeds	2.5-10 deg θ /min	
backgrounds	stationary crystal at $\pm 0.5^\circ$	
2θ limits, deg	6-140	6-58
criterion for observation	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1508	4153
unique total data	1780	8779
crystal dimensions	0.26 \times 0.16 \times 0.26 mm	0.19 \times 0.21 \times 0.29 mm

active in CO₂ activation, are monofunctional systems. They realize both the fixation⁹ and the dimerization of CO₂,⁶ even if only one structural report shows the presence of the intact metal-bonded CO₂.⁹ Rather recently, we discovered a new class of CO₂ reversible carriers, which contain CO₂ in its intact form.¹⁰ They closely approach the requirement of a bifunctional system, since they contain both acid and basic centers.¹¹

Herein we report the reactions of CO₂ with Cp₂M(CO)₂ and [Cp₂TiCl]₂ (Cp = η^5 -C₅H₅; M = Ti, Zr), the reactivity of which can be described in terms of their carbene and free-radical-like nature. These reactions give rise to the deoxygenation and disproportionation of CO₂, and produce an unprecedented tetranuclear carbonato complex of titanium(III) and a cyclic trimer of the bis(cyclopentadienyl)oxozirconium(IV).

Experimental Section

Materials. [Cp₂TiCl]₂,¹² Cp₂Ti(CO)₂,¹³ and Cp₂Zr(CO)₂¹⁴ were prepared by published procedures. Carbon dioxide was UPP oxygen-free gas. ¹³CO₂ was prepared by reaction of Ba¹³CO₃ (90% isotopic purity) with H₂SO₄.

Physical and Analytical Measurements. Elemental analyses were performed by the microanalytical laboratory at the University of Pisa. Infrared spectra were obtained from Nujol and PTFE (polytrichloroethylene) mulls between KBr plates using a Perkin-Elmer 282 spectrometer. ¹H NMR spectra were obtained from a Varian EM 360 spectrometer. CDCl₃ was used as the NMR solvent with Me₄Si as the reference.

General Procedures. Owing to the air sensitivity of the complexes all preparations were carried out under a dry and oxygen-free nitrogen or carbon dioxide atmosphere, using standard Schlenk techniques. Toluene was dried and distilled over Na under a nitrogen atmosphere prior to use.

Reaction of [Cp₂TiCl]₂ with CO₂. A toluene solution of [Cp₂TiCl]₂ (1.3 g, 3.0 mmol) was charged in a 125-mL rocking autoclave with 1 atm of N₂, then pressurized with 10 atm of CO₂. The mixture was heated for 18 h at 90 °C with shaking. The gas chromatographic analysis of the gases gave 2.5 mmol of CO (based on the N₂/CO ratio). For the most part, [Cp₂TiCl]₂O (11) was obtained from the autoclave, while a further amount was recovered from the toluene evaporated to 10 mL (ca 80%). The yield of 11 and CO ranges, under these conditions, for five different runs, from 60 to 90%.

Reaction of Cp₂Ti(CO)₂ with CO₂. A 500-mL flask containing a toluene (50 mL) solution of Cp₂Ti(CO)₂ (1.03 g, 4.40 mmol) was filled with CO₂ until saturation at room temperature. Then, when closed, the solution, heated at 52 °C for 2 days, gave a crystalline,

light-green solid (yield ca. 85%). It can be recrystallized from boiling toluene, in which it gives a deep-blue solution. It is very sensitive to air. Anal. Calcd for [(Cp₂Ti)₂(CO₃)₂]. C₄₂H₄₀O₆Ti₄: C, 60.60; H, 4.84; Ti, 23.02. Found: C, 60.18; H, 5.17; Ti, 23.0; μ_{eff} = 1.70 μ_B per titanium at 293 K. V displays two bands (PTFE) at 1475 m-s and 1425 v-s, br cm⁻¹ due to CO₃²⁻, as confirmed by isotope labeling. Decomposed with dry HCl in toluene, V gave CO₂ and a green suspension, from which, upon treatment with CHCl₃, Cp₂TiCl₂ was recovered in quantitative yield.

Reaction of Cp₂Ti(CO)₂ with ¹³CO₂. A 100-mL flask containing a toluene (20 mL) solution of Cp₂Ti(CO)₂ (1.1 g, 4.70 mmol) was filled with ¹³CO₂ (ca. 2.2 mmol) (from Ba¹³CO₃, 90% isotopic purity) and heated at 64 °C for 3 days. The gases at the end of the reaction were absorbed into an isooctane solution (20 mL) of Cp₂V (0.18 g), which was readily transformed into the corresponding Cp₂VCO.¹⁵ The CO/¹³CO molar ratio deduced from the IR bands (isooctane solution) at ν_{12CO} 1895, ν_{13CO} 1853 cm⁻¹ is nearly 4. Cp₂V reacts with CO₂, but only under rather drastic conditions. From the toluene solution, [(Cp₂Ti)₂(¹³CO₃)₂] was recovered (ca. 50%) as a green, crystalline solid. With ¹³CO₃²⁻, the two bands found in V are at 1432 m-s and 1385 v-s, br cm⁻¹. IR data on V and [(Cp₂Ti)₂(¹³CO₃)₂] are from PTFE mulls.

Reaction of Cp₂Zr(CO)₂ with CO₂. Cp₂Zr(CO)₂ (0.7 g, 2.53 mmol) was dissolved in toluene (50 mL) and the solution saturated with CO₂ at room temperature. Heating for 4 days at 74 °C gave a very small amount of a light-yellow powder which was filtered out, keeping the solution hot. On cooling, a white, crystalline solid was obtained which was recrystallized from toluene (ca. 50%). On drying, the solid loses crystallization solvent. Anal. Calcd for Cp₂ZrO, C₁₀H₁₀OZr: C, 50.59; H, 4.25. Found: C, 50.20; H, 4.21. The ¹H NMR spectrum (CDCl₃) displays a single sharp peak at τ 3.75.

X-ray Data Collection and Structure Refinement for [(Cp₂Ti)₂(CO₃)₂]. The crystal examined was wedged into thin-walled glass capillaries and sealed under nitrogen. Preliminary X-ray examination (from rotation and Weissenberg photographs) showed the crystal to be mounted along the [101] axis of an orthorhombic unit cell. A summary of the crystal data and intensity data collection is given in Table I. Lattice constants came from a least-squares refinement of the 2θ values for 36 reflections having $2\theta > 94^\circ$.

Data were collected at room temperature using a single crystal Siemens AED automated diffractometer. The pulse height discriminator was set to accept 90% of the Cu K α peak. The intensity of a standard reflection was monitored every 20 reflections as a check on crystal and instrument stability. No significant change in the measured intensity of this reflection was observed during data collection. For intensity and background, the "five-point technique"¹⁶ was used.

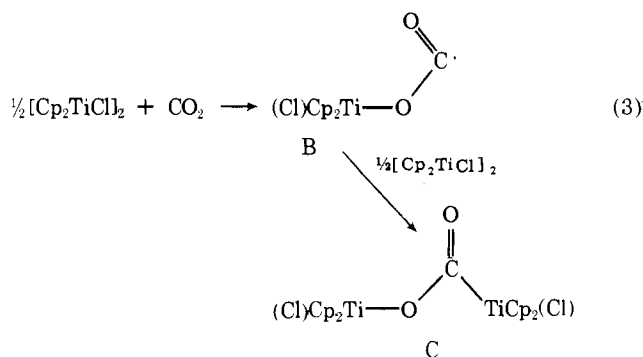
A total of 3286 nonunique data (two octants, $6^\circ < 2\theta < 140^\circ$) were measured, which reduce to 1780 unique reflections after a sort and merge procedure.¹⁷ The intensities were reduced to a set of relative

Table III. Positional Parameters ($\times 10^4$) and Their Estimated Standard Deviations for $(\text{Cp}_2\text{ZrO})_3\cdot\text{C}_7\text{H}_8$

atom ^a	x/a	y/b	z/c	atom	x/a	y/b	z/c
Zr(1)	1441 (1)	-302 (0)	2589 (0)	C(35)	5100 (11)	4206 (8)	4361 (8)
Zr(2)	1754 (1)	1078 (0)	4131 (0)	C(36)	6333 (11)	4103 (8)	4758 (8)
Zr(3)	3762 (1)	1216 (0)	2465 (0)	C(37)	8075 (16)	3240 (14)	5395 (12)
C(1)	-148 (12)	-713 (6)	1449 (7)	C(311)	5174 (14)	3603 (13)	4336 (11)
C(2)	-861 (11)	-716 (8)	2074 (8)	C(321)	5931 (14)	4206 (13)	4551 (11)
C(3)	-992 (10)	-26 (10)	2303 (7)	C(331)	7178 (14)	4123 (13)	4937 (11)
C(4)	-379 (12)	411 (6)	1834 (8)	C(341)	7669 (14)	3436 (13)	5109 (11)
C(5)	148 (10)	-17 (7)	1297 (6)	C(351)	6912 (14)	2833 (13)	4894 (11)
C(6)	2128 (18)	-1590 (6)	2325 (8)	C(361)	5665 (14)	2916 (13)	4508 (11)
C(7)	3259 (12)	-1231 (6)	2526 (8)	C(371)	3769 (15)	3725 (14)	3998 (14)
C(8)	3278 (10)	-1052 (5)	3285 (7)	H(1)	128	-1186	1120
C(9)	2161 (13)	-1308 (5)	3541 (6)	H(2)	-1123	-1165	2333
C(10)	1454 (12)	-1637 (6)	2948 (10)	H(3)	-1321	132	2733
C(11)	-655 (9)	1448 (6)	3965 (9)	H(4)	-190	957	1748
C(12)	-98 (11)	1825 (6)	3420 (6)	H(5)	837	249	984
C(13)	756 (10)	2311 (5)	3772 (8)	H(6)	1631	-1834	1777
C(14)	720 (12)	2237 (7)	4546 (8)	H(7)	4000	-1109	2138
C(15)	-185 (13)	1700 (8)	4661 (7)	H(8)	4040	-757	3624
C(16)	1863 (12)	515 (10)	5470 (7)	H(9)	1886	-1262	4143
C(17)	2443 (16)	1135 (8)	5584 (6)	H(10)	465	-1878	2969
C(18)	3527 (16)	1149 (9)	5235 (9)	H(11)	-1223	1034	3774
C(19)	3633 (14)	499 (13)	4888 (6)	H(12)	-123	1768	2764
C(20)	2610 (20)	111 (6)	5058 (8)	H(13)	1438	2650	3387
C(21)	1998 (11)	2040 (9)	1806 (9)	H(14)	1180	2571	4979
C(22)	2490 (16)	1668 (6)	1225 (7)	H(15)	-486	1500	5190
C(23)	3764 (13)	1886 (7)	1189 (6)	H(16)	986	385	5696
C(24)	3996 (13)	2397 (7)	1745 (8)	H(17)	2095	1603	5914
C(25)	2922 (19)	2485 (7)	2107 (7)	H(18)	4038	1634	5244
C(26)	6207 (11)	1491 (7)	2658 (14)	H(19)	4353	246	4531
C(27)	5493 (9)	1165 (7)	3300 (7)	H(20)	2300	-458	4911
C(28)	5637 (8)	475 (6)	3149 (6)	H(21)	993	1969	1971
C(29)	5707 (10)	383 (7)	2381 (8)	H(22)	2327	1239	968
C(30)	6054 (12)	1008 (13)	2080 (8)	H(23)	4467	1687	789
O(1)	1158 (4)	230 (3)	3532 (3)	H(24)	4920	2700	1875
O(2)	2753 (4)	345 (3)	2212 (3)	H(25)	2800	2860	2597
O(3)	3042 (4)	1423 (2)	3444 (3)	H(26)	6425	1961	2748
C(31)	6811 (11)	3409 (8)	4897 (8)	H(27)	6089	1269	3821
C(32)	6056 (11)	2817 (8)	4639 (8)	H(28)	5217	40	3481
C(33)	4823 (11)	2920 (8)	4242 (8)	H(29)	5491	-148	2115
C(34)	4345 (11)	3614 (8)	4103 (8)	H(30)	6117	984	1433

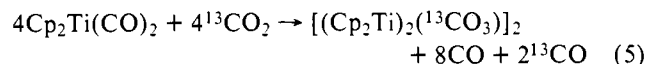
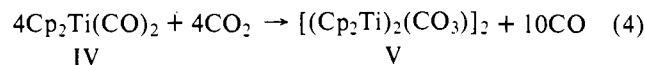
^a The atoms from C(31) to C(371) have occupancy factors of 0.5.

which dimerizes to a "pinacol" derivative, III.²⁴ Reaction 1 is expected to have a rather similar pathway (eq 3), where B could dimerize to an oxalato derivative or undergo the attack

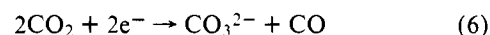


by a new free radical titanium(III), so producing the dimer C. Formation of CO and $[\text{Cp}_2\text{TiCl}]_2\text{O}$ in reaction 1 is likely expected to pass through an intermediate like C. It is rather difficult to infer how this kind of CO_2 transformation depends on the electronic configuration of the metal. It would be interesting, in any case, to compare these results with those obtained employing carbene-like titanium(II) and zirconium(II) derivatives, $\text{Cp}_2\text{M}(\text{CO})_2$ ($\text{M} = \text{Ti}, \text{Zr}$). These complexes should be considered authentic sources of the carbene, "Cp₂M", unit.²⁵

The results occurring between $\text{Cp}_2\text{Ti}(\text{CO})_2$ and CO_2 are given in eq 4. The transformation undergone by CO_2 during this reaction (see Experimental Section) was followed by the use of $^{13}\text{CO}_2$ producing $^{13}\text{CO}_3^{2-}$ and ^{13}CO , as represented by the equation



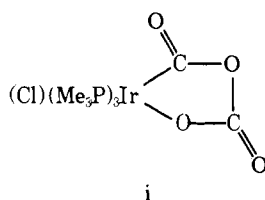
Thus the titanium(II)-promoted transformation of CO_2 corresponds to its disproportionation:²⁶⁻²⁸



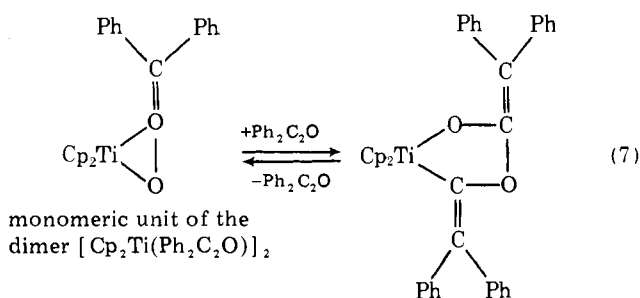
While chemical evidence suggests the presence of the carbonato ligand in V, and the magnetic moment agrees with the presence of titanium(III) ($1.70 \mu_B$ per titanium at 293 K), the molecular complexity along with the bonding mode of CO_3^{2-} is deduced from an X-ray analysis carried out on V (vide infra). Both magnetic and IR data do not correspond to those reported for the supposed carbonato dimer $\{(\text{Cp}_2\text{Ti})_2(\text{CO}_3)_2\}$,²⁹ which displays a magnetic moment lower than $1 \mu_B$ per titanium at room temperature and C-O stretchings occurring at higher frequencies [1570 sh , 1530 s , and 1355 s cm^{-1}] while V shows bands with a rather complex envelope at 1475 m-s and 1425 s cm^{-1} , which are shifted at 1432 m-s and 1385 s cm^{-1} by

isotope labeling in [(Cp₂Ti)₂(¹³CO₃)₂] (see Figure 1). These vibrational spectra data differ significantly from those reported for a di-μ₂-carbonato complex of molybdenum, Mo₂(CO₃)₂·(CO)₂(PPh₂Me)₆,²⁶ in which the carbonato absorbs at 1835 cm⁻¹, while they compare very well with those reported for Rh₂(CO₃)(PPh₃)₅.³⁰ Very recently, CO₂ was used as carbonylating agent in the synthesis of Cp₂Ti(CO)₂, starting from Cp₂TiCl₂ and zinc dust. This reaction affords, moreover, carbonato complexes of titanium(III), such as (Cp₂Ti)₂(CO₃)·2ZnCl₂·2THF and [(Cp₂Ti(CO₃))₂Zn], the nature of which, however, is not yet defined.³¹

The genesis of V could be rather interesting, in view of the metal-induced transformations of CO₂. While it was found that CO₂ reacting with transition metal complexes often produces metal carbonates,^{6,9,26-28,30} the metal-promoted disproportionation, as depicted in reaction 6, was never definitely proved before.³⁰ Hypotheses concerning its pathway are rather scanty, the most attractive between them being proposed by Herskovitz, who isolated a dimer of the CO₂ coordinated on Ir metal.⁶ A sketch of the structure of this CO₂ dimer complexed on the metal is shown in i. It was variously suggested that the di-

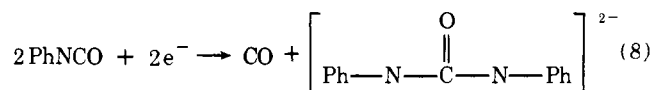


merization was the key step of the CO₂ disproportionation. This hypothesis finds further support in our case from the results of the reactions occurring between Cp₂Ti(CO)₂ and CO₂-equivalent molecules, PhN=C=O³² and Ph₂C=C=O.³³ The reaction of Ph₂C₂O with Cp₂Ti(CO)₂ is a stepwise process producing an η²C₂O metal anchored diphenylketene which adds a second molecule of Ph₂C₂O. The two diphenylketene molecules give a metallocycle which is highly reminiscent of the dimer of the CO₂.³³ Thus Ph₂C₂O seems



to simulate the steps through which it can be assumed to pass the CO₂ titanium-promoted disproportionation.

While Ph₂C₂O allowed the isolation of structural models for the stepwise CO₂ addition to the metal, PhNCO undergoes, like CO₂, a titanium-promoted disproportionation to give CO and diphenylureylene ligand (eq 8). Indeed the reaction be-



tween Cp₂Ti(CO)₂ and PhNCO produces carbon monoxide and diphenylureylene complexes of titanium.³²

As the metal-promoted CO₂ transformations depend not only on the electronic properties, but also on the nature of the metal, it should be suggested by the comparison between the results of reaction 4 and those obtained by reacting Cp₂Zr(CO)₂ with CO₂. Dicarbonyl VI, when treated for 4 days at 74 °C in toluene with CO₂, causes the deoxygenation

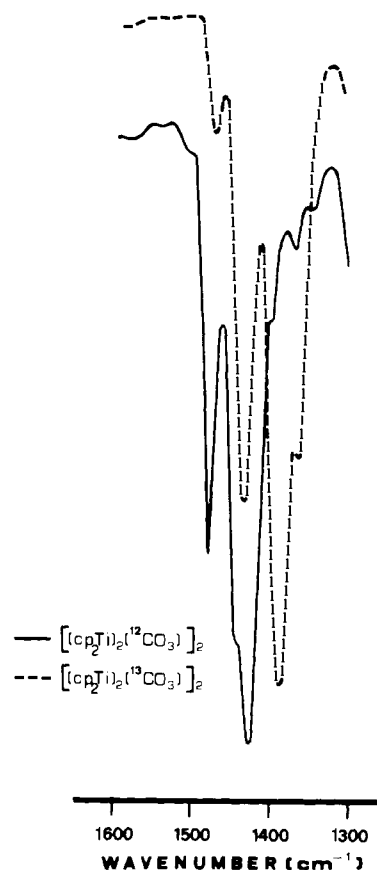


Figure 1.

of CO₂, affording the zirconyl complex VII (eq 9). VII is obtained as white crystals from toluene, which is present as crystallization solvent, and is readily lost in vacuo. VII comes along with a small amount of a light-yellow product, which is suspected to be the polymeric form of the biscyclopentadienylzirconyl derivative. The nature of VII is hard to define from chemical and spectroscopic evidence. The mass spectrum is generally uninformative as concerns the molecular complexity of VII, as was found for (Cp₂ZrCl)₂O,³⁴ while the IR spectrum exhibits an intense, broad absorption band between 760 and 790 cm⁻¹, which is assignable to metal-oxygen stretching frequencies and is diagnostic for group 4A organometallic compounds containing a M-O-M linkage. However, this band could be attributed either to the zirconyl unit or to the asymmetric mode of the Zr-O-Zr unit.³⁴⁻³⁶ The X-ray analysis, carried out on its solvated form (Cp₂ZrO)₃·C₇H₈, definitely clarified the nature of VII (vide infra). The high tendency to form a Zr-O bond and, specially, a Zr-O-Zr unit dominates the biscyclopentadienyl chemistry. In this context, it would be interesting to recall the unusual formation of formaldehyde and [(Cp₂ZrCl)₂O] when Cp₂Zr(H)Cl is reacted with CO₂,³⁷ while all the other transition metal hydrides afford, in the same reaction, the corresponding formiato derivatives.^{1,38}

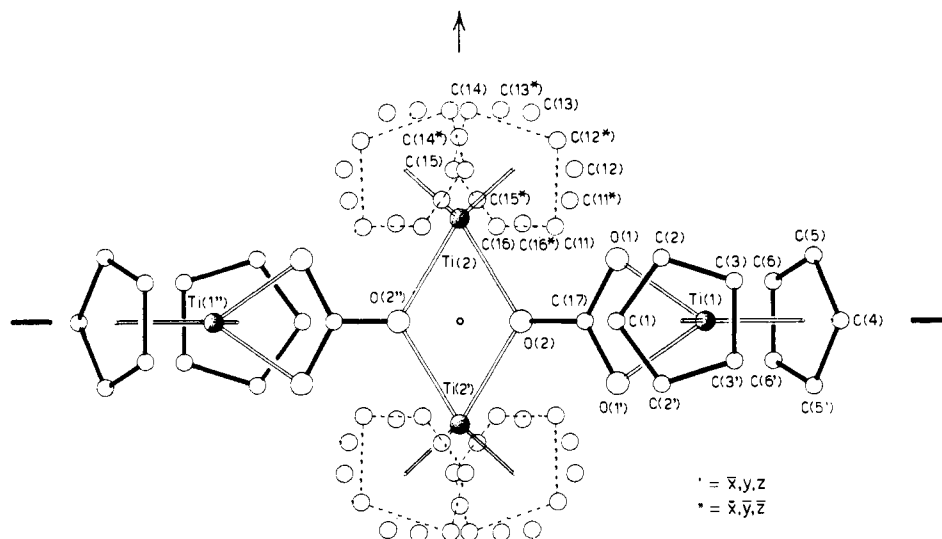
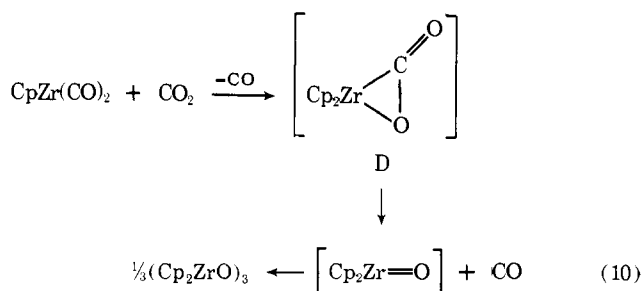
At this point, hypotheses on the origin of (Cp₂ZrO)₃ cannot find a wide justification, because of the paucity of the zirconium(II) chemistry.³⁹ This notwithstanding, it would be reasonable to assume as a key step of reaction 9 the addition of the carbene-like Cp₂Zr unit to CO₂, generating a 1:1 adduct (eq 10). The evolution of D as depicted, rather than the addition of a further CO₂ molecule, is one of the most expected possibilities based on the high oxygen affinity of zirconium. The

of CO₂, affording the zirconyl complex VII (eq 9). VII is obtained as white crystals from toluene, which is present as crystallization solvent, and is readily lost in vacuo. VII comes along with a small amount of a light-yellow product, which is suspected to be the polymeric form of the biscyclopentadienylzirconyl derivative. The nature of VII is hard to define from chemical and spectroscopic evidence. The mass spectrum is generally uninformative as concerns the molecular complexity of VII, as was found for (Cp₂ZrCl)₂O,³⁴ while the IR spectrum exhibits an intense, broad absorption band between 760 and 790 cm⁻¹, which is assignable to metal-oxygen stretching frequencies and is diagnostic for group 4A organometallic compounds containing a M-O-M linkage. However, this band could be attributed either to the zirconyl unit or to the asymmetric mode of the Zr-O-Zr unit.³⁴⁻³⁶ The X-ray analysis, carried out on its solvated form (Cp₂ZrO)₃·C₇H₈, definitely clarified the nature of VII (vide infra). The high tendency to form a Zr-O bond and, specially, a Zr-O-Zr unit dominates the biscyclopentadienyl chemistry. In this context, it would be interesting to recall the unusual formation of formaldehyde and [(Cp₂ZrCl)₂O] when Cp₂Zr(H)Cl is reacted with CO₂,³⁷ while all the other transition metal hydrides afford, in the same reaction, the corresponding formiato derivatives.^{1,38}

Table IV. Bond Distances (Å) and Angles (deg), with Estimated Standard Deviations, for $[(Cp_2Ti)_2(CO_3)]_2^a$

Ti(1)-O(1)	2.128 (3)	Ti(2)-O(2)	2.183 (2)	Ti(1)-C(1)	2.353 (8)	Ti(1)-C(4)	2.355 (7)
Ti(1)-Cp(1)	2.051 (5)	Ti(2)-Cp(3)	2.094 (15)	Ti(1)-C(2)	2.352 (6)	Ti(1)-C(5)	2.366 (6)
Ti(1)-Cp(2)	2.061 (6)	C(17)-O(1)	1.268 (4)	Ti(1)-C(3)	2.365 (5)	Ti(1)-C(6)	2.396 (5)
		C(17)-O(2)	1.301 (6)	av	2.359 (3)	av	2.380 (3)
Ti(2)-C(11)	2.406 (10)	Ti(2)-C(11)*	2.388 (17)	C(1)-C(2)	1.362 (9)	C(4)-C(5)	1.406 (8)
Ti(2)-C(12)	2.401 (9)	Ti(2)-C(12)*	2.361 (20)	C(2)-C(3)	1.360 (11)	C(5)-C(6)	1.374 (8)
Ti(2)-C(13)	2.411 (10)	Ti(2)-C(13)*	2.423 (19)	C(3)-C(3')	1.397 (15)	C(6)-C(6')	1.382 (13)
Ti(2)-C(14)	2.435 (11)	Ti(2)-C(14)*	2.460 (21)	av	1.365 (6)	av	1.390 (5)
Ti(2)-C(15)	2.401 (8)	Ti(2)-C(15)*	2.399 (15)				
Ti(2)-C(16)	2.442 (9)	Ti(2)-C(16)*	2.356 (23)				
av	2.415 (4)	av	2.397 (8)				
The C-C average distances in the disordered rings around Ti(2) are 1.43 (1), 1.42 (1), 1.42 (1), 1.43 (1), 1.44 (1), 1.40 (1); mean value 1.42.							
O(1)-Ti(1)-O(1')	61.3 (1)	O(2)-Ti(2)-O(2'')	69.1 (1)	O(1)-C(17)-O(2)	121.2 (3)		
O(1)-Ti(1)-Cp(1)	108.7 (2)	O(2)-Ti(2)-Cp(3)	110.1 (5)	O(1)-C(17)-O(1')	117.7 (5)		
O(1)-Ti(1)-Cp(2)	108.9 (2)	O(2)-Ti(2)-Cp(3')	109.6 (4)	Ti(1)-O(1)-C(17)	90.5 (2)		
Cp(1)-Ti(1)-Cp(2)	136.1 (3)	Cp(3)-Ti(2)-Cp(3')	131.3 (6)				
Ti(2)-O(2)-C(17)	124.5 (1)	C(1)-C(2)-C(3)	108.7 (7)	C(4)-C(5)-C(6)	107.0 (6)		
Ti(2)-O(2)-Ti(2'')	111.0 (2)	C(2)-C(3)-C(3')	107.3 (7)	C(5)-C(6)-C(6')	109.0 (6)		
		C(2)-C(1)-C(2')	108.1 (7)	C(5)-C(4)-C(5')	108.1 (6)		
		av	108.0 (3)	av	108.0 (3)		

^a $\bar{x}, \bar{y}, \bar{z}; '' = \bar{x}, \bar{y}, \bar{z}; ''' = x, \bar{y}, \bar{z}$. All the average values have been calculated using the formulas $\mu_{av} = \sum_i (\mu_i / \sigma_i^2) / \sum_i 1 / \sigma_i^2$, $\sigma_{av} = \sqrt{1 / \sum_i (1 / \sigma_i^2)}$, where μ_i are the individual observations and σ_i are the standard deviations for them.

**Figure 2.** A view of the molecular structure of $[(Cp_2Ti)_2(CO_3)]_2$, showing the atomic numbering scheme.

zirconyl unit, $Zr=O$, never identified,⁴⁰ could be the reasonable precursor both of the trimer VII and of a polymeric form.

Solid-State Structure of $[(Cp_2Ti)_2(CO_3)]_2$. The molecular structure of $[(Cp_2Ti)_2(CO_3)]_2$ and the atom numbering scheme are shown in Figure 2, while bond distances and angles are given in Table IV.

The structure consists of tetrameric units having crystallographic C_{2h} symmetry. The crystallographic mirror plane is orthogonal to the twofold axis passing through Ti(2) and Ti(2') (see Figure 2). Excluding the Cp rings and Ti(1), all the atoms

of the tetramer lie in a plane from which Ti(1) is displaced by 0.09 Å. The Cp rings are bonded to the titanium atoms in a bent arrangement through a pentahapto coordination mode and those around Ti(1) have staggered conformations. The chemically interesting structural features concern the backbone of the tetranuclear complex. The four Cp_2Ti units are bridged by two CO_3^{2-} ligands. Thus there are two different kinds of titanium(III) in the complex. The Ti(2)-Ti(2') distance [3.597 (2) Å] rules out a possible metal-metal interaction, excluded on the basis of the magnetic measurement $\mu_{eff} = 1.70 \mu_B$ per titanium at 293 K, which shows, moreover, no antiferromagnetic interaction between titanium atoms. No other carbonato compounds similar to that found here have previously been structurally characterized. A more useful comparison can be done, as concerns the CO_3^{2-} unit, with other compounds containing a tridentate bridging carbonato group.^{26,30,41} Here, as in the other structures, the carbonato moiety is essentially planar. The four-membered ring formation around Ti(1) causes the carbonato O-C-O bond angle to decrease from 120° to 117.7 (5)°, while the O(1')-Ti-O(1) angle of 61.3 (1)° is similar to those found for the same four-membered ring in other carbonato complexes.³⁰ As concerns

Table V. Bond Distances (Å) and Bond Angles (deg), with Estimated Standard Deviations, for (Cp₂ZrO)₃-C₇H₈

Zr(1)-O(1)	1.961 (6)	Zr(2)-O(1)	1.957 (6)	Zr(3)-O(2)	1.950 (6)
Zr(1)-O(2)	1.960 (5)	Zr(2)-O(3)	1.966 (5)	Zr(3)-O(3)	1.955 (5)
Zr(1)-Cp(1)	2.28 (1)	Zr(2)-Cp(3)	2.28 (1)	Zr(3)-Cp(5)	2.29 (1)
Zr(1)-Cp(2)	2.28 (1)	Zr(2)-Cp(4)	2.26 (1)	Zr(3)-Cp(6)	2.28 (1)
Zr(1)-C(1)	2.56 (1)	Zr(2)-C(11)	2.55 (1)	Zr(3)-C(21)	2.56 (1)
Zr(1)-C(2)	2.56 (1)	Zr(2)-C(12)	2.57 (1)	Zr(3)-C(22)	2.56 (1)
Zr(1)-C(3)	2.55 (1)	Zr(2)-C(13)	2.57 (1)	Zr(3)-C(23)	2.55 (1)
Zr(1)-C(4)	2.55 (1)	Zr(2)-C(14)	2.54 (1)	Zr(3)-C(24)	2.55 (1)
Zr(1)-C(5)	2.56 (1)	Zr(2)-C(15)	2.54 (1)	Zr(3)-C(25)	2.57 (1)
av	2.556 (5)	av	2.554 (5)	av	2.558 (5)
Zr(1)-C(6)	2.55 (1)	Zr(2)-C(16)	2.55 (1)	Zr(3)-C(26)	2.55 (1)
Zr(1)-C(7)	2.55 (1)	Zr(2)-C(17)	2.57 (1)	Zr(3)-C(27)	2.55 (1)
Zr(1)-C(8)	2.56 (1)	Zr(2)-C(18)	2.52 (2)	Zr(3)-C(28)	2.57 (1)
Zr(1)-C(9)	2.56 (1)	Zr(2)-C(19)	2.48 (2)	Zr(3)-C(29)	2.54 (1)
Zr(1)-C(10)	2.56 (1)	Zr(2)-C(20)	2.52 (1)	Zr(3)-C(30)	2.53 (1)
av	2.556 (5)	av	2.540 (5)	av	2.548 (5)
C(1)-C(2)	1.36 (2)	C(11)-C(12)	1.35 (2)	C(21)-C(22)	1.36 (2)
C(1)-C(5)	1.36 (2)	C(11)-C(15)	1.35 (2)	C(21)-C(25)	1.33 (2)
C(2)-C(3)	1.36 (2)	C(12)-C(13)	1.36 (2)	C(22)-C(23)	1.37 (2)
C(3)-C(4)	1.35 (2)	C(13)-C(14)	1.36 (2)	C(23)-C(24)	1.36 (2)
C(4)-C(5)	1.38 (2)	C(14)-C(15)	1.39 (2)	C(24)-C(25)	1.33 (2)
av	1.36 (1)	av	1.36 (1)	av	1.35 (1)
C(6)-C(7)	1.35 (2)	C(16)-C(17)	1.30 (2)	C(26)-C(27)	1.32 (2)
C(6)-C(10)	1.34 (2)	C(16)-C(20)	1.33 (2)	C(26)-C(30)	1.35 (3)
C(7)-C(8)	1.36 (2)	C(17)-C(18)	1.31 (2)	C(27)-C(28)	1.34 (2)
C(8)-C(9)	1.35 (2)	C(18)-C(19)	1.36 (3)	C(28)-C(29)	1.36 (2)
C(9)-C(10)	1.35 (2)	C(19)-C(20)	1.33 (3)	C(29)-C(30)	1.34 (3)
av	1.35 (1)	av	1.32 (1)	av	1.34 (1)
O(1)-Zr(1)-O(2)	97.4 (2)	O(1)-Zr(2)-O(3)	97.7 (2)	O(2)-Zr(3)-O(3)	97.3 (2)
O(1)-Zr(1)-Cp(1)	106.9 (3)	O(1)-Zr(2)-Cp(3)	109.2 (3)	O(2)-Zr(3)-Cp(5)	108.3 (4)
O(1)-Zr(1)-Cp(2)	108.7 (4)	O(1)-Zr(2)-Cp(4)	107.2 (5)	O(2)-Zr(3)-Cp(6)	108.2 (4)
O(2)-Zr(1)-Cp(1)	108.6 (4)	O(3)-Zr(2)-Cp(3)	106.7 (3)	O(3)-Zr(3)-Cp(5)	107.3 (4)
O(2)-Zr(1)-Cp(2)	108.0 (4)	O(3)-Zr(2)-Cp(4)	109.5 (4)	O(3)-Zr(3)-Cp(6)	108.6 (4)
Cp(1)-Zr(1)-Cp(2)	124.0 (5)	Cp(3)-Zr(2)-Cp(4)	123.6 (5)	Cp(5)-Zr(3)-Cp(6)	123.9 (5)
Zr(1)-O(1)-Zr(2)	142.2 (3)	Zr(1)-O(2)-Zr(3)	143.0 (3)	Zr(2)-O(3)-Zr(3)	142.4 (3)
C(1)-Zr(1)-C(2)	30.9 (4)	C(11)-Zr(2)-C(12)	30.5 (4)	C(21)-Zr(3)-C(22)	30.8 (5)
C(1)-Zr(1)-C(5)	30.8 (4)	C(11)-Zr(2)-C(15)	30.7 (4)	C(21)-Zr(3)-C(25)	30.0 (5)
C(2)-Zr(1)-C(3)	30.8 (5)	C(12)-Zr(2)-C(13)	30.8 (3)	C(22)-Zr(3)-C(23)	31.2 (5)
C(3)-Zr(1)-C(4)	30.7 (5)	C(13)-Zr(2)-C(14)	30.8 (5)	C(23)-Zr(3)-C(24)	31.0 (4)
C(4)-Zr(1)-C(5)	31.2 (4)	C(14)-Zr(2)-C(15)	31.7 (4)	C(24)-Zr(3)-C(25)	30.0 (5)
av	30.9 (2)	av	30.9 (2)	av	30.6 (2)
C(6)-Zr(1)-C(7)	30.8 (5)	C(16)-Zr(2)-C(17)	29.6 (5)	C(26)-Zr(3)-C(27)	30.1 (6)
C(6)-Zr(1)-C(10)	30.4 (5)	C(16)-Zr(2)-C(20)	30.4 (5)	C(26)-Zr(3)-C(30)	30.8 (6)
C(7)-Zr(1)-C(8)	30.9 (4)	C(17)-Zr(2)-C(18)	29.9 (5)	C(27)-Zr(3)-C(28)	30.4 (4)
C(8)-Zr(1)-C(9)	30.6 (4)	C(18)-Zr(2)-C(19)	31.6 (6)	C(28)-Zr(3)-C(29)	30.8 (4)
C(9)-Zr(1)-C(10)	30.6 (4)	C(19)-Zr(2)-C(20)	30.8 (6)	C(29)-Zr(3)-C(30)	30.6 (6)
av	30.7 (2)	av	30.4 (2)	av	30.6 (2)
C(2)-C(1)-C(5)	107.7 (11)	C(12)-C(11)-C(15)	108.3 (10)	C(22)-C(21)-C(25)	108.2 (13)
C(1)-C(2)-C(3)	107.8 (12)	C(11)-C(12)-C(13)	108.9 (11)	C(21)-C(22)-C(23)	107.5 (11)
C(2)-C(3)-C(4)	109.2 (12)	C(12)-C(13)-C(14)	107.7 (10)	C(22)-C(23)-C(24)	106.2 (11)
C(3)-C(4)-C(5)	107.2 (12)	C(13)-C(14)-C(15)	107.2 (11)	C(23)-C(24)-C(25)	109.1 (12)
C(4)-C(5)-C(1)	108.1 (11)	C(14)-C(15)-C(11)	107.9 (12)	C(24)-C(25)-C(21)	109.0 (12)
av	108.0 (5)	av	108.0 (5)	av	107.9 (5)
C(7)-C(6)-C(10)	108.3 (12)	C(17)-C(16)-C(20)	107.9 (13)	C(27)-C(26)-C(30)	107.9 (14)
C(6)-C(7)-C(8)	107.9 (12)	C(16)-C(17)-C(18)	109.7 (14)	C(26)-C(27)-C(28)	109.6 (12)
C(7)-C(8)-C(9)	107.3 (10)	C(17)-C(18)-C(19)	107.1 (15)	C(27)-C(28)-C(29)	106.3 (10)
C(8)-C(9)-C(10)	108.5 (11)	C(18)-C(19)-C(20)	106.7 (14)	C(28)-C(29)-C(30)	108.5 (12)
C(9)-C(10)-C(6)	108.1 (12)	C(19)-C(20)-C(16)	108.5 (14)	C(29)-C(30)-C(26)	107.7 (14)
av	108.0 (5)	av	108.0 (6)	av	107.9 (5)

the C-O bond distances, the comparison can be restricted to the complexes containing a tridentate bridging carbonato group. In two of these,⁴¹ the C-O bond lengths related to the four-membered ring formation are significantly longer than the third one [Cu(NH₃)₂CO₃, 1.307 (3) and 1.299 (3) vs. 1.245 (3) Å; (Ph₄Sb)₂CO₃, 1.308 (13) and 1.293 (13) vs. 1.275 (13) Å] while in complex V the C-O bond distance for the oxygen chelating titanium is significantly shorter [1.268 (4) Å] than the third C-O bond length [1.301 (6) Å]. As shown in Table IV, all angles involving the centroids of the cyclopentadienyl rings, the C-C(Cp) and the Ti-C(Cp) bond

lengths, are close to the values given for related compounds.⁴²

Solid-State Structure of (Cp₂ZrO)₃-C₇H₈. The molecular in Figure 3. Zirconium and oxygen atoms give rise to a nearly planar six-membered ring, the displacement from the mean plane through the six atoms being Zr(1), 0.004; Zr(2), 0.000; Zr(3), 0.000; O(1), 0.015; O(2), 0.018; O(3), -0.030 Å. The Zr-O bond lengths range from 1.950 (6) to 1.966 (5) Å and average 1.959 (3) Å, while the three Zr-O-Zr angles are very close to the mean value of 142.5 (2)°. Zr-O bond distances agree well with values given for the dinuclear [Cp₂ZrCl]₂O⁴³

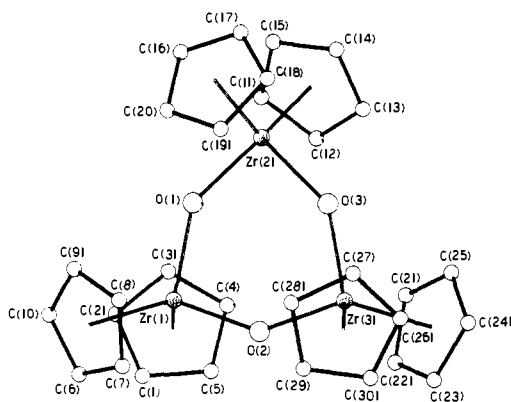


Figure 3. A view of the molecular structure of $(\text{Cp}_2\text{ZrO})_3$, showing the atomic numbering scheme.

[Zr–O, 1.94 (1) and 1.95 (1) Å], while Zr–O–Zr angle values are highly affected by the ring formation. The rather short Zr–O bond distance and the ring planarity are on behalf of the existence of a rather significant metal–oxygen double bond contribution. Tilting cyclopentadienyl rings, which are planar within the experimental errors, are η^5 bonded to zirconium atoms. They exhibit an eclipsed conformation around Zr(1) and Zr(2), while those around Zr(3) are midway (neither eclipsed nor staggered). The planes containing the normals to the Cp rings at the metal atoms are nearly perpendicular to the molecular plane, the dihedral angles between the planes being 89.1, 87.4, and 88.5° around Zr(1), Zr(2), and Zr(3), respectively.

As is shown in Table V, the Zr–C distances and Cp–Zr–Cp angles [Zr(1), 124.0 (5); Zr(2), 123.6 (5); Zr(3), 123.9 (5)°] fall in the range given for related Cp_2Zr derivatives.⁴⁴ The C–C(Cp) bond distances range from 1.31 (2) to 1.39 (2) Å. Even if a value of 1.43 Å is expected for a thermally rigid system, these values are common for compounds in which a large degree of vibrational motion is found. It may be interesting to note that this structure is highly significant as concerns the open question on the existence of the zirconyl unit.⁴⁰ The simultaneous presence of the Zr–O band at 760–790 cm^{-1} and the trimeric nature of VII rule out the possibility of using the IR spectrum to infer the presence of the monomeric zirconyl unit $\text{Zr}=\text{O}$. Its “inexistence” finds its counterpart in the “instability” of the monomeric acetaldehyde and formaldehyde, which give very similar cyclic trimers, the paraldehyde and the trioxane, respectively. Another helpful comparison that can be made in this context is with the hypothetical $\text{R}_2\text{Si}=\text{O}$ unit,⁴⁵ whose hydration, cyclization, and polymerization are parallel to those found for $\text{Zr}=\text{O}$. X-ray structural data for cyclopentadienyl compounds containing M–O–M units are relatively scarce, even if it is a growing area in this field. The previous reports concern the structures of $[\text{Cp}_2\text{TiCl}]_2\text{O}$,⁴⁶ $[\text{CpTiCl}_2]_2\text{O}$,⁴⁷ $[\text{CpTiOCl}]_4$,⁴⁸ $[\text{Cp}_6\text{Ti}_6\text{O}_8]$,⁴⁹ $[\text{Cp}_2\text{ZrCl}]_2\text{O}$,⁴³ and $[\text{Cp}_2\text{HfCH}_3]_2\text{O}$,⁵⁰ while complexes containing a M_3O_3 six-membered ring could not be found. Generally, these complexes exhibit M–O bond distances shorter than those observed for typical oxygen-donor ligands, and this effect is usually attributed to sp or sp^2 hybridization of the bridging oxygen atom and ($d_\pi\text{--}p_\pi$) interaction with the metal. Ring formation imposes Zr–O–Zr angles in VII far from linearity, 142.5 (2)°, and this is reflected in the smaller M–O multiple bond contribution.

Conclusions

Carbon dioxide undergoes a deoxygenation to carbon monoxide both with $[\text{Cp}_2\text{TiCl}]_2$ and $\text{Cp}_2\text{Zr}(\text{CO})_2$ to give μ -oxo complexes $[\text{Cp}_2\text{TiCl}]_2\text{O}$ and $[\text{Cp}_2\text{ZrO}]_3$, respectively. $[\text{Cp}_2\text{ZrO}]_3$, which is formally a trimer of the monomeric zir-

conyl complex, $\text{Cp}_2\text{Zr}=\text{O}$, contains a nearly planar six-membered ring $[\text{Zr}_3\text{O}_3]$. The green compound produced by the reaction of $\text{Cp}_2\text{Ti}(\text{CO})_2$ with CO_2 thus has been characterized as a bridging carbonate complex, $[(\text{Cp}_2\text{Ti})_2(\text{CO}_3)]_2$, on the basis of vibrational spectra, chemical evidences, and X-ray analysis. The use of $^{13}\text{C}\text{O}_2$ allowed us to identify, without doubt, the route to the titanium–carbonate complex, as being the disproportionation of CO_2 to CO and CO_3^{2-} . Parallel studies, carried out employing CO_2 equivalent molecules, allow us to suggest some pathways for these CO_2 metal-promoted transformations, deoxygenation, and disproportionation.

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Supplementary Material Available: A listing of structure factor amplitudes for $[(\text{Cp}_2\text{Ti})_2(\text{CO}_3)]_2$ and $(\text{Cp}_2\text{ZrO})_3$ and the thermal parameters and the equations of least-squares planes (Tables VI and VII) (80 pages). Ordering information is given on any current mast-head page.

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ENDOR Investigation of Internal Dynamics in Cyclopropyl Galvinoxyl Radicals

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Abstract: The ESR and ENDOR spectra of cyclopropyl-substituted galvinoxyls exhibit temperature-dependent line positions and line widths. This behavior could be interpreted by assuming two different types of dynamic processes to be present, giving rise to temperature-dependent β -proton hyperfine couplings and to line-shape effects, respectively. The latter process could be described by a jump model for the hindered rotation of the aroxy rings within the galvinoxyl moiety. Barriers to internal rotation and activation parameters of the jump processes have been evaluated. The measured hyperfine coupling constants were assigned to molecular positions; the signs of the couplings could be determined by means of the electron-nuclear-nuclear TRIPLE resonance technique. Possible mechanisms of the dynamic processes and the equilibrium geometries of the radicals are briefly discussed.

Introduction

The magnetic resonance methods ESR and ENDOR have proved to be of unique value in the elucidation of the structure of organic free radicals. Besides the determination of electron spin distributions and equilibrium conformations, e.g., twist angles, they permit an insight into the internal dynamics of molecules.¹ Such dynamic processes can affect the widths of spectral lines provided the characteristic time of the interconversions is comparable to the ESR/ENDOR time scale (10^{-9} – 10^{-4} s).² Quite different mechanisms can be responsible for the intramolecular dynamic behavior: hindered rotation,³ ring inversion,⁴ pyramidal atomic inversion,⁵ intramolecular electron transfer,⁶ ion pairing,⁷ or torsional oscillations.⁸ There are two distinct effects with respect to the temperature-dependent appearance of the spectra. Firstly, β -proton hyperfine coupling constants often show a marked temperature dependence due to torsional oscillations of sterically hindered alkyl groups.⁹ Secondly, line shapes can be temperature dependent because the molecule is involved in a rate process modulating isotropic hyperfine couplings, the rates being temperature dependent.¹⁰ Furthermore, intermolecular exchange effects, i.e., chemical and Heisenberg exchange, may be a cause of line broadening.

In the present paper we report on the syntheses and ESR/ENDOR studies of cyclopropyl and cycloprop[*a*]acenaphthylenyl galvinoxyls. Since we are currently interested in studying the internal dynamics in substituted galvinoxyl radicals,^{11,12} we found it worthwhile to investigate in detail the different types of dynamic processes conceivable in cyclopropyl galvinoxyl, e.g., hindered rotation of the cyclopropyl group and the phenoxyl groups. Another aspect was to gather further

information on the spin-transfer mechanism, i.e., spin polarization or hyperconjugation, into the cyclopropyl substituent. For that purpose, the possibility of relative sign determination of the hyperfine couplings by means of the electron-nuclear-nuclear TRIPLE resonance technique¹³ appeared to be of special value. In order to increase the bulkiness of the substituent, we have extended our investigation to cycloprop[*a*]acenaphthylenyl galvinoxyl.

Experimental Section

Preparation of Compounds. The galvinoxyl precursors, i.e., the galvinoxyls, were prepared from cyclopropanecarboxylic acid (to give **1b**), from 6b,7a-dihydro-7H-cycloprop[*a*]acenaphthylene-7-carboxylic acid (to give **2b**), and from the respective deuterated carboxylic acid¹⁴ (to give **3b**) by using our organometallic synthetic pathway described elsewhere.¹⁵ Corresponding to this procedure, the esterified carboxylic acids **1a–3a** were treated with (2,6-di-*tert*-butyl-4-lithium phenoxy)trimethylsilane, followed by elimination of the protecting trimethylsilyl group. The NMR spectra of all compounds are consistent with the structures given in Figure 1. In particular, the possibility of a rearrangement could be ruled out (protons of the three-membered ring, **1b**: δ_A 0.61 ppm, δ_B 1.01 ppm, δ_X 2.33 ppm, $J_{cis} = 8$ Hz, $J_{trans} = 4.5$ Hz; **2b**: A_2X spin system, δ_A 3.15 ppm, δ_X 2.32 ppm, $J_{AX} = 3.5$ Hz). The results for **2b** prove the *exo* configuration of the galvinoxyl (trans position of the protons) in accordance with previous NMR studies of the carboxylic acid **2a** (methyl ester).¹⁶ Moreover, the galvinoxyls **1c–3c** yielded the parent galvinoxyls on reduction.¹⁵ The elemental analyses differ slightly from the usual criterion of $\leq 0.3\%$ deviation, since removal of residual solvent molecules calls for elevated temperatures causing decomposition of the galvinoxyls.

[(3,5-Di-*tert*-butyl-4-hydroxyphenyl)(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)methyl]cyclopropane (**1b**). Cyclopropanecarboxylic acid ethyl ester (0.64 g) was treated with a mixture of 5.0