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C=O and C=C Bond Activation in Diphenylketene Promoted by Dicarbonylbis(η-cyclopentadienyl)titanium(II)

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The reaction of $(cp)_2Ti(CO)_2$ with diphenylketene can be described as a two-step process, the first one giving a 1:1 adduct, $[(cp)_2Ti(Ph_2C_2O)]_2$ (III) (cp = η^5-C_5H_5), followed by the reversible addition of a second Ph_2C_2O molecule, producing $(cp)_2Ti(Ph_2C_2O)_2$ (IV). The X-ray analysis showed, as an interesting structural feature, that Ph_2C_2O is η^2-C,O anchored to titanium in III·2THF, whose dimeric nature comes from the sharing of the oxygen atoms between two titaniums. The addition of a second diphenylketene to III gave a new kind of titanocycle $(cp)_2\underline{TiOC(CPh_2)OC}(CPh_2)$ (IV). The X-ray structural analysis showed that the geometry of the heterocyclic ring is very similar to that found for the dimer of CO_2 in $IrCl(PMe_3)_3(C_2O_4)$. The C=C bond cleavage is achieved on the coordinated Ph_2C_2O, by reacting III with protic acids, while IV gives, through the hydrolysis of the metallocyclic unit, the vinyl ester derivative $Ph_2C{=}CHOC(O)CHPh_2$. Crystallographic details for $[(cp)_2Ti(Ph_2C_2O)]_2 \cdot 2THF$ are space group $P\bar{1}$ (triclinic), $a = 9.990$ (1) Å, $b = 11.058$ (2) Å, $c = 10.820$ (2) Å, $\alpha = 73.86$ (2)°, $\beta = 94.98$ (2)°, $\gamma = 98.85$ (1)°, $V = 1133.2$ Å^3, and $Z = 1$. The final R factor is 6.9% for 3544 observed reflections. Crystallographic details for $(cp)_2\underline{TiOC(CPh_2)OC}(CPh_2)$ are space group $I2/a$ (monoclinic), $a = 24.527$ (4) Å, $b = 11.327$ (2) Å, $c = 20.370$ (3) Å, $\beta = 95.45$ (2)°, $V = 5633.4$ Å^3, and $Z = 8$. The final R factor is 6.1% for 1154 observed reflections.

Introduction

The metal-promoted activation of ketenes can be strictly related to the problem of CO_2 activation by transition-metal complexes.[1,2] Although it is a different process, the problem of the CO_2 fixation is also not yet understood.[3] It is impossible to state, a priori, the requirements that the metal must meet in order to induce a metal–CO_2 interaction. Some useful information can be inferred using model molecules[4] which can imitate the elusive CO_2 and provide information on the influence of the metal, on the attaching mode, and on the evolution of the coordinated species. Moreover, the change in the reactivity induced on molecules widely used in organic synthesis is especially attractive for new selective synthetic routes. In this regard it will be useful to remember that ketenes (specially the more stable, monomeric diphenylketene) can be model molecules for studying the selective site of attack by different metals, which eventually give bimetallic complexes, as well as for studying C=O and C=C bond cleavage, in deoxygenation[5-7] and decarbonylation reactions.[8,9] A brief account of this work has appeared.[10]

Experimental Section

Unless otherwise stated, all reactions described were carried out under an atmosphere of purified nitrogen. Infrared spectra were recorded on Perkin-Elmer 283 and 337 spectrophotometers, and NMR spectra were recorded on a Varian EM-360 spectrometer. Absorption or evolution of CO was measured volumetrically as previously described.[11] Dicarbonylbis(η-cyclopentadienyl)titanium(II) was prepared by one of the methods previously reported.[12] Diphenylketene was prepared and purified following a reported procedure.[13]

Preparations. Bis-μ-(η^2-diphenylketene-*C*,*O*)-bis[bis(η-cyclopentadienyl)titanium] (III). To a hexane (900 cm^3) solution of $(cp)_2Ti(CO)_2$ (2.61 g, 11.5 mmol), neat diphenylketene was added (2.31 g, 12.3 mmol). The solution was heated for 1 h at about 60 °C. The solution color changed to light orange and, on cooling, an orange microcrystalline solid was obtained. This was washed three times with Et_2O (ca. 88%). Anal. Calcd for $[(cp)_2Ti(Ph_2C_2O)]_2$, $C_{48}H_{40}O_2Ti_2$: C, 77.41; H, 5.37; Ti, 12.90. Found: C, 78.09; H, 5.43; Ti, 12.8. The same reaction was carried out in tetrahydrofuran, THF. A THF solution of $(cp)_2Ti(CO)_2$ (2.24 g, 10.44 mmol) and diphenylketene (2.05 g, 10.56 mmol) was heated for 2 h at about 60 °C. After cooling, the deep orange crystals formed were washed with THF (ca. 56%). Anal. Calcd for $[(cp)_2Ti(Ph_2C_2O)]_2 \cdot 2THF$, $C_{56}H_{56}O_4Ti_2$: C, 75.67; H, 6.31; Ti, 10.81. Found: C, 74.75; H, 6.03; Ti, 11.03. The X-ray analysis was carried out using these crystals.

Both complexes are poorly soluble in benzene. Higher solubility is shown by the complex containing THF. Its solubility in THF is around 5%. III and III·2THF are thermally stable both in the solid state and in toluene. III·2THF was refluxed for 4 h in toluene without any change.

The IR spectrum does not show any absorption above 1600 cm^{-1}, and the CO stretching band cannot be unequivocably assigned. ^1H NMR spectrum in THF-d_8 vs. Me_4Si: τ 4.44 (10 H, s, cp), 3.0 (10 H, b, mult, Ph). ^1H NMR spectrum in $(CD_3)_2CO$, where the compound is slightly soluble: τ 4.32 (s, cp), 2.87 (b, mult Ph).

Reaction of $[(cp)_2Ti(Ph_2C_2O)]_2$ with Acids. (a) Reaction with Dry HCl. $[(cp)_2Ti(Ph_2C_2O)]_2$ (0.33 g, 0.44 mmol) suspended in toluene (10 cm^3) and reacted with dry HCl gave $(cp)_2TiCl_2$ (90%).

(b) Reaction with Aqueous HCl. III·2THF (0.318 g, 0.36 mmol) dissolved in THF (20 cm^3) was reacted with an aqueous solution of concentrated HCl (0.1 cm^3). Gas evolution took place immediately and the solution became yellow-green. The gas was shown (chromatography) to be CO only. The solution was evaporated to dryness and the residue recovered with toluene. It contained Ph_2CH_2 and $(Ph_2CH)_2$. The first was determined by GLC (ca. 21%), and the second was separated through chromatography on silica gel (benzene) (ca. 65%). In a second run, the yield of Ph_2CH_2 was ca. 30% and the yield of $(Ph_2CH)_2$ was 55%. While the $Ph_2CH_2/(Ph_2CH)_2$ ratio is practically fortuitous for many experiments, the overall yield in hydrocarbons is higher than 85%.

Synthesis of $(cp)_2Ti(Ph_2C_2O)_2$ (IV). A THF (50 cm^3) solution of $(cp)_2Ti(CO)_2$ (2.5 g, 10.68 mmol) was reacted with an excess of diphenylketene (7.75 g, 39.94 mmol) and heated at 60 °C for 1 h. Ether was added (150 cm^3) after cooling of the solution to room temperature. After the mixture was allowed to stand for 24 h, black crystals were obtained (ca. 30%). Anal. Calcd for $(cp)_2Ti(Ph_2C_2O)_2$: C, 80.56; H, 5.30; Ti, 8.48. Found: C, 80.30; H, 5.30; Ti, 8.40. The yield of the reaction can be improved using toluene as solvent and hexane for precipitating the product, but a less pure and microcrystalline compound is usually obtained. No significant absorption in the IR spectrum above 1600 cm^{-1} has been observed. ^1H NMR (C_6D_6 vs. Me_4Si): τ 4.28 (10 H, s, cp), 3.0 (20 H, b, mult, Ph).

Hydrolysis of IV. A toluene (10 cm^3) solution of $(cp)_2Ti(Ph_2C_2O)_2$ (IV) (0.54 g, 0.95 mmol) treated with dry HCl gave immediately $(cp)_2TiCl_2$, which was filtered out. The solution [chromatography on silica gel with benzene (50%) and hexane (50%)] gave $Ph_2C{=}CH{-}OCO{-}CHPh_2$, mp 94–95 °C. Anal. Calcd for $C_{28}H_{22}O_2$: C, 86.15; H, 5.64. Found: C, 85.71; H, 6.05 (ca. 67%). IR spectrum: ν_{CO} (Nujol) 1750 cm^{-1} (s). ^1H NMR (CCl_4 vs. Me_4Si): τ 5.12 (1 H, s), 2.93 (b, mult, 20 H), 2.47 (1 H, s). Mass spectrum (m/e^+): 152, 167, 194, 196, 390.

Reaction of III with Diphenylketene. $[(cp)_2Ti(Ph_2C_2O)]_2$ (III) (0.47 g, 0.63 mmol) was suspended in toluene (20 cm^3) and heated (70 °C) with stirring in the presence of diphenylketene (1.1 g, 5.67 mmol) for 1 h. The solid dissolved giving a deep black solution. When cooled,

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Table I. Atomic Coordinates ($\times 10^4$ for Nonhydrogen and $\times 10^3$ for Hydrogen Atoms), with Estimated Standard Deviations in Parentheses, for $[Ti(C_5H_5)_2(Ph_2C_2O)]_2 \cdot 2C_4H_8O$

	x/*a*	*y*/*b*	*z*/*c*		*x*/*a*	*y*/*b*	*z*/*c*	*U*, Å^2
Ti	857 (1)	3742 (1)	4880 (1)	H(1)	167 (9)	592 (9)	283 (9)	100 (29)
C(1)	2247 (4)	5319 (4)	3320 (4)	H(2)	306 (9)	565 (9)	528 (9)	79 (29)
C(2)	2927 (4)	5215 (4)	4517 (4)	H(3)	375 (10)	386 (9)	584 (9)	95 (29)
C(3)	3286 (4)	3987 (5)	4968 (5)	H(4)	313 (10)	270 (9)	402 (9)	110 (30)
C(4)	2849 (4)	3344 (4)	4037 (6)	H(5)	184 (9)	415 (9)	196 (9)	97 (29)
C(5)	2181 (4)	4164 (4)	3004 (4)	H(6)	−186 (10)	237 (9)	598 (9)	81 (29)
C(6)	−923 (4)	2303 (3)	6110 (4)	H(7)	12 (10)	288 (9)	761 (9)	71 (29)
C(7)	143 (5)	2480 (4)	6979 (4)	H(8)	224 (10)	212 (9)	698 (9)	76 (29)
C(8)	1255 (5)	2010 (4)	6699 (5)	H(9)	137 (10)	129 (9)	526 (9)	99 (29)
C(9)	834 (5)	1489 (3)	5644 (5)	H(10)	−116 (10)	145 (9)	470 (9)	77 (29)
C(10)	−486 (4)	1690 (3)	5274 (4)	H(22)	28 (8)	212 (7)	276 (8)	40 (25)
O(1)	−635 (2)	4817 (2)	4063 (2)	H(23)	49 (8)	66 (8)	162 (8)	80 (25)
C(11)	−614 (3)	4029 (3)	3358 (3)	H(24)	−113 (8)	54 (8)	−27 (8)	82 (24)
C(12)	−1350 (3)	3962 (3)	2259 (3)	H(25)	−270 (8)	203 (8)	−85 (8)	69 (25)
C(21)	−1251 (3)	3012 (3)	1578 (3)	H(26)	−285 (8)	349 (8)	17 (8)	71 (25)
C(22)	−382 (4)	2068 (3)	1998 (4)	H(32)	−88 (8)	622 (8)	40 (8)	45 (24)
C(23)	−367 (4)	1137 (4)	1371 (4)	H(33)	−236 (8)	761 (8)	−64 (8)	117 (24)
C(24)	−1202 (5)	1108 (4)	300 (4)	H(34)	−475 (8)	721 (8)	17 (8)	88 (24)
C(25)	−2038 (5)	2036 (4)	−159 (4)	H(35)	−554 (8)	545 (7)	181 (8)	57 (24)
C(26)	−2078 (4)	2964 (4)	465 (4)	H(36)	−381 (8)	410 (7)	293 (8)	92 (24)
C(31)	−2307 (3)	4925 (3)	1708 (3)	H(411)	651	91	403	320 (36)
C(32)	−1906 (4)	6010 (4)	745 (4)	H(412)	675	77	248	223 (27)
C(33)	−2782 (5)	6906 (4)	237 (5)	H(421)	493	187	200	188 (23)
C(34)	−4071 (5)	6724 (5)	696 (5)	H(422)	428	120	354	224 (33)
C(35)	−4482 (4)	5648 (5)	1649 (5)	H(431)	399	25	128	282 (36)
C(36)	−3611 (4)	4748 (4)	2146 (4)	H(432)	300	−16	264	344 (38)
O(2)	5803 (9)	−735 (9)	3694 (9)	H(441)	398	−179	341	325 (38)
C(41)	6055 (11)	521 (11)	3256 (14)	H(442)	503	−132	209	285 (33)
C(42)	4772 (14)	1014 (8)	2775 (12)					
C(43)	4022 (15)	16 (9)	2315 (15)					
C(44)	4678 (18)	−1026 (14)	2856 (18)					

the solution gave, by addition of hexane (110 cm^3), black crystals of $(cp)_2Ti(Ph_2C_2O)_2$ (ca. 30%).

The conversion of III in IV can be followed via NMR spectroscopy: $[(cp)_2Ti(Ph_2C_2O)]_2 \cdot 2THF$ (0.09 g, 0.1 mmol) suspended in C_6D_6 (2 cm^3) in the presence of Ph_2C_2O (0.35 g, 1.8 mmol) was refluxed for 1 h 30 min, whereupon a black solution was obtained whose ^1H NMR spectrum is identical with that of an authentic sample of $(cp)_2Ti(Ph_2C_2O)_2$.

Conversion of IV in III and Diphenylketene. $(cp)_2Ti(Ph_2C_2O)_2$ (0.55 g, 0.97 mmol) dissolved in a mixture of hexane (80 cm^3) and toluene (20 cm^3) was refluxed for 2 h. The solution became light orange and gave on cooling $[(cp)_2Ti(Ph_2C_2O)]_2$ (ca. 70%). The free diphenylketene was determined via IR spectroscopy (ca. 75%) (ν_{CO} 2095 cm^{-1}).

X-ray Data. The crystal data follow. For III·2THF, $C_{48}H_{40}O_2Ti_2 \cdot 2C_4H_8O$: fw 888.9, $a = 9.990$ (1) Å, $b = 11.058$ (2) Å, $c = 10.820$ (2) Å, $\alpha = 73.86$ (2)°, $\beta = 94.98$ (2)°, $\gamma = 98.85$ (1)°,[45] $V = 1133.2$ Å^3, $Z = 1$, $d_{calcd} = 1.302$ g cm^{-3}, $F(000) = 468$, $\mu = 34.8$ cm^{-1} (Cu Kα), triclinic, space group $P\bar{1}$ (from structural analysis). For IV, $C_{38}H_{30}O_2Ti$: fw 566.6, $a = 24.527$ (4) Å, $b = 11.327$ (2) Å, $c = 20.370$ (3) Å, $\beta = 95.45$ (2)°, $V = 5633.4$ Å^3, $Z = 8$, $d_{calcd} = 1.336$ g cm^{-3}, $F(000) = 2368$, $\mu = 3.5$ cm^{-1} (Mo Kα), monoclinic, space group $I2/a$[46] (from systematic absences). Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained by least-squares refinement of the 2θ values of 19 reflections for III·2THF ($2\theta > 40°$) and 34 reflections for IV ($2\theta > 20°$).

The crystals used for data collection, sealed in glass capillaries under nitrogen, had dimensions 0.40 × 0.24 × 0.32 mm for III·2THF and 0.13 × 0.24 × 0.50 mm for IV. They were mounted with the [001] axis along the ϕ axis of the diffractometer. Intensity data were collected on the "on-line" single-crystal automated Siemens AED diffractometer using nickel-filtered Cu K$\bar{\alpha}$ radiation (λ 1.5418 Å) at a takeoff angle of 6° for III·2THF and niobium-filtered Mo K$\bar{\alpha}$ radiation (λ 0.7107 Å) at a takeoff angle of 4° for IV. The pulse-height discriminator was set to accept 90% of the Cu K$\bar{\alpha}$ or Mo K$\bar{\alpha}$ peak. The moving-counter-moving-crystal scan technique was employed with a drive speed related to the number of counts on the peak (lowest speed 2.5°/min). One reflection was remeasured after every 20 reflections for both compounds as a check on crystal and instrument stability. No significant change in the measured intensities of these reflections was observed during data collection. For intensities and background the "five-point technique"[14] was used. For III·2THF a total of 4276 independent reflections was measured in the interval $6° < 2\theta < 140°$; of these, 3545 having $I > 2\sigma(I)$ were considered observed and used in the analysis. For IV the number of independent reflections was 4937 ($5° < 2\theta < 50°$), 1157 of which [$I > 2\sigma(I)$] were used in the analysis ($\sigma^2(I)$ = (total counts) + (0.01 × intensity)^2).

The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[15] No correction for absorption was applied [μr = 0.5 for III·2THF and 0.03 for IV] and therefore the thermal coefficients are influenced by this omission, in particular for III·2THF.

Solution and Refinement of the Structure of III·2THF.[16] Initial coordinates for the one independent titanium atom and one independent oxygen atom were obtained from a vector analysis of a three-dimensional Patterson function. Two successive Fourier syntheses yielded the positions of all other nonhydrogen atoms. Refinement was by full-matrix least squares, isotropically down to $R = 12.4\%$ and anisotropically down to $R = 8.6\%$. A subsequent difference Fourier map revealed all hydrogen atoms but those associated to tetrahydrofuran, which were subjected to two cycles of isotropic refinement. The tetrahydrofuran hydrogen atoms were introduced as fixed-atom contributions with free isotropic temperature factors and idealized positional parameters (calculated after each cycle) constrained to fixed values. In the last stage of the refinement no parameters shifted by more than 0.3 times its standard deviation and the refinement was considered to have converged at $R = 6.9\%$, one reflection (100) probably affected by counting errors and/or extinction being rejected.[47]

A final difference map showed no peaks with electron density greater than 0.3 e Å^{-3}. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$ and the reflections were weighted according to the scheme $w^{-1} = [\sigma^2(F_o) + 0.005F_o^2]$ based on counting statistics. The atomic scattering factors were those of ref 17 for Ti, those of Cromer and Mann[18] for O and C, and those of Stewart, Davidson, and Simpson[19] for H. The final atomic coordinates are listed in Table I.

Solution and Refinement of the Structure of IV.[16] The structure was solved by the heavy-atom method as described for III·2THF. The

Table II. Atomic Coordinates ($\times 10^4$ for Nonhydrogen Atoms), with Estimated Standard Deviations in Parentheses, for $Ti(C_5H_5)_2(Ph_2C_2O)_2$

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Ti	797 (1)	2288 (2)	894 (1)	C(25)	1995 (8)	4455 (17)	3864 (9)
O(1)	1382 (3)	3355 (8)	1161 (4)	C(26)	1963 (7)	4253 (14)	3193 (8)
O(2)	1276 (3)	2841 (9)	2225 (4)	C(31)	1763 (6)	5715 (12)	1577 (7)
C(11)	1422 (6)	3665 (14)	1808 (7)	C(32)	1532 (7)	5842 (15)	947 (7)
C(12)	1608 (5)	4756 (11)	2032 (6)	C(33)	1686 (8)	6776 (16)	569 (7)
C(13)	1003 (5)	1838 (12)	1929 (6)	C(34)	2059 (8)	7621 (16)	796 (8)
C(14)	990 (5)	896 (12)	2327 (6)	C(35)	2270 (7)	7480 (16)	1426 (9)
C(1)	255 (7)	3947 (18)	543 (10)	C(36)	2143 (7)	6540 (17)	1806 (8)
C(2)	263 (6)	3892 (13)	1237 (9)	C(41)	1283 (6)	783 (12)	2982 (6)
C(3)	17 (6)	2860 (17)	1423 (6)	C(42)	1813 (7)	1124 (13)	3123 (7)
C(4)	−157 (6)	2287 (16)	835 (9)	C(43)	2092 (7)	997 (16)	3735 (9)
C(5)	−25 (7)	2902 (18)	321 (8)	C(44)	1844 (8)	540 (17)	4246 (8)
C(6)	1368 (8)	685 (16)	767 (7)	C(45)	1297 (8)	188 (17)	4123 (8)
C(7)	1530 (6)	1560 (17)	340 (10)	C(46)	1019 (6)	323 (14)	3504 (8)
C(8)	1082 (7)	1782 (13)	−122 (7)	C(51)	646 (6)	−130 (13)	2094 (7)
C(9)	686 (6)	956 (14)	−6 (7)	C(52)	86 (7)	−77 (12)	2007 (7)
C(10)	859 (7)	292 (12)	568 (8)	C(53)	−229 (6)	−1053 (16)	1793 (7)
C(21)	1662 (5)	4958 (12)	2752 (6)	C(54)	21 (8)	−2095 (14)	1675 (7)
C(22)	1420 (6)	5956 (14)	2986 (7)	C(55)	575 (8)	−2188 (15)	1792 (8)
C(23)	1458 (7)	6144 (15)	3666 (8)	C(56)	880 (6)	−1219 (16)	2003 (7)
C(24)	1743 (8)	5444 (18)	4092 (7)				

	x/a	*y/b*	*z/c*	*U*, Å		*x/a*	*y/b*	*z/c*	*U*, Å
H(1)	0.043	0.462	0.026	0.19 (12)	H(32)	0.122	0.521	0.075	0.05 (5)
H(2)	0.044	0.455	0.158	0.13 (7)	H(33)	0.151	0.684	0.006	0.23 (9)
H(3)	−0.004	0.255	0.192	0.09 (5)	H(34)	0.216	0.833	0.049	0.15 (13)
H(4)	−0.038	0.146	0.079	0.11 (7)	H(35)	0.256	0.813	0.163	0.18 (10)
H(5)	−0.011	0.268	−0.020	0.16 (8)	H(36)	0.235	0.642	0.231	0.23 (8)
H(6)	0.163	0.036	0.118	0.03 (4)	H(42)	0.202	0.148	0.273	0.13 (7)
H(7)	0.192	0.200	0.038	0.13 (7)	H(43)	0.252	0.127	0.384	0.13 (8)
H(8)	0.105	0.246	−0.049	0.07 (5)	H(44)	0.205	0.043	0.473	0.22 (9)
H(9)	0.030	0.081	−0.030	0.02 (4)	H(45)	0.109	−0.020	0.452	0.23 (10)
H(10)	0.064	−0.039	0.081	0.05 (5)	H(46)	0.060	0.006	0.342	0.05 (5)
H(22)	0.120	0.657	0.265	0.08 (6)	H(52)	−0.010	0.075	0.210	0.09 (7)
H(23)	0.124	0.691	0.386	0.07 (6)	H(53)	−0.068	−0.095	0.172	0.13 (7)
H(24)	0.178	0.566	0.461	0.23 (10)	H(54)	−0.023	−0.283	0.152	0.11 (6)
H(25)	0.220	0.388	0.423	0.06 (5)	H(55)	0.076	−0.304	0.170	0.26 (10)
H(26)	0.218	0.351	0.301	0.07 (6)	H(56)	0.132	−0.133	0.211	0.02 (4)

positions of the atoms were refined first isotropically and then anisotropically only for the titanium atom and the oxygen atoms by several full-matrix least-squares cycles to give a discrepancy index R = 9.3%. The hydrogen atoms could not be accurately located in a difference map and so were introduced in their geometrically calculated positions. These positions corresponded to a residual electron density of ca. 0.7–1.0 e Å^{-3}. Two successive cycles with the contribution of the hydrogen atoms (only their isotropic temperature factors were allowed to vary) gave R = 7.7%. All nonhydrogen atoms were then refined anisotropically to convergence in two "blocked" (two blocks) full-matrix least-squares cycles to R = 0.061, three reflections having $F_o >> F_c$ (004, $\bar{2}$06, 008) being rejected. This result was considered satisfactory in view of the low number of observations with respect to the number of parameters. The final difference Fourier map showed no significant peaks. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found.

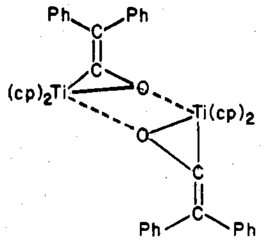
The function minimized was $\sum w|\Delta F|^2$ with unit weights, the weighting scheme $w^{-1} = [\sigma^2(F_o)^4 + |g|F_o^2]$ attempted for different g values giving unsatisfactory results. Scattering curves are the same as used previously. The final atomic coordinates are listed in Table II.

Results and Discussion

Chemical Studies. Dicarbonylbis(η-cyclopentadienyl)titanium(II), $Ti(cp)_2(CO)_2$ (I) (cp = η^5-C_5H_5), reacts with 1 mol of diphenylketene in THF or hexane solution at 60 °C, releasing 2 mol of CO to give a 1:1 $Ph_2C{=}C{=}O/(cp)_2Ti$ adduct:[20]

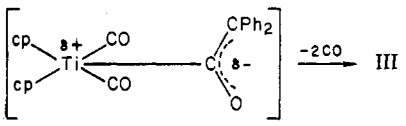
$$\underset{\text{I}}{(cp)_2Ti(CO)_2} + \underset{\text{II}}{Ph_2C{=}C{=}O} \xrightarrow[-2CO]{} \underset{\text{III}}{{}^1/_2[(cp)_2Ti(Ph_2C_2O)]_2} \quad (1)$$

III was obtained as deep orange crystals from THF, containing 1 mol of THF/mol of Ti, and as a microcrystalline powder in higher yield from hexane. III is diamagnetic and has been characterized by elemental and spectroscopic analyses. The presence of the intact Ph_2C_2O moiety has not been inferred either from spectroscopic data or from the reaction of III with protic acids (vide infra). The molecular complexity was deduced from the X-ray analysis, which first of all indicates that Ph_2C_2O is η^2-C,O bonded to titanium. These results explain the absence of any CO stretching band above 1600 cm^{-1} in the IR spectrum. A sketch of III shows its main structural features: the η^2-C,O bonded diphenylketene unit and the dimerization achieved through the oxygen atoms shared by two titaniums.

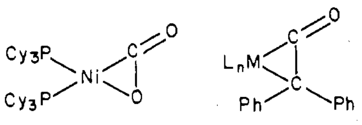


III

The high reactivity of I with electrophilic substrates is a quite general behavior of this dicarbonyl derivative and can be easily explained on the basis of the highly nucleophilic properties found for d^2–$(cp)_2MX_2$ systems.[21] Reaction 1 can be interpreted as occurring through a nucleophilic attack by the titanium(II) on the electrophilic carbon of diphenylketene:



This step is, as usual, followed by the loss of two CO per titanium and by the addition of the carbenoid unit $(cp)_2Ti$ to the C=O bond. We must underline that of all the "titanocenes" described until now, none contains the monomeric $(cp)_2Ti$ unit,[22] so I can be regarded as the most authentic source of the $(cp)_2Ti$ carbene, which is stabilized by the two easily leaving CO groups. The high affinity of the $(cp)_2Ti$ unit for C=O units gave rise to a novel bonding mode of diphenylketene, acetyl,[21] and diphenylureylene[23] ligands. The structure of III looks like a model structure for the addition of CO_2 to a transition metal, being reminescent of the structure of the $(PCy_3)_2NiCO_2$,[24] A (Cy = cyclohexyl).

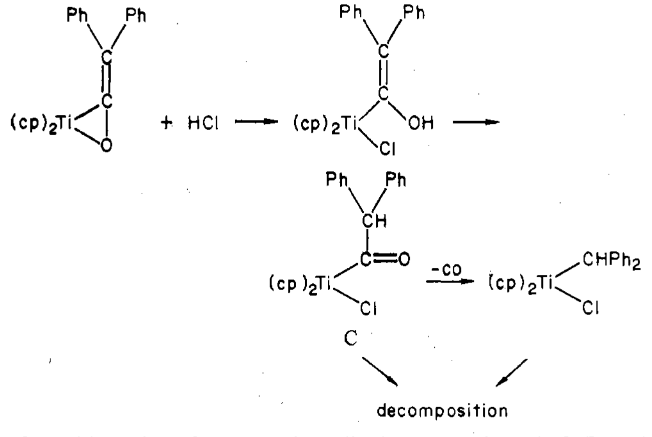


A B

The addition of the carbenoid-like metal unit, $Pt(PPh_3)_2$,[25] and $Mn(cp)(CO)_2$[26] to Ph_2C_2O occurs at the C=C bond giving a metallocyclopropanone structure (B) (ν_{CO} 1700–1800 cm^{-1}). Apart from a lower reactivity, no significant changes were observed for an η^2-C,C bonded Ph_2C_2O.[27] In this connection, an interesting test could be the reaction of III with protic acids:

$$\underset{\text{III}}{[(cp)_2Ti(Ph_2C_2O)]_2} + n\text{HCl} \xrightarrow[-2CO]{} (cp)_2TiCl_2 + Ph_2CH_2 + (Ph_2CH)_2 \quad (2)$$

Reaction 2, exemplified for HCl, gave the same results independently of the source of protons (ROH, HCl etc.). The yield in hydrocarbons is practically quantitative, and the evolution of CO, no other gas being present, was gas-volumetrically controlled. The products expected from the reaction of Ph_2C_2O with protons are diphenylacetic acid or its derivatives. One experimental observation can help us in describing the probable pathway of this C=C bond cleavage. The hydrolysis carried out under rigorously pure nitrogen gave first a green solution, probably containing a titanium(III) derivative which, however, was impossible to identify.



C could produce free organic radicals, generating Ph_2CH_2 and $(Ph_2CH)_2$, through the homolytic cleavage of the Ti–COR bond or, more likely, the decarbonylation of C[28] could give the corresponding alkyl which normally decomposes via a free-radical pathway.[29]

The attack of the carbene-like $(cp)_2Ti(CO)_2$ on the C=O bond of Ph_2C_2O can be strictly related to the adduct between Ph_2C_2O and trivalent phosphorus derivatives.[30,31] These adducts evolve by deoxygenation of Ph_2C_2O, giving Ph_2C_2, which is formed through the rearrangement of a diphenylvinylidene carbene intermediate. The utilization of deoxygenating agents, such as $P(OEt)_3$, for many unsaturated units, mainly N=O, is very well-known in synthetic organic chemistry.[32] This reaction has its parallel in inorganic chemistry, where metal carbonyls[33] or other metal complexes are used as deoxygenating agents.[34] The deoxygenation of diphenylketene was observed for every attempt in which its complexation was tried in combination with metal carbonyls. The deoxygenation was realized by the activated CO giving CO_2 and the resulting diphenylvinylidene carbene being trapped by coordination to two metal centers.[5,6] The reaction of $(cp)_2Ti(CO)_2$ with Ph_2C_2O, on the contrary, stops at the addition product, III, which was heated in refluxing toluene for 4 h without any change. Reaction of I with nitro and nitroso derivatives gave, like trivalent phosphorus derivatives, azo and azooxi derivatives but no isolation of addition products was possible.[35] This parallel chemistry between trivalent phosphorus and $(cp)_2Ti(CO)_2$ will be further emphasized afterward.

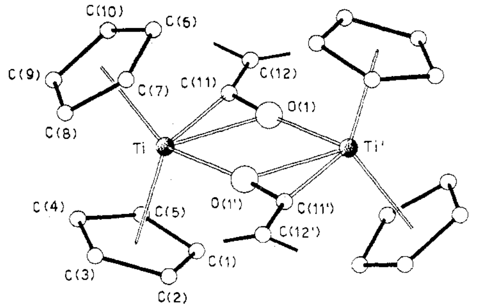


Figure 1. View of the molecular structure of the dimer $[(cp)_2Ti(Ph_2C_2O)]_2$. The phenyl rings have been omitted for clarity.

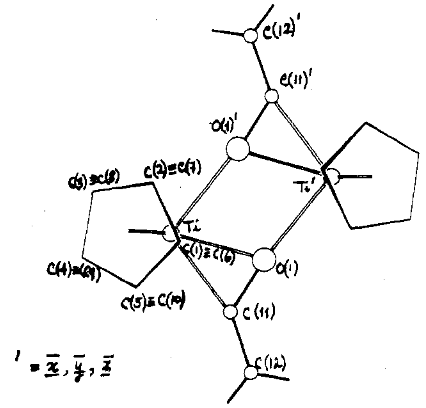


Figure 2. Projection of the dimer $[(cp)_2Ti(Ph_2C_2O)]_2$ onto the plane perpendicular to the ring(centroid)$_1$–Ti–ring(centroid)$_2$ plane. Phenyl rings have been omitted.

Ketenes seem to be the ideal source of the carbene ligands. A dissociative oxidative addition to the C=C bond is not yet known. Decarbonylation of diphenylketene was successful and gave organic products, whose origin can be explained through the intermediate formation of the corresponding carbene.[7-9] Reaction 2 carried out on the coordinated Ph_2C_2O can be considered as a special case of the C=C bond activation promoted by a transition metal.

Structural Properties of III. The molecular structure of III illustrating the atom-labeling scheme is shown in Figure 1. The final interatomic distances and angles are given in Table III. The crystal structure is composed of dimers of the basic unit $(cp)_2Ti(Ph_2C_2O)$. The monomeric unit consists of η^2-C,O diphenylketene bonded to the $(cp)_2Ti$ unit, and the dimerization is achieved through an oxygen shared by two centrosymmetric titanium atoms. The dimer possesses a crystal-

Table III. Bond Distances[a] (Å) and Angles (deg), with Estimated Standard Deviations in Parentheses, for $[Ti(C_5H_5)_2(Ph_2C_2O)]_2 \cdot 2C_4H_8O$[b]

Distances

Ti-C(1)	2.417 (4)	Ti-C(6)	2.414 (4)	C(1)-C(2)	1.393 (6)	C(6)-C(7)	1.386 (6)	O(2)-C(41)	1.33 (2)
Ti-C(2)	2.415 (4)	Ti-C(7)	2.414 (4)	C(1)-C(5)	1.402 (7)	C(6)-C(10)	1.403 (6)	O(2)-C(44)	1.44 (2)
Ti-C(3)	2.396 (4)	Ti-C(8)	2.388 (5)	C(2)-C(3)	1.401 (7)	C(7)-C(8)	1.386 (7)	C(41)-C(42)	1.47 (2)
Ti-C(4)	2.407 (5)	Ti-C(9)	2.394 (4)	C(3)-C(4)	1.392 (8)	C(8)-C(9)	1.421 (7)	C(42)-C(43)	1.42 (2)
Ti-C(5)	2.416 (4)	Ti-C(10)	2.399 (4)	C(4)-C(5)	1.418 (7)	C(9)-C(10)	1.378 (6)	C(43)-C(44)	1.38 (2)
av	2.410 (4)	av	2.403 (5)	av	1.401 (6)	av	1.394 (8)		
Ti-O(1)	2.037 (2)	O(1)-C(11)	1.311 (4)	C(21)-C(22)	1.413 (5)	C(31)-C(32)	1.384 (5)		
Ti-C(11)	2.099 (3)	C(11)-C(12)	1.357 (4)	C(21)-C(26)	1.409 (5)	C(31)-C(36)	1.392 (5)		
Ti-O(1′)	2.250 (3)	C(12)-C(21)	1.460 (5)	C(22)-C(23)	1.384 (6)	C(32)-C(33)	1.389 (7)		
Ti-cp(1)	2.095 (4)	C(12)-C(31)	1.505 (5)	C(23)-C(24)	1.373 (6)	C(33)-C(34)	1.386 (7)		
Ti-cp(2)	2.088 (4)			C(24)-C(25)	1.380 (7)	C(34)-C(35)	1.374 (8)		
				C(25)-C(26)	1.383 (6)	C(35)-C(36)	1.387 (7)		
				av	1.393 (7)	av	1.386 (3)		

Angles

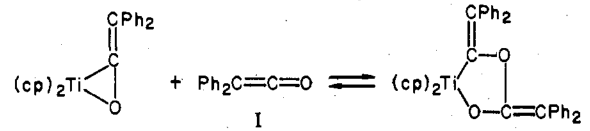
C(1)-Ti-C(2)	33.5 (1)	C(6)-Ti-C(7)	33.4 (2)	C(1)-C(2)-C(3)	108.1 (4)	C(6)-C(7)-C(8)	109.3 (4)
C(1)-Ti-C(5)	33.7 (2)	C(6)-Ti-C(10)	33.9 (1)	C(2)-C(3)-C(4)	107.9 (4)	C(7)-C(8)-C(9)	106.4 (4)
C(2)-Ti-C(3)	33.9 (2)	C(7)-Ti-C(8)	33.5 (2)	C(3)-C(4)-C(5)	108.5 (4)	C(8)-C(9)-C(10)	108.8 (4)
C(3)-Ti-C(4)	33.7 (2)	C(8)-Ti-C(9)	34.6 (2)	C(4)-C(5)-C(1)	106.7 (4)	C(9)-C(10)-C(6)	107.6 (4)
C(4)-Ti-C(5)	34.2 (2)	C(9)-Ti-C(10)	33.4 (2)	C(5)-C(1)-C(2)	108.8 (4)	C(10)-C(6)-C(7)	107.9 (4)
av	33.7 (1)	av	33.8 (2)	av	108.0 (4)	av	108.0 (5)
O(1)-Ti-O(1′)	67.7 (1)	cp(1)-Ti-O(1′)	104.7 (2)	Ti-O(1)-Ti′	116.0 (1)		
C(11)-Ti-O(1)	36.9 (1)	cp(1)-Ti-C(11)	103.9 (2)	Ti-O(1)-C(11)	74.1 (2)		
C(11)-Ti-O(1′)	104.7 (1)	cp(2)-Ti-O(1)	114.2 (2)	Ti-C(11)-O(1)	69.0 (2)		
cp(1)-Ti-cp(2)	131.2 (2)	cp(2)-Ti-O(1′)	104.5 (2)	Ti-C(11)-C(12)	161.9 (3)		
cp(1)-Ti-O(1)	112.9 (2)	cp(2)-Ti-C(11)	105.4 (2)	O(1)-C(11)-C(12)	128.8 (3)		
C(11)-C(12)-C(21)	123.4 (3)	C(21)-C(22)-C(23)	122.0 (4)	C(31)-C(32)-C(33)	120.7 (4)	C(41)-O(2)-C(44)	102 (1)
C(11)-C(12)-C(31)	118.2 (3)	C(22)-C(23)-C(24)	120.5 (4)	C(32)-C(33)-C(34)	120.2 (5)	C(42)-C(41)-O(2)	109 (1)
C(21)-C(12)-C(31)	118.4 (3)	C(23)-C(24)-C(25)	119.1 (4)	C(33)-C(34)-C(35)	119.7 (5)	C(41)-C(42)-C(43)	103 (1)
C(12)-C(21)-C(22)	123.4 (3)	C(24)-C(25)-C(26)	121.1 (4)	C(34)-C(35)-C(36)	120.1 (4)	C(42)-C(43)-C(44)	105 (1)
C(12)-C(21)-C(26)	120.7 (3)	C(25)-C(26)-C(21)	121.4 (4)	C(35)-C(36)-C(31)	120.9 (4)	C(43)-C(44)-O(2)	111 (1)
C(12)-C(31)-C(32)	120.4 (3)	C(26)-C(21)-C(22)	115.9 (3)	C(36)-C(31)-C(32)	118.5 (3)		
C(12)-C(31)-C(36)	121.2 (3)	av	119.5 (1.1)	av	119.8 (5)		

[a] The C-H distances range from 0.80 to 1.15 Å. [b] A prime indicates $\bar{x}$, $1 - y$, $1 - z$.

lographic C_i (1) symmetry. The molecular plane (not crystallographic) defined by Ti, O(1), C(11), and O(1′) bisects the cp–Ti–cp angle. The cyclopentadienyl rings are planar (Table V)[48] and their mutual orientation is nearly eclipsed (Figure 2). The average cp ring C–C distances are 1.401 (3) and 1.394 (3) Å, with an average ring angle of 108.0 (2)°. The Ti–C(cp) distances vary from 2.388 (5) to 2.417 (4) Å [mean values 2.410 (2) and 2.403 (2) Å]. The Ti–cp(centroid) distances are 2.095 (4) and 2.088 (4) Å, and the cp(centroid)–Ti–cp(centroid) angle is 131.2 (2)°. This geometry is similar to that in many other $Ti(cp)_2$ complexes, containing η^5 bonded cyclopentadienyls.[36] The more significant parameters associated with Ph_2C_2O coordinated to titanium are reported in Figure 3 (monomeric unit), together with the parameters identifying the same ligand η^2-C,C bonded in $(cp)Mn(CO)_2(Ph_2C_2O)$,[26] and the acetyl ligand η^2-C,O bonded to titanium in $(cp)_2Ti(COMe)Cl$.[21]

A relevant C–O bond distance can be inferred from other η^2-C,O bonded ligands, such as CO_2 in $Ni(PCy_3)_2CO_2$ (D).[24] It is interesting to note that Ph_2C_2O repeats in III the attachment mode of CO_2 in D. The C–O bond distance is in the range of the C–O single bond, conserving only a slight character of double bond.[37] The rather anomalous lengthening of the C=C distance indicates the long-range metal-induced effect, which can be represented through a delocalization of double-bond character over the C–C–O unit. THF is present as crystallization solvent.[38]

Complex III can undergo a reversible ring-expansion reaction on treatment with an excess of Ph_2C_2O in toluene, from which IV is obtained as a black crystalline solid:



(3)

monomeric unit in III I IV

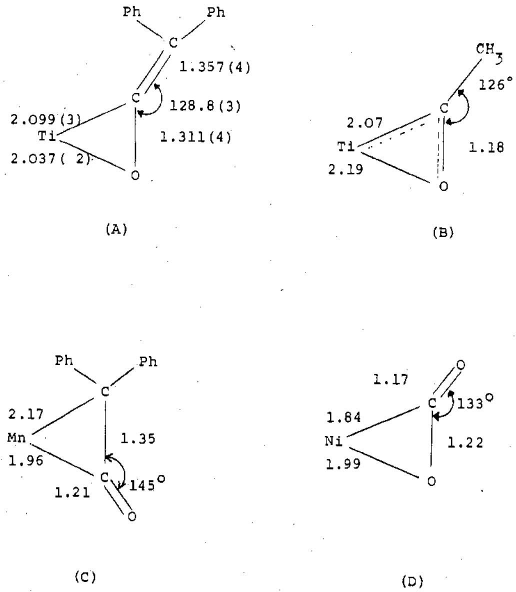


Figure 3.

IV can be synthesized directly from $(cp)_2Ti(CO)_2$ reacted with a large excess of Ph_2C_2O both in THF and in toluene. It was found that heating IV in toluene–hexane in the absence of Ph_2C_2O gives back III while I is released. The spectroscopic properties of IV give little information about its structure, but the hydrolysis gave $Ph_2C{=}CHOCOCHPh_2$, which is the rearranged organic part of the metallocycle. Novel features and properties of IV, including genesis and evolution, will be discussed on the basis of the molecular and crystal structure.

Structural Properties of IV. The crystal structure of IV consists of discrete molecules separated by van der Waals contacts. The molecular structure illustrating the atom-

Table IV. Bond Distances (Å) and Angles (deg), with Estimated Standard Deviations, for Ti$(C_5H_5)_2(Ph_2C_2O)_2$

Distances

Ti–C(1)	2.37 (2)	Ti–C(6)	2.32 (2)	Ti–cp(1)	2.04 (2)		
Ti–C(2)	2.38 (2)	Ti–C(7)	2.36 (2)	Ti–cp(2)	2.03 (2)		
Ti–C(3)	2.37 (2)	Ti–C(8)	2.32 (2)	Ti–O(1)	1.92 (1)		
Ti–C(4)	2.33 (2)	Ti–C(9)	2.37 (2)	Ti–C(13)	2.18 (1)		
Ti–C(5)	2.34 (2)	Ti–C(10)	2.37 (2)				
av[a]	2.36 (1)	av	2.35 (1)				
O(1)–C(11)	1.36 (2)	C(12)–C(31)	1.50 (2)	C(1)–C(2)	1.41 (3)	C(6)–C(7)	1.40 (3)
O(2)–C(11)	1.33 (2)	C(13)–C(14)	1.34 (2)	C(1)–C(5)	1.42 (3)	C(6)–C(10)	1.35 (3)
O(2)–C(13)	1.42 (2)	C(14)–C(41)	1.46 (2)	C(2)–C(3)	1.38 (2)	C(7)–C(8)	1.40 (2)
C(11)–C(12)	1.38 (2)	C(14)–C(51)	1.49 (2)	C(3)–C(4)	1.39 (2)	C(8)–C(9)	1.39 (2)
C(12)–C(21)	1.48 (2)			C(4)–C(5)	1.32 (3)	C(9)–C(10)	1.42 (2)
				av	1.38 (2)	av	1.39 (1)
C(21)–C(22)	1.38 (2)	C(31)–C(32)	1.36 (2)	C(41)–C(42)	1.36 (2)	C(51)–C(52)	1.37 (2)
C(21)–C(26)	1.37 (2)	C(31)–C(36)	1.37 (2)	C(41)–C(46)	1.40 (2)	C(51)–C(56)	1.38 (2)
C(22)–C(23)	1.40 (2)	C(32)–C(33)	1.38 (2)	C(42)–C(43)	1.37 (2)	C(52)–C(53)	1.39 (2)
C(23)–C(24)	1.32 (3)	C(33)–C(34)	1.37 (3)	C(43)–C(44)	1.36 (3)	C(53)–C(54)	1.36 (2)
C(24)–C(25)	1.38 (3)	C(34)–C(35)	1.35 (2)	C(44)–C(45)	1.40 (3)	C(54)–C(55)	1.36 (3)
C(25)–C(26)	1.38 (2)	C(35)–C(36)	1.37 (3)	C(45)–C(46)	1.38 (2)	C(55)–C(56)	1.37 (2)
av	1.38 (1)	av	1.37 (1)	av	1.38 (1)	av	1.37 (1)

Angles

C(1)–Ti–C(2)	34.6 (7)	C(6)–Ti–C(7)	34.8 (6)	O(1)–Ti–C(13)	77.0 (4)
C(1)–Ti–C(5)	35.1 (7)	C(6)–Ti–C(10)	33.5 (6)	O(1)–Ti–cp(1)	108.9 (5)
C(2)–Ti–C(3)	33.9 (6)	C(7)–Ti–C(8)	34.8 (6)	O(1)–Ti–cp(2)	106.9 (5)
C(3)–Ti–C(4)	34.4 (6)	C(8)–Ti–C(9)	34.3 (5)	C(13)–Ti–cp(1)	105.0 (6)
C(4)–Ti–C(5)	32.9 (6)	C(9)–Ti–C(10)	34.9 (5)	C(13)–Ti–cp(2)	110.0 (6)
av	34.1 (5)	av	34.5 (4)	cp(1)–Ti–cp(2)	134.3 (7)
Ti–O(1)–C(11)	115.0 (8)	C(11)–O(2)–C(13)	115.6 (1.0)	C(2)–C(1)–C(5)	104.0 (1.6)
Ti–C(13)–C(14)	138.9 (1.0)	C(11)–C(12)–C(21)	117.6 (1.2)	C(1)–C(2)–C(3)	110.2 (1.5)
Ti–C(13)–O(2)	106.2 (8)	C(11)–C(12)–C(31)	122.6 (1.2)	C(2)–C(3)–C(4)	105.3 (1.4)
O(2)–C(13)–C(14)	114.6 (1.1)	C(21)–C(12)–C(31)	119.8 (1.1)	C(3)–C(4)–C(5)	110.9 (1.6)
O(2)–C(11)–O(1)	116.0 (1.3)	C(13)–C(14)–C(41)	125.7 (1.2)	C(4)–C(5)–C(1)	109.5 (1.6)
O(2)–C(11)–C(12)	121.1 (1.2)	C(13)–C(14)–C(51)	118.3 (1.2)	av	107.9 (1.5)
O(1)–C(11)–C(12)	122.9 (1.3)	C(41)–C(14)–C(51)	116.0 (1.2)		
C(7)–C(6)–C(10)	110.8 (1.5)	C(22)–C(21)–C(26)	118.3 (1.3)	C(32)–C(31)–C(36)	117.3 (1.4)
C(6)–C(7)–C(8)	107.1 (1.4)	C(21)–C(22)–C(23)	118.5 (1.4)	C(31)–C(32)–C(33)	119.7 (1.5)
C(7)–C(8)–C(9)	106.4 (1.4)	C(22)–C(23)–C(24)	122.7 (1.6)	C(32)–C(33)–C(34)	123.7 (1.4)
C(8)–C(9)–C(10)	109.8 (1.3)	C(23)–C(24)–C(25)	119.4 (1.5)	C(33)–C(34)–C(35)	114.9 (1.6)
C(9)–C(10)–C(6)	105.5 (1.4)	C(24)–C(25)–C(26)	118.8 (1.6)	C(34)–C(35)–C(36)	122.9 (1.7)
av	107.9 (1.2)	C(25)–C(26)–C(21)	122.1 (1.5)	C(35)–C(36)–C(31)	121.5 (1.5)
		av	119.8 (1.0)	av	120.0 (1.5)
C(42)–C(41)–C(46)	116.6 (1.3)	C(52)–C(51)–C(56)	116.5 (1.4)	C(12)–C(21)–C(22)	117.9 (1.2)
C(41)–C(42)–C(43)	123.1 (1.4)	C(51)–C(52)–C(53)	121.7 (1.4)	C(12)–C(21)–C(26)	123.7 (1.3)
C(42)–C(43)–C(44)	121.1 (1.6)	C(52)–C(53)–C(54)	119.8 (1.5)	C(12)–C(31)–C(32)	123.5 (1.3)
C(43)–C(44)–C(45)	117.6 (1.6)	C(53)–C(54)–C(55)	119.7 (1.6)	C(12)–C(31)–C(36)	119.2 (1.3)
C(44)–C(45)–C(46)	120.9 (1.6)	C(54)–C(55)–C(56)	119.9 (1.6)	C(14)–C(41)–C(42)	123.1 (1.2)
C(45)–C(46)–C(41)	120.7 (1.5)	C(55)–C(56)–C(51)	122.3 (1.5)	C(14)–C(41)–C(46)	120.3 (1.3)
av	119.9 (1.2)	av	120.0 (1.1)	C(14)–C(51)–C(52)	122.6 (1.3)
				C(14)–C(51)–C(56)	120.7 (1.3)

[a] All average values have been calculated using the formulas

$$x_m = \frac{\Sigma N_i x_i}{\Sigma w_i} \qquad \sigma_i = \left(\frac{1}{N-1}\left(\frac{\Sigma w_i x_i^2}{\Sigma w_i}\right) - x_m^2 + \frac{1}{\Sigma w_i}\right)^{1/2} \qquad w_i = \sigma_i^{-2}$$

where x_i are the individual observations and σ_i are their standard deviations.

numbering scheme is shown in Figure 4. Each titanium is η^5 bonded to two C_5H_5 rings that are bent back to make a cavity in the horizontal plane (not crystallographic) for the metallocycle moiety. The molecule has no crystallographic symmetry. Interatomic distances and angles are given in Table IV. The two cyclopentadienyl rings are closely planar (Table V[48]) and the differences in the C–C bond lengths are not significant. They exhibit a nearly staggered configuration (Figure 5).

Distances from titanium to the ring centers are 2.03 (2) and 2.04 (2) Å, and the cp(centroid)–Ti–cp(centroid) angle is 134.3 (7)°. This geometry is similar to that in many other Ti(cp)$_2$ complexes.[36]

The five-membered heterocyclic ring system shows many interesting features. It must be noticed that it is a practically unknown organic moiety coordinated to a transition metal. Far from being planar, it shows an envelope-like conformation with Ti deviating 0.67 Å from the best plane through C(11), O(2), C(13), and O(1) (Table V[48]). The value of 2.18 (1) Å for Ti–C(13) falls in the range of the Ti–C(sp^2) known distances: 2.172 (5) and 2.141 (5) Å in (cp)$_2$TiC$_4$Ph$_4$,[36] 2.27 Å in (cp)$_2$TiPh$_2$,[39] 2.107 (7) and 2.230 (7) Å in (cp)$_2$Ti(Ph$_2$C$_2$)(CO),[40] 2.099 (3) Å in [(cp)$_2$Ti(Ph$_2$C$_2$O)]$_2$·2THF. All C–O bond distances are much more reminiscent of a single rather than a double C–O bond, and they compare very well with the long C–O bond in carboxylic acids and esters [1.358 (5) Å].[37] The lengthening of the C–O bond from III to IV is persuasive evidence of the olefinic-like nature of the C=O unit in bonding titanium in III. Further support for the notion that Ph_2C_2O can be considered a model molecule for CO_2 in its reaction with transition metals results from a comparison between the geometries of the two heterocycles Ti$(Ph_2C_2O)_2$ and Ir(C_2O_4)[41] (Figure 6). The organic moiety built up by the dimerization of CO_2 coordinated to a transition metal looks

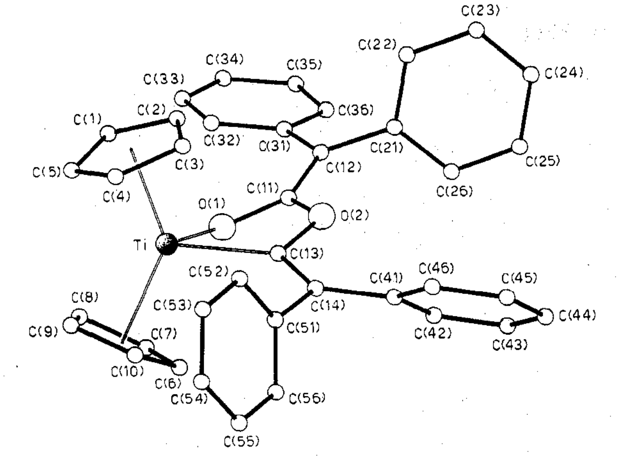


Figure 4. A view of the molecular structure of $(cp)_2Ti(Ph_2C_2O)_2$.

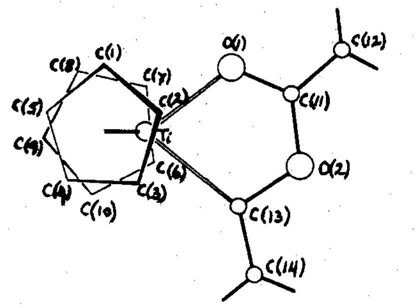


Figure 5. Projection of the structure of $(cp)_2Ti(Ph_2C_2O)_2$ onto the plane perpendicular to the ring(centroid)$_1$–Ti–ring(centroid)$_2$ plane. Phenyl rings have been omitted.

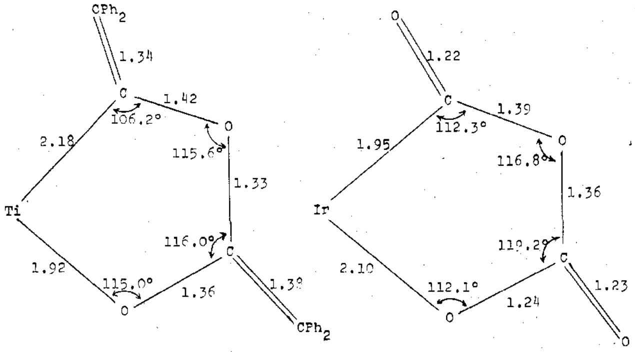


Figure 6. Geometry of the five-membered heterocyclic ring system in $(cp)_2Ti(Ph_2C_2O)_2$ (IV) and $IrCl(C_2O_4)(PMe_3)_3$.

like the dimer obtained through the opening of the C═O bonds of diphenylketene.

As the reaction between $(cp)_2Ti(CO)_2$ and Ph_2C_2O is initiated by the addition of the nucleophilic titanium(II) to Ph_2C_2O, so the basic oxygen in III could bond a second molecule of Ph_2C_2O through the electrophilic carbon. Cyclization via Ti–O bond formation affords IV. Some years ago, the reactions of η-carboxo complexes with other unsaturated molecules to yield five-membered metallocycles received some attention.[42] The suspected two steps in the dimerization of Ph_2C_2O promoted by trivalent phosphorus[30,31] and CO_2 promoted by $IrCl(C_8H_{14})(PMe_3)_3$[41] have their models in reactions 1 and 3. Moreover, the final compounds can be considered structural models for the supposed intermediates. It must be emphasized that a dimerization process like (4), promoted by metals, can be the key explanation of the evolution from many intermediate CO_2 complexes of carbon monoxide and carbonato complexes.[3,41] Very likely, the metal-induced decomposition of alkyl and aryl isocyanates by basic metals[23,43] to carbon monoxide and ureylene ligands RN–CO–NR could pass through the steps observed in the reaction of $(cp)_2Ti(CO)_2$ with Ph_2C_2O.

It is very well-known that electronically rich metals provide the activation for C═O functions, but in the absence of the reactive multiple C–C bonds.[44] The example reported concerns the selective attack by a metal on the C═O bond in the presence of a highly reactive C═C bond.

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Registry No. $(cp)_2Ti(CO)_2$, 12129-51-0; Ph_2C═CH—OCO—$CHPh_2$, 67073-67-0; III·2THF, 66350-87-6; IV, 66350-86-5.

Supplementary Material Available: Listings of structure factor amplitudes, least-squares planes (Table V), and anisotropic thermal parameters (Tables VI and VII) for III·2THF and IV (51 pages). Ordering information is given on any current masthead page.

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(46) The unit cell parameters, reduced to the standard setting $C2/c$ (No. 15), are $a = 30.358$ (5) Å, $b = 11.327$ (2) Å, $c = 20.370$ (3) Å, and $\beta = 126.46$ (3)°. The transformation matrix from the $I2/a$ to $C2/c$ orientation is $(101//0\bar{1}0//00\bar{1})$. Coordinates of equivalent positions for the nonstandard $I2/a$ setting are $(0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2)$ +; x, y, z; $\bar{x}, \bar{y}, \bar{z}$; ${}^1/_2 - x, y, \bar{z}$; ${}^1/_2 + x, \bar{y}, z$.
(47) Absorption corrections were not applied in view of the rather low absorbance ($\mu\bar{r}$ ca. 0.5) and the irregular shape of the sample examined.
(48) Supplementary material.

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Isolation of the Ion Pair $NaCo(CO)_4$ Promoted by an Inorganic Ligand: Structure and Properties of $[(Co(salen))_2NaCo(CO)_4THF]$

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A THF (tetrahydrofuran) solution of sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na, reacts reversibly with carbon monoxide giving a monocarbonylic species, Co(salen)NaCO, rapidly evolving under a CO atmosphere to a compound containing $NaCo(CO)_4$ as a complexed ion pair, $[(Co(salen))_2NaCo(CO)_4THF]$ (III). The structure of III has been solved by single-crystal X-ray diffraction methods. Crystallographic details for III are as follows: space group $P\bar{1}$ (triclinic), $a = 12.356$ (3) Å, $b = 13.207$ (3), Å, $c = 17.576$ (4) Å, $\alpha = 92.83$ (2)°, $\beta = 121.55$ (2)°, $\gamma = 116.69$ (2)°, $V = 2025.8$ Å^3, and $Z = 2$. The final R factor is 4.9% for 2849 observed reflections. The most interesting feature of the structure is the fact that III is a complex of Na^+ octahedrally surrounded by six oxygen atoms provided by two Co(salen) groups, acting as bidentate chelating ligands, THF, and $Co(CO)_4^-$ bonded to Na^+ through one of the carbonylic oxygens. The $Co(CO)_4^-$ has essentially an undistorted tetrahedral symmetry. The IR spectrum in the solid state (Nujol) showed well-resolved bands at 2003, 1917, 1890, and 1867 cm^{-1}.

Introduction

Ion-pairing effects on chemical reactivity of transition-metal organic anions have received very limited attention. Recently, Collman delineated the importance of ion pairing on the reactivity of $Na_2Fe(CO)_4$,[2] whose solid-state X-ray analysis showed the existence of a solvent-separated ion pair and a contact ion pair.[3,4]

While the usual reaction of cobalt(I) square-planar complexes with carbon monoxide gives rise to the corresponding stable monocaronyl derivatives,[5] the reaction with sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na (I),[6-8] allows the isolation of the polynuclear system $[(Co(salen))_2NaCo(CO)_4THF]$ (III), containing the complexed ion pair $NaCo(CO)_4$. Moreover, while it is very well-known that crown ethers complex ion pairs,[9] using "inorganic ligands", such as a set of bicovalent oxygens bonded to a transition metal, it is possible to achieve parallel results.[10-15] Thus ion-pair units may be encapsulated in a cage formed by the oxygen atoms of different coordination compounds.[10-15] These complexes represent structural models for polynuclear and/or polyfunctional systems, whose utilization in molecular activation processes might be important.[16] $NaCo(CO)_4$ was shown by Edgell et al. to consist of an equilibrium of solvent-separated and contact ion pairs, such as $(CO)_3CoCo^-\cdots Na^+$ in THF.[17] We report in this study the genesis and the X-ray analysis of III showing the $(CO)_3CoCONa$ ion pair sequestered by the inorganic ligand *N,N'*-ethylenebis(salicylideniminato)cobalt(II), Co(salen).

Experimental section

All the reactions were carried out under an atmosphere of purified nitrogen or carbon monoxide. Solvents were purified by standard methods. Infrared spectra were recorded on Perkin-Elmer 282 and 337 spectrometers. Absorption or evolution of carbon monoxide was measured volumetrically. The magnetic measurements were carried out with a Gouy balance. *N,N'*-Ethylenebis(salicylideniminato)cobalt(II), Co(salen),[18] and sodium *N,N'*-ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na,[5] were prepared as previously described.

Carbonylation of Sodium *N,N'*-Ethylenebis(salicylideniminato)cobaltate(I), Co(salen)Na. A THF (400 mL) suspension of Co(salen) (13.5 g, 41.5 mmol) was reacted with sodium sand (1.028 g, 44.7 mmol). The suspension gave, on stirring, in 3 h, a deep green solution. The presence of small amounts of solid was eliminated by filtration. The green solution was stirred under CO for another 13 h at atmospheric pressure and room temperature. The color changed slowly from green to red-maroon. The volume of the solution was reduced to 150 mL and, by addition of toluene (200 mL), a red crystalline solid was obtained. This was recrystallized from THF/toluene. Heating must be avoided, because the solid can release free Co(salen). The solid contained small amounts of toluene, which could be found on heating at 180 °C and determined by GLC (ca. 3.7%). This gave rise to the observed differences in the analytical data. Anal. Calcd for $[(Co(salen))_2NaCo(CO)_4]$, $C_{36}H_{28}N_4O_8Co_3Na$: C, 51.18; H, 3.31; N, 6.63. Found: C, 51.81; H, 3.78; N, 5.88. The IR spectrum (Nujol) shows bands at 2003 (vw) and 1920 (m–s) cm^{-1} and a large rather unresolved band at 1880–1860 cm^{-1}. $\mu_{eff}(293\ K) = 2.55\ \mu_B$ per Co(salen) unit. By addition of Et_2O to the deep red solution, suitable crystals for X-ray analysis of $[(Co(salen))_2NaCo(CO)_4THF]$ were obtained. Anal. Calcd for $[(Co(salen))_2NaCo(CO)_4THF]$, $C_{40}H_{36}H_4O_9Co_3Na$: C, 52.40; H, 3.93; N, 6.11. Found: C, 52.30; H, 4.01; N, 6.01. The IR spectrum (Nujol) shows four well-resolved bands at 2003 (w), 1917 (m–s), 1890 (s), and 1867 (s) cm^{-1}. The solid, decomposed with a pyridine solution of I_2, gave 3.68 mol of CO/mol of complex.

Preparation of $[(Co(salen))_2NaCo(CO)_4]$ from $NaCo(CO)_4$. $Co_2(CO)_8$ (1.05 g, 3.07 mmol) was dissolved in toluene and reacted with sodium sand (0.195 g, 8.4 mmol) and Hg (1 mL). In 3 h a gray powder was formed. The solvent was evaporated to dryness and the Hg eliminated when the solid was dissolved in THF (100 mL). Co(salen) (5.8 g, 17.8 mmol) in excess was added to the solution on stirring for 20 min. The excess of Co(salen) was filtered out and the solution gave, by addition of toluene (200 mL), a deep red crystalline

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