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Metal-Promoted C–C Bond Formation from One-Carbon Functional Groups: Modeling Study for Reductive Coupling of Carbon Dioxide

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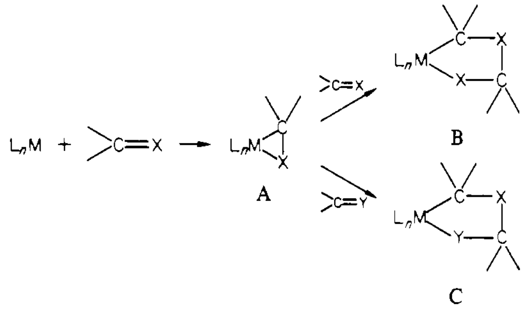
Bis(η^5-cyclopentadienyl)dicarbonyltitanium(II), $Cp_2Ti(CO)_2$ (Cp = η^5-C_5H_5), undergoes an oxidative addition by two molecules of diethyl ketomalonate (DEKM) with loss of the two CO groups and formation of the "symmetric" metallacycle $\underline{Cp_2Ti\text{-}O\text{-}C(R_2)\text{-}C(R_2)\text{-}O}$ (I) (R = $CO_2C_2H_5$). The pinacol-like structure of the ligand O,O′ bonded to titanium(IV) is shown by the NMR spectrum and confirmed by the X-ray analysis. The overall structure is that found for other Cp_2Ti complexes, where the metal bonds a bidentate chelating ligand. The chelate ring has a gauche conformation, the carbon atoms being displaced by 0.18 Å on opposite sites from the Ti,O,O′ plane. *p*-Tolylcarbodiimide (*p*-TCD) is reductively coupled by $Cp_2Ti(CO)_2$ to tetra-*p*-tolyloxalylamidine, which acts as a dinucleating ligand bonding two Cp_2Ti units, containing titanium in the +3 oxidation state (1.74 μ_B per titanium at 293 K) $[Cp_2Ti(p\text{-TCD})]_2$ (II). The nature of the ligand, whose resemblance with other electronically delocalized systems is noteworthy, was clarified by an X-ray analysis. The C–N distances in the metallacycle rings have been, practically, found identical; the mean value of 1.331 (3) Å indicates a significant double-bond character. The dinucleating ligand, except for the *p*-tolyl groups, is perfectly planar with the two titanium atoms displaced by 0.34 Å in the opposite sites of the ligand plane. Iodine converts complex II to the corresponding diamagnetic titanium(IV) compound $[Cp_2Ti(p\text{-TCD})]_2(I_3)_2$. The oxidation of II carried out with tetracyanoethylene (TCNE) affords a probable charge-transfer complex, $[Cp_2Ti(p\text{-TCD})]_2(TCNE)_2$, containing the radical anion $TCNE^{-}\cdot$, the presence of which is deduced from the IR spectrum (ν_{CN}(Nujol) = 2145 (s) and 2185 (ms) cm^{-1}) and from the magnetic moment suggesting the presence of two unpaired electrons per unit. A mechanism is proposed for this rather unusual metal-promoted reductive coupling of DEKM and *p*-TCD. Crystallographic details for complex I: space group *C*2/*c* (monoclinic); $a = 8.264$ (1) Å, $b = 30.455$ (3) Å, $c = 11.612$ (1) Å, $\beta = 96.33$ (1)°, $V = 2904.7$ Å^3, $Z = 4$, $D_{calcd} = 1.311$ g cm^{-3}. The final *R* factor is 0.068 for 1342 observed independent reflections. Crystallographic details for complex II: space group $P\bar{1}$ (triclinic); $a = 12.408$ (1) Å, $b = 10.449$ (1) Å, $c = 8.179$ (1) Å, $\alpha = 103.56$ (1)°, $\beta = 94.29$ (1)°, $\gamma = 94.23$ (1)°, $V = 1023.4$ Å^3, $Z = 1$, $D_{calcd} = 1.299$ g cm^{-3}. The final *R* factor is 0.061 for 3468 observed independent reflections.

Introduction

Much of the interest in organometallic chemistry is, at present, centered on the role of metals promoting C–C bond formation from molecules containing one carbon atom such as carbon monoxide and carbon dioxide. A modeling study in this area is represented by the reactivity of various metal centers with functional groups that maintain some characteristics of carbon monoxide and carbon dioxide. A rather rich harvest of information is so far available on the reaction between group 8 metals in low oxidation state with ketones or imines.[1,2] These results can be summarized in the scheme shown in eq 1 which exemplifies the formation of π complexes

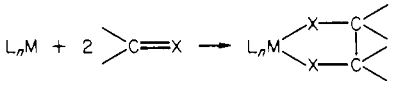


(1)

X = O, NR

such as A and their reaction with the same C=X) or other functional groups (C=Y) yielding "asymmetric" metallacycles B and C.[2] With regard to this, we must point out that a metallacycle such as B would be the intermediate step in the metal-induced disproportionation of some cumulenes, X=C=X.[3]

The group 8 metals were so far unable to promote the reductive coupling of ketones and imines[2,4] and the consequent C–C bond formation seen in eq 2.



(2)

D

Reductive coupling of functional groups other than >C=C< and –C≡C– is rather limited and it has a common feature of being promoted by early-transition-metal complexes. So we find that nitriles are reductively coupled by Cp_2TiR (Cp = η^5-C_5H_5; R = alkyl or aryl),[5] niobium and tantalum complexes,[6] and $(C_5Me_5)Zr$,[7] while ketones undergo the same transformation by the action of $CpTiCl_2$.[8] This is in line with the pinacolic reduction of ketones accomplished by metallic magnesium and zinc.

The occurrence of the functional group transformation seen in reaction 2 bears a relevant importance as a modeling study both for the reduction of CO_2 to oxalic acid and for the reduction of ketones to pinacols and olefins.[9] Such ketone

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transformations are usually accomplished with use of reduced titanium species of undefined chemical composition.

We report here a detailed study on the reductive coupling of the diethyl ketomalonate (DEKM) and *p*-tolylcarbodiimide (*p*-TCD) accomplished by $Cp_2Ti(CO)_2$. Moreover, the reductive coupling of two molecules of *p*-TCD produces a dinucleating ligand with interesting electronic and chemical features. The dependence of reaction 2 on the nature of the metal and of the organic molecule bearing the functional group will be discussed. A brief account of this work was recently reported.[10]

Experimental Section

All the operations described were carried out under an atmosphere of purified nitrogen. Infrared spectra were recorded with a Perkin-Elmer 282 spectrophotometer, and NMR spectra were recorded on a Varian EM-360 spectrometer. Evolution of CO was measured volumetrically. Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) was prepared by one of the methods previously reported.[11] Commercially available diethyl ketomalonate (DEKM) and *p*-tolylcarbodiimide (*p*-TCD) were purified by distillation and crystallization, respectively, before use.

Reaction of $Cp_2Ti(CO)_2$ with Diethyl Ketomalonate. Method A. A diethyl ether (30 mL) solution of $Cp_2Ti(CO)_2$ (0.90 g, 3.84 mmol) is reacted with DEKM (1.8 mL, 11.79 mmol) and the resulting solution is gently heated. The solution color changes from red-brown to green. After 10 min, a fast gas evolution starts and red-maroon crystals form. After 2 h, the solid is collected and washed with Et_2O (ca. 30%). ^1H NMR spectrum shows the presence of Et_2O of crystallization.

Method B. A benzene (20 mL) solution of $Cp_2Ti(CO)_2$ (1.4 g, 5.98 mmol) treated with DEKM (1.9 mL, 12.45 mmol) is heated at ~35 °C for 1 h and then kept for 15 h at room temperature. Crystals suitable for X-ray analysis are present (ca. 20%). The IR spectrum (Nujol) shows a strong broad C=O band centered at 1740 cm^{-1}, which is practically the same as that found in the spectrum of the free ligand. ^1H NMR ($CDCl_3$ vs. Me_4Si): τ 3.38 (s, Cp, 10 H), 5.63 (q, CH_2, 8 H), 8.66 (t, CH_3, 12 H). Anal. Calcd for $Cp_2Ti(DEKM)_2 \cdot 0.6C_6H_6$, $C_{27.6}H_{33.6}O_{10}Ti$: C, 57.82; H, 5.86. Found: C, 57.60; H, 5.95. The content of C_6H_6, which is always present, is variable.

Reaction of $Cp_2Ti(CO)_2$ with *p*-Tolylcarbodiimide. A toluene (20 mL) solution containing $Cp_2Ti(CO)_2$ (0.85 g, 3.63 mmol) and *p*-tolylcarbodiimide (1.7 g, 7.65 mmol) is heated for 2 h at 70 °C. The solution becomes green-maroon and gives deep red-violet crystals (0.8 g, 55%). Anal. Calcd for $[Cp_2Ti(p\text{-}TCD)]_2$, $C_{50}H_{48}N_4Ti_2$: C, 75.0; H, 6.0; N, 7.0. Found: C, 74.80; H, 5.95; N, 7.11. The yield of the complex can be increased by adding hexane to the toluene solution. The solid is only slightly soluble in the usual organic solvents, where it gives green solutions.

The reaction between $Cp_2Ti(CO)_2$ and *p*-TCD is very slow at room temperature. The IR spectrum (Nujol) does not show C=N bands above 1550 cm^{-1}. The magnetic moment is 1.74 μ_B per titanium at 293 K.

Reaction of $[Cp_2Ti(p\text{-}TCD)]_2$ with Iodine. The addition of I_2 (1.0 g, 3.94 mmol) to a THF (30 mL) suspension of $[Cp_2Ti(p\text{-}TCD)]_2$ causes a fast dissolution of the complex, producing a solution which gives $[Cp_2Ti(p\text{-}TCD)]_2(I_3)_2$ as a deep green microcrystalline solid (93% yield). Anal. Calcd for $C_{50}H_{48}N_4I_6Ti_2$: C, 38.42; H, 3.07; N, 3.59; I, 48.76. Found: C, 38.2; H, 3.0; N, 3.45; I, 49.2. The IR spectrum is quite similar to that of complex VII. The crystalline solid may contain some THF of crystallization, but this is lost very easily. The ^1H NMR spectrum $[CO(CD_3)_2$ vs. $Me_4Si]$ shows the presence of one THF molecule per titanium: τ 7.59 (s, Me, 6 H), 2.33 (m, Cp and Ph).

Reaction of $[Cp_2Ti(p\text{-}TCD)]_2$ with Tetracyanoethylene. When a THF (30 mL) suspension of $[Cp_2Ti(p\text{-}TCD)]_2$ (1.18 g, 1.47 mmol) is reacted with tetracyanoethylene (TCNE) (0.41 g, 3.20 mmol), suddenly the dissolution of the solid occurs. A microcrystalline green solid forms in a few minutes, which is washed with THF (ca. 80%). Anal. Calcd for $[(Cp_2Ti(p\text{-}TCD))]_2(TCNE)_2$, $C_{62}H_{48}N_{12}Ti_2$: C, 70.45; H, 4.55; N, 15.91. While C and H percentages always fall in the expected range, we did not get reproducible values for N. Found for A: C, 69.94; H, 4.36; N, 15.60. Found for **B**: C, 70.67; H, 5.08; N, 12.42. The IR spectrum (Nujol), which is very similar to those of complexes VII and VIII in the region 1550–400 cm^{-1}, displays two strong bands at 2145 (s) and 2185 (ms) cm^{-1}. The magnetic moment is 1.73 μ_B at 293 K per titanium.

Table I. Summary of Crystal Data and Intensity Collection

	$[Cp_2Ti(DEKM)_2] \cdot 0.6C_6H_6$	$[Cp_2Ti(p\text{-}TCD)]_2$
a, Å	8.264 (1)	12.408 (1)
b, Å	30.455 (3)	10.449 (1)
c, Å	11.612 (1)	8.179 (1)
α, deg	90	103.56 (1)
β, deg	96.33 (1)	94.29 (1)
γ, deg	90	94.23 (1)
Z	4	1
M_r	573.3	800.8
D_{calcd}, g/cm^3	1.311	1.299
space group	*C*2/*c*	$P\bar{1}$
radiation	Ni-filtered Cu Kα radiation (λ = 1.5418 Å)	Ni-filtered Cu Kα radiation (λ = 1.5418 Å)
μ, mm^{-1}	2.94	3.63
scan type	θ–2θ	θ–2θ
scan range	±5° from peak center	±5° from peak center
scan speeds, deg θ/min	2.5/10	2.5/10
backgrounds	stationary cryst at ±0.5°	stationary cryst at ±0.5°
2θ limits, deg	6–120	6–140
criterion for observn	$I > 2\sigma(I)$	$I > 2\sigma(I)$
unique obsd data	1342	3468
unique total data	2160	3859
cryst dimens, mm	0.08 × 0.24 × 0.32	0.16 × 0.40 × 0.59

X-ray Data Collection and Structure Refinement. $Cp_2Ti(DEKM)_2 \cdot 0.6C_6H_6$. A summary of crystal data and intensity data collection is given in Table I. Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained by a least-squares refinement of the 2θ values of 25 reflections (2θ > 80°). The crystal examined was wedged into a thin-walled glass capillary which was sealed under nitrogen. Data were collected at room temperature with use of a single-crystal Siemens automated diffractometer. The pulse-height discriminator was set to accept 90% of the Cu Kα peak. One reflection was remeasured after 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"[12] was used. The structure amplitudes were obtained after the usual Lorentz and polarization reduction, and the absolute scale was established by Wilson's method.[13] No correction for absorption was applied ($\mu\bar{r}$ = 0.2).

The structure was solved by the heavy-atom technique,[14] the titanium atom being assumed to lie on a twofold axis of the centrosymmetric space group *C*2/*c*, as indicated by the number of molecules in the unit cell (*Z* = 4). The Fourier map confirmed this assumption and revealed all the atoms of the complex molecule. Refinement was by full-matrix least squares isotropically down to *R* = 0.17 and then anisotropically down to *R* = 0.11. The subsequent difference map showed a disorder about the ethyl group C(14)–C(15). Attempts to deal with this in terms of partial occupancy were successful only for the methyl carbon C(15), which was considered statistically distributed

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Table II. Final Atomic Fractional Coordinates (×10⁴) for $Cp_2Ti(DEKM)_2 \cdot 0.6C_6H_6$[a]

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Ti	5000	4952 (1)	2500	C(15A)	5018 (35)	2634 (9)	531 (24)
O(1)	4769 (5)	4470 (1)	1437 (3)	C(15B)	6025 (51)	2574 (13)	1448 (36)
O(2)	6212 (6)	3866 (2)	255 (4)	C(16)	452 (9)	3866 (4)	297 (8)
O(3)	5176 (7)	3327 (2)	1240 (5)	C(17)	182 (13)	3673 (4)	−791 (10)
O(4)	2072 (6)	3773 (2)	2423 (4)	C(21)	0000	2778 (9)	2500
O(5)	2201 (6)	3963 (2)	603 (4)	C(22)	1342 (28)	2582 (8)	2266 (18)
C(1)	7865 (8)	5039 (3)	3074 (6)	C(23)	1377 (36)	2115 (9)	2250 (23)
C(2)	7716 (8)	4914 (3)	1915 (7)	C(24)	0000 (–)	1866 (12)	2500
C(3)	6899 (10)	5235 (3)	1275 (6)	H(1)	8373 (97)	4895 (25)	3789 (69)
C(4)	6577 (10)	5572 (3)	2020 (9)	H(2)	8030 (98)	4654 (27)	1595 (62)
C(5)	7143 (10)	5442 (3)	3135 (7)	H(3)	6623 (95)	5204 (25)	492 (65)
C(11)	4633 (7)	4049 (2)	1820 (5)	H(4)	6026 (100)	5801 (26)	1782 (67)
C(12)	5469 (8)	3742 (2)	1018 (6)	H(5)	7023 (97)	5568 (25)	3758 (66)
C(13)	2824 (8)	3906 (2)	1677 (6)	H(161)	−292 (122)	4176 (28)	265 (77)
C(14)	5954 (20)	3010 (3)	514 (14)	H(162)	129 (117)	3653 (28)	756 (82)

[a] Estimated standard deviations in parentheses. The site occupancy factors for the disordered carbon atom and the benzene atoms are 0.60 for C(15A), 0.40 for C(15B), 0.30 for C(21) and C(24), and 0.60 for C(22) and C(23).

over two positions, C(15A) and C(15B). The refinement attempted to the noncentrosymmetric space group *Cc* to remove the disorder was not satisfactory due to the high correlations between parameters and inexplicable distortions in bond distances and angles. This confirmed the original choice of the space group. Refinement of the site occupation factors for the two "partial" carbon atoms led to values of 0.60 and 0.40 for C(15A) and C(15B), respectively. A benzene solvent molecule lying on a twofold axis was found to be present in a successive difference map. The stoichiometric complex/solvent molar ratio was established by the X-ray analysis as a consequence of three facts: (i) the abnormally high isotropic thermal parameters reached by benzene carbons when considered in the molar ratio 1/1, i.e., with site occupancy factors of 1 for the atoms in general positions and 0.5 for those lying on the twofold axis, (ii) the lack of convergency for such a model ($R = 0.11$), and (iii) the packing inconsistency between benzene molecule and methyl carbon in the C(15B) position (15B)···C(22)($1 - x, y, {}^1/_2 - z$) = 2.50 (4) Å]. This suggested for the solvent molecule the use of a site occupation factor of 0.6 equal to that of the C(15A) carbon. With this assumption the isotropic refinement of benzene carbons and disordered atoms converged to the final *R* value of 0.068 for the 1342 observed data. The hydrogen atoms associated with the cyclopentadienyl ring and the C(16) ethyl carbon atom were located on a difference map and subjected to one cycle of isotropic refinement. In the last stage of the refinement no parameter shifted by more than 0.4 its standard deviation.

A final difference map showed no unusual features with no peaks greater than 0.3 e Å^{-3} and no holes lower than −0.2 e Å^{-3}. The effects of the anomalous dispersion were included in all structure factor calculations. No evidence for secondary extinction was found. The atomic scattering factors used were those of ref 15 for Ti, those of ref 16 for O, N, and C, and those of ref 17 for H. The function minimized in the least-squares calculations was $\sum w|\Delta F|^2$, and the reflections were weighted according to the scheme $w^{-1} = (\sigma^2|F| + 0.004F^2)$ on the basis of counting statistics. The final coordinates and thermal parameters are listed in Tables II and III.

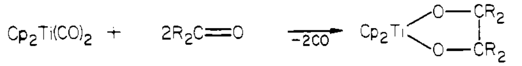
[Cp$_2$Ti(*p*-TCD)]$_2$. A summary of crystal data and intensity data collection is given in Table I. Cell dimensions were determined from rotation and Weissenberg photographs; the values quoted were obtained by a least-squares refinement of the 2θ values (2θ > 100°) of 31 reflections. Data collection and data reduction techniques have been described above.[14] No correction for absorption was applied ($\mu\bar{r}$ = 0.5).

The structure was solved by the heavy-atom technique, starting from a three-dimensional Patterson map. All the nonhydrogen atoms were located in two successive Fourier syntheses. Refinement was by full-matrix least squares first isotropically down to $R = 0.16$, and then anisotropically down to $R = 0.08$. A difference Fourier map, calculated at this stage, revealed electron density concentrations appropriately located for the hydrogen atoms including one for each methyl group. The positions of the other four methyl hydrogens were calculated with the assumption of C–H bond distances of 1.09 Å and an sp^3 hybridization for carbons. All the hydrogen atoms were included in the subsequent refinement as fixed contributors with isotropic thermal parameters fixed at 0.08 Å. Refinement stopped at $R = 0.061$, no parameter shifting by more than 0.4 times its standard deviation in the last cycle. A final difference Fourier map showed no peaks above the general background. 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-sqares calculations was $\sum w|\Delta F|^2$ and the reflections were weighted according to the scheme $w^{-1} = (\sigma^2|F| + 0.004F^2)$ on the basis of counting statistics. The atomic scattering factors used were as indicated above. The final atomic coordinates and thermal parameters are listed in Tables IV and V.

Results and Discussions

Bis(η^5-cyclopentadienyl)dicarbonyltitanium(II), $Cp_2Ti(CO)_2$ (Cp = η^5-C_5H_5), reacts with diethyl ketomalonate (DEKM) in solvents such as C_6H_6 and Et_2O at 30–40 °C, losing carbon monoxide and producing red-maroon crystals of I (eq 3).



(3)

DEKM
(R = COOC$_2$H$_5$)

I, Cp$_2$Ti(DEKM)$_2$

Complex I crystallizes with molecules of solvent. The nature of I was mainly clarified by the ^{1}H NMR spectrum and by the X-ray analysis which was performed on $Cp_2Ti(DEKM)_2 \cdot 0.6C_6H_6$. The yield of I reaches 40% only when a large excess of DEKM over $Cp_2Ti(CO)_2$ is used. The NMR spectrum of the reaction mixture shows the presence of some paramagnetic species, appearing with a green color of the solution. All these data are consistent with the presence of some titanium(III) and the occurrence of concurrent reactions, in spite of the fact that we were unable to identify any complex different from I.

The genesis of I, which resembles the key intermediate proposed to be present in the titanium-promoted deoxygenation of carbonyls, deserves a detailed comment.[18,19] Moreover, this would give suggestions concerning the factors affecting the metal-induced C–C bond formation from >C=X functional groups including CO$_2$.

A synthetic result resembling that reported in reaction 3 is obtained in the reaction between benzophenone and CpTiCl$_2$[8] (see eq 4). The proposed mechanism is based on the nature of the isolated complex III and on the free-radical

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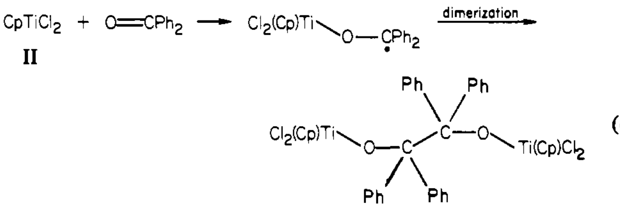
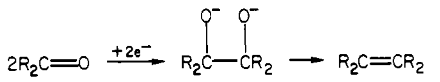


II

(4)

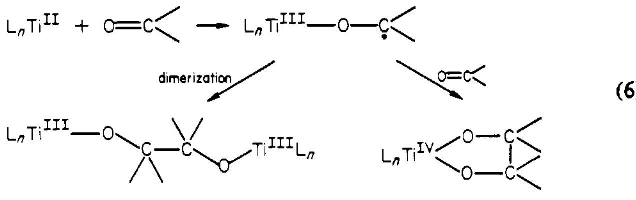
III

nature of II. A quite related process is the deoxygenation of carbonyls accomplished by low-valent titanium species of undefined structure (eq 5). Whether the reaction stops at



$$2R_2C{=}O \xrightarrow{+2e^-} R_2\overset{O^-}{C}{-}\overset{O^-}{C}R_2 \longrightarrow R_2C{=}CR_2 \qquad (5)$$

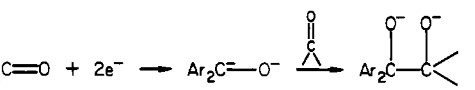
the pinacol or whether it proceeds to the olefin, a common multistep free-radical-like mechanism, as that given in reaction 4, was proposed.[19] This is seen in the scheme of eq 6 for a



(6)

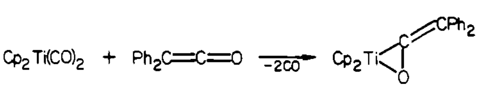
IV

titanium(II) species. An alternative mechanistic hypothesis, suggested for aryl ketones, considers the pinacolic coupling as involving[20] a biectronic reduction of the carbonyl dianion and its nucleophilic addition to another carbonyl (eq 7).



$$Ar_2C{=}O + 2e^- \longrightarrow Ar_2\ddot{C}^{-}{-}O^- \xrightarrow{>C=O} Ar_2\overset{O^-}{C}{-}\overset{O^-}{C}{<} \qquad (7)$$

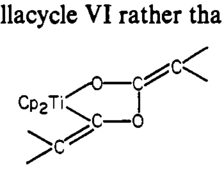
The reaction occurring between $Cp_2Ti(CO)_2$ and diphenylketene (DPK) can be considered a bielectronic reduction of a carbonylic group. Reaction 8 affords a η^2-C,O metal-bonded



(8)

V

DPK[21] formally reduced to the corresponding dianion. It adds to the C=O of another DPK molecule giving, however, the "asymmetric" metallacycle VI rather than the symmetric one



VI

resulting from a head-to-head linkage between the two >C=O groups, as expected from reaction 7. The genesis of VI can be reasonably ascribed to the nucleophilic attack of the metal-bonded oxygen in V on the electrophilic carbon of another >C=O group. This "asymmetric" metallacycle formation was always observed in the reaction between group 8 metals, which usually undergo bielectronic oxidative-addition reactions, and activated ketones or imines.[2,4]

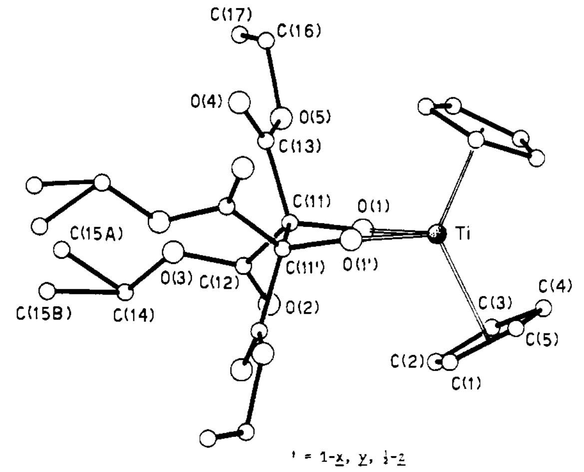
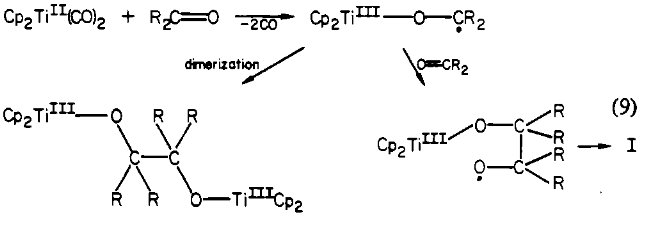


Figure 1. View of the molecular structure of $Cp_2Ti(DEKM)_2$.

Some of the considerations outlined above suggest that a free-radical-like mechanism, which is mainly a feature of early transition metals in low oxidation state, leads to a C–C bond formation while a two-electron reduction affords only a head-to-tail linkage of the same functional groups. A possible mechanism for reaction 1 is based on the nature of I as well as on the appearance of some paramagnetic species and on the influence which the DEKM/titanium ratio has on the yield of I.

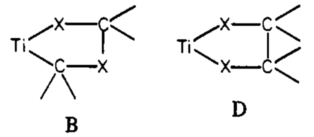
The monoelectronic reduction of DEKM would produce a radical, which can either dimerize or add another molecule or DEKM giving I (see eq 9). A concurrent process such as



(9)

R = COOC$_2$H$_5$

dimerization may account the low yield of I. In both cases, the C–C bond formation is achieved as the consequence of a free-radical process. On the basis of the discussion reported, it seems that the control of the titanium-induced dimerization of a functional group, >C=X, if head-to-tail (B) or head-to-head (D), would mainly depend on the reduction potential of the functional group itself.[22]



B D

Functional groups which can be formally reduced by titanium(II) to the corresponding dianion will produce metallacycles of structure B or products whose genesis is explained by a precursor like B. While DPK gives the metallacycle B, phenyl isocyanate and CO_2 undergo the so-called disproportionation[3] which probably passes through a head-to-tail dimerization of the C=O group. Less reducible molecules such

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(20) McMurry, J. E.; Fleming, M. P.; Kees, K. L.; Krepski, L. R. *J. Org. Chem.* **1978**, *43*, 3255.

(21) Fachinetti, G.; Biran, C.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1978**, *100*, 1921; *Inorg. Chem.* **1978**, *17*, 2995.

(22) Reduction potentials, determined under the same conditions, for the organic species involved in the processes discussed here are difficult to find. Nevertheless, a qualitative evaluation can be done on the basis of the reduction potentials concerning organic molecules bearing similar functional groups: Meites, L.; "Polarographic Techniques", 2nd ed.; Interscience: New York, 1965. "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. VII, Chapter 1; Vol. XII, Chapter 1.

Table IV. Final Atomic Fractional Coordinates (×10^4) for $[Cp_2Ti(p\text{-}TCD)]_2$[a]

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Ti	1089 (1)	2390 (1)	2360 (1)	C(26)	−2159 (2)	1376 (3)	2510 (4)
N(1)	−1335 (1)	−382 (2)	−1048 (2)	C(27)	−4388 (3)	3713 (6)	3318 (8)
N(2)	−489 (1)	1469 (2)	1154 (3)	H(1)	223	3182	−852
C(30)	−528 (2)	312 (2)	25 (3)	H(2)	315	4997	1680
C(1)	930 (2)	3395 (3)	−39 (4)	H(3)	2321	5139	3521
C(2)	969 (3)	4395 (3)	1452 (5)	H(4)	3439	3409	1651
C(3)	1992 (3)	4479 (3)	2305 (6)	H(5)	2181	2061	−1052
C(4)	2581 (3)	3509 (4)	1378 (6)	H(6)	−61	950	4396
C(5)	1928 (3)	2845 (4)	−85 (5)	H(7)	−717	2758	4873
C(6)	580 (7)	1532 (6)	4619 (5)	H(8)	967	4728	5431
C(7)	201 (4)	2753 (6)	4893 (5)	H(9)	2845	3464	5509
C(8)	1055 (3)	3637 (4)	5253 (4)	H(10)	2270	1185	4694
C(9)	2020 (3)	3033 (4)	5185 (4)	H(12)	−3390	−1048	−611
C(10)	1718 (6)	1685 (4)	4805 (4)	H(13)	−5032	−74	−1641
C(11)	−2278 (2)	217 (2)	−1455 (3)	H(15)	−3113	2656	−3287
C(12)	−3309 (2)	−291 (3)	−1237 (4)	H(16)	−1412	1610	−2322
C(13)	−4224 (2)	259 (5)	−1723 (5)	H(171)	−5975	1615	−2863
C(14)	−5153 (3)	1335 (4)	−2436 (5)	H(172)	−5115	1967	−4271
C(15)	3117 (3)	1841 (3)	−2678 (5)	H(173)	−5052	2973	−2201
C(16)	−2200 (2)	1272 (3)	−2214 (4)	H(22)	−1193	3752	687
C(17)	−5156 (4)	1953 (7)	−2943 (8)	H(23)	−2903	4567	1450
C(21)	−1469 (2)	2016 (2)	1638 (3)	H(25)	−3660	1381	3662
C(22)	−1725 (2)	3219 (3)	1315 (4)	H(26)	−2017	522	2852
C(23)	−2668 (3)	3750 (3)	1864 (5)	H(271)	−5094	3016	3199
C(24)	−3358 (2)	3127 (4)	2713 (5)	H(272)	−4589	4433	2594
C(25)	−3102 (2)	1950 (4)	3061 (5)	H(273)	−4221	4234	4638

[a] Estimated standard deviations in parentheses.

as DEKM and *p*-TCD[22] could accept only one electron in the first step of their interaction with titanium(II). The evolution of the radical produced by the action of the metal will give in any case a head-to-head linking of the two functional groups. The description of the structure of I, which is a key product in the reductive coupling of carbonylic groups promoted by various titanium species in low oxidation state, is given below.[9,18,19]

Description of the Structure of $Cp_2Ti(DEKM)_2$. The structure consists of discrete molecules $Cp_2Ti(DEKM)_2$ having crystallographic C_2 symmetry (Figure 1). The twofold axis runs through titanium and bisects the C(11)–C(11′) bond. The planar cyclopentadienyl rings are η^5 bonded to titanium in a bent arrangement, and the plane Ti,O(1),O(1′) (prime = 1 − x, y, $^1/_2 - z$) is nearly orthogonal to that containing the Cp ring normals (Cp–Ti–Cp′ = 130.3 (4)°), the dihedral angle being 85.0°. The structural parameters concerning the Cp_2Ti unit and ester groups fall in the usual range,[3,21,23] if excluding those relative to the ethyl groups affected by disorder or high thermal motion. The atomic positions of the benzene molecule are poorly defined. The organic part derived from the coupling of two diethyl ketomalonato molecules gives an O,O′-bonded metallacycle

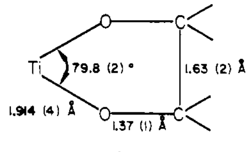

Table VI. Bond Distances (Å) and Angles (Deg) for $Cp_2Ti(DEKM)_2\cdot 0.6C_6H_6$[a,b]

(a) In the Complex Molecule			
Ti–C(1)	2.403 (7)	C(1)–C(2)	1.39 (1)
Ti–C(2)	2.418 (7)	C(1)–C(5)	1.37 (1)
Ti–C(3)	2.392 (8)	C(2)–C(3)	1.36 (1)
Ti–C(4)	2.395 (9)	C(3)–C(4)	1.39 (1)
Ti–C(5)	2.371 (9)	C(4)–C(5)	1.39 (1)
Ti–O(1)	1.914 (4)	C(14)–O(3)	1.48 (2)
Ti–Cp	2.088 (9)	C(14)–C(15A)	1.38 (3)
C(11)–O(1)	1.37 (1)	C(14)–C(15B)	1.71 (4)
C(11)–C(11′)	1.63 (2)	C(13)–O(4)	1.19 (1)
C(11)–C(12)	1.54 (1)	C(13)–O(5)	1.31 (1)
C(11)–C(13)	1.55 (1)	C(16)–O(5)	1.48 (1)
C(12)–O(2)	1.19 (1)	C(16)–O(17)	1.39 (2)
C(12)–O(3)	1.32 (1)		
C(1)–Ti–C(2)	33.5 (3)	C(2)–C(1)–C(5)	107.6 (7)
C(2)–Ti–C(3)	32.9 (3)	C(1)–C(2)–C(3)	108.5 (8)
C(3)–Ti–C(4)	33.7 (3)	C(2)–C(3)–C(4)	108.0 (7)
C(4)–Ti–C(5)	33.8 (3)	C(3)–C(4)–C(5)	107.7 (8)
C(5)–Ti–C(1)	33.4 (3)	C(4)–C(5)–C(1)	108.2 (7)
O(1)–Ti–O(1′)	79.8 (2)	C(11)–C(12)–O(2)	124.1 (6)
O(1)–Ti–Cp	105.8 (3)	C(11)–C(12)–O(3)	111.1 (6)
O(1)–Ti–Cp′	111.9 (3)	O(2)–C(12)–O(3)	124.7 (7)
Cp–Ti–Cp′	130.3 (4)	C(12)–O(3)–C(14)	114.5 (7)
Ti–O(1)–C(11)	121.1 (3)	O(3)–C(14)–C(15A)	105 (2)
O(1)–C(11)–C(11′)	106.3 (7)	O(3)–C(14)–C(15B)	98 (2)
O(1)–C(11)–C(12)	108.4 (5)	C(11)–C(13)–O(4)	126.3 (6)
C(12)–C(11)–C(11′)	116.3 (7)	C(11)–C(13)–O(5)	109.8 (5)
C(12)–C(11)–C(13)	104.9 (5)	O(4)–C(13)–O(5)	123.8 (6)
C(13)–C(11)–C(11′)	110.9 (7)	C(13)–O(5)–C(16)	118.3 (6)
C(13)–C(11)–O(1)	110.0 (5)	O(5)–C(16)–C(17)	111.0 (7)
(b) In the Solvent Molecule			
C(21)–C(22)	1.31 (4)	C(22)–C(21)–C(22′)	126 (3)
C(22)–C(23)	1.42 (4)	C(21)–C(22)–C(23)	118 (2)
C(23)–C(24)	1.42 (4)	C(22)–C(23)–C(24)	121 (3)
		C(23′)–C(24)–C(23)	116 (3)

[a] The distances involving hydrogens range from 0.86 (8) to 1.13 (9) Å. [b] Prime = 1 − x, y, $^1/_2 - z$.

The most relevant structural parameters concern this unit (Table VI). The chelate ring has a gauche conformation with C(11) and C(11′) deviating 0.18 Å from the opposite sites of the Ti,O(1),O(1′) plane. The Ti–O and C–O distances within the metallacycle, which compare well with those reported for $Cp_2Ti(DPK)_2$,[21] have the usual single-bond character. The abnormal lengthening of the C(11)–C(11′) bond distances was found in some oxalato complexes, in which, however, sp^2 rather than sp^3 carbons are involved.[24] Bond distances and angles

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(23) Fachinetti, G.; Floriani, C.; Marchetti, F.; Mellini, M. *J. Chem. Soc., Dalton Trans.* **1978**, 1398. Fachinetti, G.; Floriani, C.; Stoeckli-Evans, H. *Ibid.* **1977**, 2297. Atwood, J. L.; Hunter, W. E.; Alt, H.; Rausch, M. D. *J. Am. Chem. Soc.* **1976**, *98*, 2454. Atwood, J. L.; Stone, K. E.; Alt, H.; Hrneir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367.

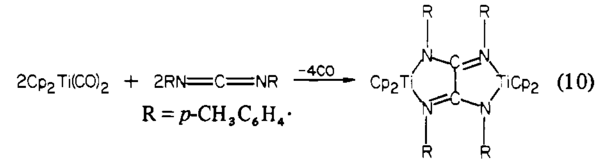
Table VII. Bond Distances (Å) and Angles (Deg) for $[Cp_2Ti(p\text{-}TCD)]_2$[a,b]

Ti–C(1)	2.435 (4)	Ti–C(6)	2.342 (6)	Ti–N(1′)	2.176 (2)	N(1)–C(30)	1.328 (2)
Ti–C(2)	2.392 (4)	Ti–C(7)	2.384 (4)	Ti–N(2)	2.173 (2)	N(2)–C(30)	1.333 (3)
Ti–C(3)	2.391 (4)	Ti–C(8)	2.424 (3)	Ti–Cp(1)	2.101 (4)	C(30)–C(30′)	1.504 (6)
Ti–C(4)	2.405 (4)	Ti–C(9)	2.426 (3)	Ti–Cp(2)	2.089 (4)	N(1)–C(11)	1.421 (3)
Ti–C(5)	2.448 (4)	Ti–C(10)	2.386 (5)			N(2)–C(21)	1.425 (3)
C(1)–C(2)	1.403 (4)	C(6)–C(7)	1.367 (9)	C(11)–C(12)	1.388 (4)	C(21)–C(22)	1.398 (4)
C(1)–C(5)	1.402 (5)	C(6)–C(10)	1.402 (11)	C(11)–C(16)	1.387 (4)	C(21)–C(26)	1.386 (4)
C(2)–C(3)	1.388 (5)	C(7)–C(8)	1.320 (8)	C(12)–C(13)	1.383 (5)	C(22)–C(23)	1.392 (4)
C(3)–C(4)	1.403 (5)	C(8)–C(9)	1.393 (6)	C(13)–C(14)	1.384 (7)	C(23)–C(24)	1.363 (6)
C(4)–C(5)	1.398 (5)	C(9)–C(10)	1.386 (6)	C(14)–C(15)	1.399 (5)	C(24)–C(25)	1.379 (6)
				C(15)–C(16)	1.391 (5)	C(25)–C(26)	1.409 (4)
				C(17)–C(14)	1.518 (8)	C(27)–C(24)	1.524 (6)
C(1)–Ti–C(2)	33.8 (1)	C(6)–Ti–C(7)	33.6 (2)	N(2)–Ti–N(1′)	73.6 (1)		
C(1)–Ti–C(5)	33.4 (1)	C(6)–Ti–C(10)	34.5 (3)	N(2)–Ti–Cp(1)	108.7 (1)		
C(2)–Ti–C(3)	33.7 (1)	C(7)–Ti–C(8)	31.8 (2)	N(2)–Ti–Cp(2)	108.6 (2)		
C(3)–Ti–C(4)	34.0 (1)	C(8)–Ti–C(9)	33.4 (1)	N(1′)–Ti–Cp(1)	109.7 (1)		
C(4)–Ti–C(5)	33.5 (1)	C(9)–Ti–C(10)	33.5 (1)	N(1′)–Ti–Cp(2)	109.7 (2)		
				Cp(1)–Ti–Cp(2)	131.6 (2)		
Ti–N(2)–C(30)	118.1 (1)	C(2)–C(1)–C(5)	108.3 (3)	N(1)–C(11)–C(12)	121.6 (3)	N(2)–C(21)–C(22)	121.2 (2)
Ti–N(2)–C(21)	121.6 (1)	C(1)–C(2)–C(3)	107.7 (3)	N(1)–C(11)–C(16)	120.5 (2)	N(2)–C(21)–C(26)	119.6 (2)
C(21)–N(2)–C(30)	120.1 (2)	C(2)–C(3)–C(4)	108.4 (3)	C(12)–C(11)–C(16)	117.7 (3)	C(22)–C(21)–C(26)	119.2 (2)
Ti′–N(1)–C(30)	117.7 (1)	C(3)–C(4)–C(5)	108.0 (3)	C(11)–C(12)–C(13)	121.0 (4)	C(21)–C(22)–C(23)	119.6 (3)
Ti′–N(1)–C(11)	121.2 (1)	C(4)–C(5)–C(1)	107.5 (3)	C(12)–C(13)–C(14)	121.7 (3)	C(22)–C(23)–C(24)	121.8 (3)
C(11)–N(1)–C(30)	120.7 (2)	C(7)–C(6)–C(10)	109.0 (5)	C(13)–C(14)–C(15)	117.5 (3)	C(23)–C(24)–C(25)	118.9 (3)
N(1)–C(30)–N(2)	131.2 (2)	C(6)–C(7)–C(8)	107.3 (5)	C(13)–C(14)–C(17)	121.7 (4)	C(23)–C(24)–C(27)	121.7 (4)
N(1)–C(30)–C(30′)	115.8 (2)	C(7)–C(8)–C(9)	111.4 (4)	C(15)–C(14)–C(17)	120.7 (4)	C(25)–C(24)–C(27)	119.4 (4)
N(2)–C(30)–C(30′)	114.0 (2)	C(8)–C(9)–C(10)	105.8 (4)	C(14)–C(15)–C(16)	120.6 (4)	C(24)–C(25)–C(26)	120.9 (4)
		C(9)–C(10)–C(6)	106.5 (5)	C(15)–C(16)–C(11)	121.4 (3)	C(25)–C(26)–C(21)	119.6 (3)

[a] The distances involving hydrogens range from 0.89 to 1.14 Å. [b] Prime = $\bar{x}, \bar{y}, \bar{z}$.

for complex I are given in Table VI.

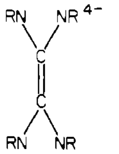
Reaction of $Cp_2Ti(CO)_2$ with *p*-TCD. $Cp_2Ti(CO)_2$ reacting with *p*-TCD produces the tetra-*p*-tolyloxalylamidine dianion, which acts as a dinucleating ligand bridging two Cp_2Ti units (eq 10). Complex VII is obtained as a deep red-violet solid, only slightly soluble in the most common organic solvents. The magnetic measurement indicates the presence of titanium(III) in accordance with the represented bond distribution within the tetradentate ligand, while the alternative bond distribution



(10)

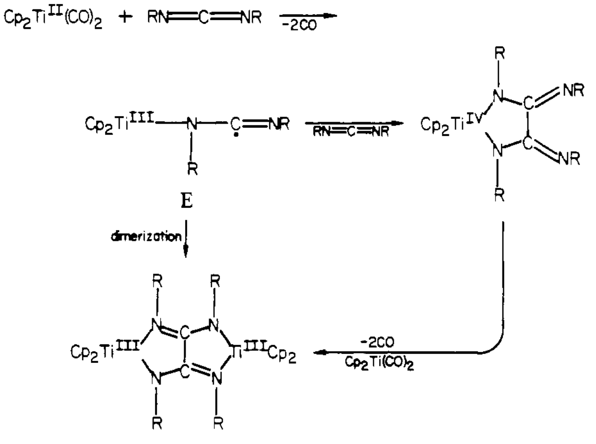
R = $p\text{-}CH_3C_6H_4\cdot$

VII



which requires the presence of titanium(IV), can be ruled out. The IR spectrum does not show C=N bands above 1550 cm^{-1} as expected on the basis of the symmetric electronic distribution over the two CN_2 units, confirmed by the X-ray analysis. The genesis of the dinucleating ligand deserves some comments. It seems to require, first of all, a free-radical activation of the *p*-TCD, and at the same time it suggests that the cumulene structure is not the factor controlling the linking model (head-to-head or head-to-tail) of the functional group. All the other cumulenes so far explored in reaction with $Cp_2Ti(CO)_2$ either produce an "asymmetric" metallacycle, DPK,[21] or undergo a disporportionation reaction, CO_2[3] and PhNCO,[3] through a probable head-to-tail dimerization. A comparison between *p*-TCD and the other cumulenes supports again the hypothesis considering the reduction potential as the factor controlling the direction of the functional group dimerization.[22]

A mechanism can be suggested for reaction 10, in which the titanium(II)–titanium(III) oxidation generates a free-radical anion. The evolution of the radical E in eq 11 is quite similar to that proposed in reaction 9.



(11)

VII, R = $p\text{-}CH_3C_6H_4\cdot$

For both paths sketched in (11), the final complex is in this case the same. The interest in reaction 10 depends even on the nature of the ligand resulting from the coupling of two *p*-TCD.

Description of the Structure of $[Cp_2Ti(p\text{-}TCD)]_2$. The complex consists of the bimetallic centrosymmetric unit shown in Figure 2. The planar cyclopentadienyl rings are η^5 bonded to titanium in a bent arrangement (Cp–Ti–Cp = 131.6 (2)°), in order to make a cavity in the molecular plane for the tetra-*p*-tolyloxalylamidine tetradentate ligand. The structural

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(24) Cavalca, L.; Chiesi-Villa, A.; Gaetani-Manfredotti, A.; Mangia, A.; Tomlinson, A. A. G. *J. Chem. Soc., Dalton Trans.* **1972**, 391.

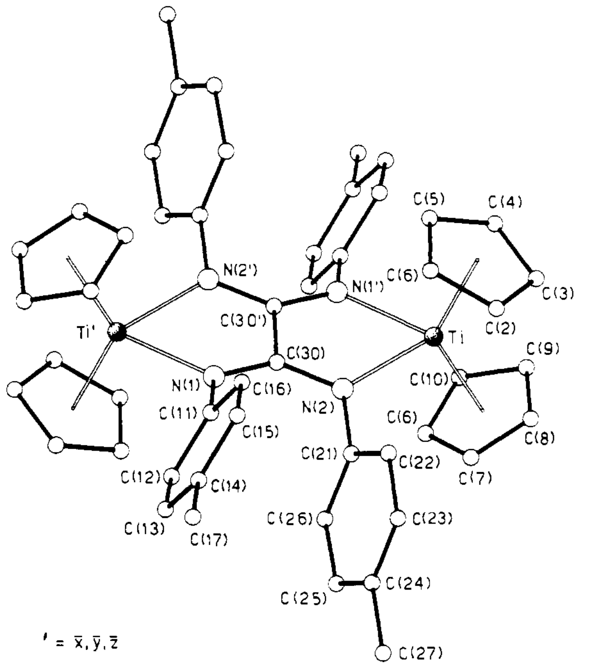
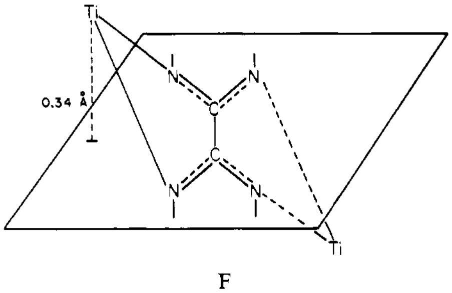


Figure 2. View of the molecular structure of $[Cp_2Ti(p\text{-}TCD)]_2$.

parameters concerning the Cp_2Ti unit[3,21,23] and the *p*-tolyl substituents fall in the usual range. The most interesting part of the molecule is the double metallacycle ring (see F). Bond distances and angles for complex VII are listed in Table VII. The C_2N_4 unit is perfectly planar, with the titanium atoms displaced by 0.34 Å above and below the N(2),C(30),C(30′)N(1′),N(1),N(2′) (prime = $\bar{x}, \bar{y}, \bar{z}$) plane. The C–N bonds are equivalent with a high double-bond character, which indicates a complete electronic delocalization over the two CN_2 units. The absence of any C=N stretching band above 1550 cm^{-1} agrees with this observation. The C–C bond distance of the C_2N_4 units is that of a single bond; bond angles around both carbons indicate an sp^2 hybridization, while the stereochemistry around the nitrogen atoms is between sp^2 and sp^3 limiting geometries. N(2) is displaced by 0.04 Å from the plane through Ti,C(30),C(21); and N(1) deviates by 0.05 Å from the Ti′,C(30),C(11) plane.



F

The interest in complex VII is mainly centered on its redox properties, which are related both to the oxidation state of the metal and to the nature of the ligand. The oxidation of VII with an excess of iodine produces a titanium(IV) complex as a deep-green microcrystalline solid, which contains THF of crystallization (see eq 12). The diamagnetism of complex

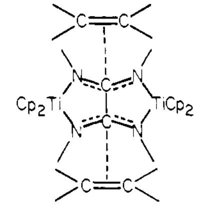
$$\underset{\text{VII}}{[Cp_2Ti(p\text{-}TCD)]_2} + 3I_2 \rightarrow \underset{\text{VIII}}{[Cp_2Ti(p\text{-}TCD)]_2(I_3)_2} \qquad (12)$$

VIII was deduced from the NMR spectrum. The IR spectrum, which is practically identical with that of VII, shows that the oxidation by I_2 affects only the oxidation state of the metal.

The nature of the dinucleating ligand is rather attractive as concerns its electronically delocalized nature, which is strongly reminiscent of the chemical properties of some tetrathiolene complexes.[25] In this perspective, we used complex VII as the electron-donor partner in the reaction with tetracyanoethylene. The oxidation of VII by the TCNE action occurs in THF with the stoichiometry given in eq 13. The

$$\underset{\text{VII}}{[(Cp_2Ti)(p\text{-}TCD)]_2} + 2TCNE \rightarrow \underset{\text{IX}}{[(Cp_2Ti)(p\text{-}TCD)]_2(TCNE)_2} \qquad (13)$$

TCNE is present as the radical anion $TCNE^-$ in complex IX, as suggested by the IR spectrum displaying two strong bands at 2185 and 2145 cm^{-1} [26] and by the magnetic moment indicating the presence of two unpaired electrons. Moreover, the IR spectrum shows the presence of the unchanged dinucleating ligand. Any kind of TCNE–metal interaction occurring through the donor nitrogen atoms gives rise to a much more complicated vibrational spectrum.[26] Therefore, we expect that the TCNE–complex interaction involves the dinucleating ligand, which is the more electron rich site of the complex, rather than the metal (X).



X, $[Cp_2Ti(p\text{-}TCD)]_2(TCNE)_2$

Conclusions. The results presented and the related discussion give some insight into the factors controlling the metal-promoted dimerization of a functional group. This can occur in a head-to-tail or head-to-head manner. This second way represents a C–C bond formation process which is the key reaction for transforming CO_2 into more carbon-rich material. Transition metals, which undergo bielectronic oxidative-addition reactions (group 8 metals mainly), promote the linkage C–X–C–X–, while the C–C bond formation X–C–C–X is the consequence of a one-electron-transfer process from the metal to the molecule to be activated. The redox potentials of the functional group and the metal (nature of the metal and its coordination sphere) are the factors determining the occurrence of either process.

We feel that the nature of the metal, however, could play the prominent role. Group 8 metals when in a low oxidation state usually undergo bielectronic oxidative-addition reactions through a non-free-radical-like mechanism and promote head-to-tail dimerizations. The greatest attention should be given to the early transition metals in low oxidation state, which undergo one- as well as two-electron-transfer processes. For these metals the energetic balance between two different electronic configurations does not have relevant importance and they should play an important role in promoting the C—C bond formation from >C=X units through a free-radical-like pathway.

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Registry No. I, 71615-89-9; VII, 71639-57-1; VIII, 75198-18-4; IX, 75197-52-3; $Cp_2Ti(CO)_2$, 12129-51-0; DEKM, 609-09-6; *p*-TCD, 726-42-1.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters (Tables III and V), and least-squares planes (Table VIII) (12 pages). Ordering information is given on any current masthead page.

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