the corresponding transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) of the Δ isomer (−)$_D$-[Co(bpy)$_3$]$^{3+}$.

Acknowledgments. One of the authors (H.K.) is grateful to Professor Yoshihiko Saito, The University of Tokyo, and Professor Yoichi Shimura, Osaka University, for helpful discussions and encouragement.

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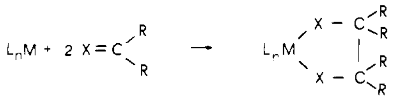
Received February 27, 1979

Reductive Coupling of Carbonyl or Imino Functional Groups by Dicarbonylbis(cyclopentadienyl)titanium(II): Model Reactions for Carbon Dioxide Dimerization and a Novel Metallacycle Formation

Sir:

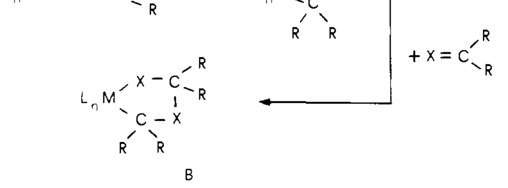
A new perspective on the utilization of transition metals in organic synthesis is represented by the reductive coupling of unsaturated functional groups other than C═C and C≡C[1] (eq 1) (where L$_n$M = low-valent transition metal complex undergoing oxidative addition reactions; X = O, NR).



(1)

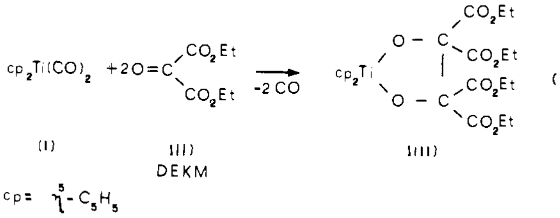
A

A wide range of electron-withdrawing substituents, R, is capable of affecting the necessary activation of the C═X bond to cause π coordination to the metal.[2] Reactions of these complexes with the same or other unsaturated substrates yield five-membered metallacycles[2] (eq 2). All of them have been found, however, to have structure B rather than structure A.[3] Reaction 1 exemplifies an unprecedented process promoted by transition metals producing a C—C single bond. Moreover, should this reductive coupling by realized with CO$_2$, this could produce the precursor of oxalic or glyoxylic acid. We have found that, while cp$_2$Ti(CO)$_2$ (I, cp = η^5-C$_5$H$_5$) causes the disproportionation of CO$_2$[4] and PhNCO,[5] it promotes the reductive coupling of CO$_2$-like molecules such as diethyl ketomalonate, DEKM, or *N,N'*-di-*p*-tolylcarbodiimide, *p*-TCD. Both can be considered as CO$_2$ equivalents,[6] since they maintain one of the main characteristics of CO$_2$, the C═O activated function or the cumulene structure. I reacts with DEKM in benzene producing red-maroon crystals of III[7] (eq 3). Analytical and NMR data, along with a preliminary X-ray analysis, are consistent with the structure reported for III.[7] The final metallacycle could be described as resulting from the reductive coupling of the ketonic function promoted by titanium(II). This result is very reminiscent of the "classic" bimolecular reduction of acetone to pinacol accomplished by metallic magnesium.[8] The titanium-induced reductive coupling of carbonyls to olefins was supposed to involve a key intermediate like III, which precedes the deoxygenation step forming olefins.[9] It is rather difficult to justify the difference in the metallacycle formation occurring with DEKM vs. diphenylketene, which is dimerized by complex I forming a metallacycle of structure B.[10]



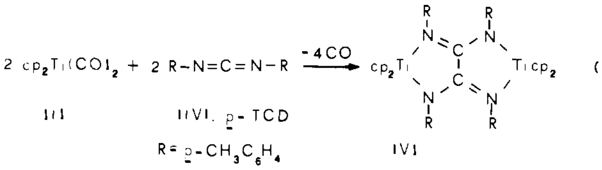
(2)

B



(3)

A second example of reductive coupling of unsaturated functional groups affording a C—C single bond is represented in reaction 4. A toluene solution of I reacts with *p*-TCD giving V.[11] Complex V is rather insoluble, paramagnetic in the solid state (1.74 μ_B per titanium at 293 K), and its IR spectrum does not show any significant band above 1600 cm^{-1} (Nujol mull). Because of the paucity and the limited usefulness of spectroscopic data, an X-ray analysis was required to elucidate the nature of the product. A knowledge of its structure is the fundamental starting point for understanding the metal-induced transformation undergone by IV.



(4)

Crystal Data. C$_{50}$H$_{48}$N$_4$Ti$_2$ (V): M = 800.8; triclinic; a = 12.408 (1), b = 10.449 (1), c = 8.179 (1) Å; α = 103.56 (1), β = 94.29 (1), γ = 94.23 (1)°; Z = 1; d_{calcd} = 1.299, d_{obsd} = 1.31 g cm^{-3} (flotation); space group $P1$. Intensity data were collected on an "on-line" single-crystal automated Siemens AED diffractometer using nickel-filtered Cu kα radiation (λ = 1.54178 A, 6° < 2θ < 140°) at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu kα peak. For intensities and background the "five-point technique"[12] was used. A total of 3468 reflections were considered observed ($I > 2\sigma(I)$) and used in the structure determination and refinement. The structure was solved by heavy-atom method and refined by full-matrix least-squares techniques[13] with anisotropic thermal parameters. The final R index was 0.061.[14]

A view of the molecular structure of V is shown in Figure

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Table I. Bond Distances (Ångstrom) and Angles (Degrees) for $[Ticp_2CN_2(C_6H_4CH_3\text{-}p)_2]_2$

Ti-C(cp)	2.414 (13)[a]	2.407 (11)[a]
Ti-cp ⊥	2.101 (4)[a]	2.089 (4)[a]
C-C(cp)	1.399 (8)[a]	1.376 (14)[a]
C-C(Ph)	1.389 (4)[a]	1.392 (6)[a]
cp(1)-Ti-cp(2)	131.6 (2)	

N(2)-Ti-N(1′)	73.6 (1)	Ti-N(1′)	2.176 (2)
Ti-N(2)-C(30)	118.1 (1)	Ti-N(2)	2.173 (2)
Ti-N(1′)-C(30′)	117.7 (1)	N(1)-C(30)	1.328 (2)
N(2)-C(30)-C(30′)	114.0 (2)	N(2)-C(30)	1.333 (3)
		C(30)-C(30′)	1.504 (6)
		N(1)-C(11)	1.421 (3)
		N(2)-C(21)	1.425 (3)

[a] Values related to crystallographically nonequivalent cyclopentadienyl and phenyl groups. All the average values have been calculated using the formulae

$$x_m = \frac{\Sigma N_i x_i}{\Sigma w_i}$$

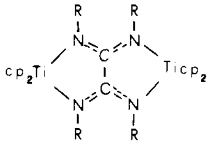
$$\sigma_m = \sqrt{\frac{1}{N-1}(\Sigma w_i x_i^2/\Sigma w_i - x_m^2) + \frac{1}{\Sigma w_i}}$$

$$w_i = \sigma_i^{-2}$$

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

1 and pertinent bond distances and bond angles are given in Table I. See the paragraph at the end of the paper regarding supplementary material. The compound consists of centrosymmetric dimeric units, $[cp_2TiCN_2(C_6H_4CH_3\text{-}p)_2]_2$. Cyclopentadienyl rings are η^5 bonded to the titanium atoms in a bent arrangement. The bridging ligand, which results from the dimerization of two *p*-TCD, acts as a tetradentate ligand chelating two centrosymmetric titaniums through the four nitrogen atoms. The titanium atoms deviate by 0.34 Å on the opposite sides of the perfect plane defined by N(2), C(30), C(30′), N(1′), N(1), and N(2′) (′ = $\bar{x}, \bar{y}, \bar{z}$). The resulting C-C (1.504 (6) Å) and C-N (1.328 (2) and 1.333 (3) Å) distances in the coupled ligand require single and partial double-bond character, respectively. While bond angles around C(30) essentially indicate a sp^2 hybridization, N(1) and N(2) deviate by −0.05 and 0.04 Å from the Ti′-C(30)-C(11) and Ti-C(30)-C(21) planes, respectively.

The structural and magnetic results indicate that the product of the reductive coupling reaction may be considered as a *N,N′,N″,N‴*-tetra-*p*-tolyloxalylamidine derivative with substantial bond delocalization all over the two CN_2 units. The



close relationship between this bridging ligand and the well-known tetrathiolene group stems from the resemblance in their structural and electronic properties.[15]

It is interesting to point out that, depending on the cumulene structure and/or on the nature of X, the reductive coupling of C=X bonds involves either a titanium(II) → titanium(IV) (reaction 3) or a Ti(II) → Ti(III) (reaction 4) oxidation process. Somewhat related and rare examples of reductive coupling of C=O and C=N functional groups affording C—C bond formation have been described to occur in the reaction between typical free-radical-like titanium(III) complexes, $(cpTiCl_2)_2$[16] and (cp_2TiR)[17] with ketones and organic cyanides, respectively.

The so far reported metal-promoted activation on DEKM[2] and carbodiimides is mainly limited to their σ[18] and π[19] coordination to a metal center. In a few cases, it was found that *N,N′*-dialkylcarbodiimides undergo a transformation into the dehydro-*N,N′,N″*-trialkylguanidino dianion, $[RN{=}C(NR)_2]^{2-}$, being complexes by the metal and isonitrile (RNC).[20] This metal-induced transformation, which resembles CO_2[4] and RNCO disproportionation,[5,21] could require as a key intermediate step the dimerization of the carbodiimide, as it was observed for CO_2,[22] into a metallacycle of structure **B**. While we emphasize the uniqueness of these titanium-induced transformations on DEKM and *p*-TCD, we point out that the mechanism by which two DEKM's or *p*-TCD's are reductively coupled is presently unknown. This notwithstanding, both reactions 3 and 4 can be considered model reactions for the reductive coupling of CO_2 to oxalic acid precursors.

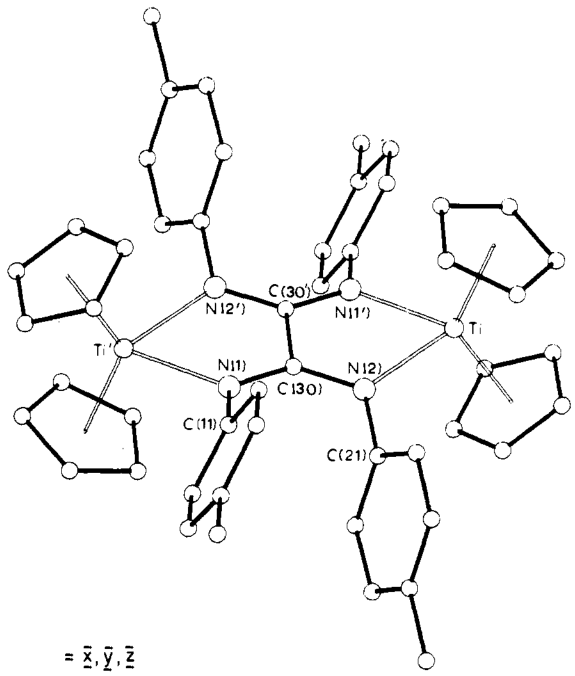


Figure 1. A view of the molecular structure of the dimer $[cp_2TiCN_2(C_6H_4CH_3\text{-}p)_2]_2$.

Acknowledgments. This work was supported by CNR (Rome). We thank Dr. G. Fachinetti for a preliminary experiment with DEKM in the early phase of the work and Dr. G. Dell'Amico for magnetic measurements.

Supplementary Material Available. The final atomic parameters (Tables II and III), bond distances and angles (Table IV), molecular structure of $[cp_2TiCN_2(C_6H_4CH_3\text{-}p)_2]_2$, and a complete listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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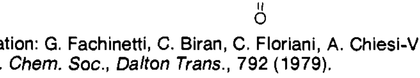
$$4\,cp_2Ti(CO)_2 + 4\,^{13}CO_2 \rightarrow [(cp_2Ti)_2(^{13}CO_3)]_2 + 2\,^{13}CO + 8\,CO$$

$$2\,CO_2 + 2\,e^- \rightarrow CO_3^{2-} + CO$$

(5) Phenyl isocyanate reacts with $cp_2Ti(CO)_2$ producing diphenylureylene $(PhNC({=}O)NPh)^{2-}$ complexes, $(cp_2Ti)_3(PhNCONPh)_2$, and $(cp_2Ti)_2(PhNCONPh)$ in a reaction which corresponds to its metal-induced dis-



$$2\,PhNCO + 2\,e^- \rightarrow [Ph{-}N{-}C({=}O){-}N{-}Ph]^{2-} + CO$$

porportionation: G. Fachinetti, C. Biran, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 792 (1979).

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(11) $cp_2Ti(CO)_2$ (1.25 g, 3.63 mmol) dissolved in toluene (30 mL) is reacted with *N,N'*-di-*p*-tolylcarbodiimide (1.7 g, 7.66 mmol). The reaction slowly occurs at room temperature. Then the solution, when heated for 2 h at 70 °C, produces deep-red crystals of V along with a green maroon solution. The crystals were washed with hexane and dried (yield, ~60%). 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, 75.28; H, 6.06; N, 6.84.
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Received February 13, 1979

MNDO Study of Tetra-*tert*-butyltetrahedrane and Tetra-*tert*-butylcyclobutadiene and of Their Thermal Interconversion

Sir:

Tetra-*tert*-butyltetrahedrane (**1**) shows a surprising thermal stability and rearranges to tetra-*tert*-butylcyclobutadiene (**2**) only at temperatures of 130 °C and above.[1] In this communication, we report on a MNDO[2] study of the structure, stability, and thermal interconversion of **1** and **2** and compare the results with those for unsubstituted tetrahedrane (**3**) and cyclobutadiene (**4**).

The optimized geometries of **1** and **2** (see Table I) show some unusual features. **1** is predicted to be a chiral molecule with T symmetry,[3] in analogy to other tetra-*tert*-butyl substituted systems.[4] Relative to the T_d conformation, each *tert*-butyl group is twisted in the same direction by 14.2°, and each methyl group by 4.8°, thereby destroying the planes of symmetry but preserving all of the rotation axes of the T_d point group. It should, however, be difficult to detect the chirality of **1** experimentally since the conformation with T_d symmetry is calculated to be only 2.6 kcal/mol above that with T symmetry which implies free internal rotation of the *tert*-butyl groups. These MNDO results confirm previous empirical force-field calculations[5] which also predict ground-state T symmetry and a low rotational barrier in **1**.

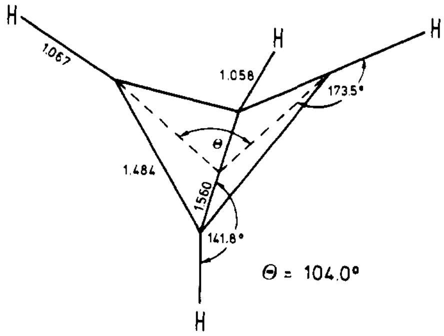

Figure 1. Optimized C_{2v} structure of the MNDO-CI_0 transition state for the reaction **3** → **4**.

Table I. Calculated Heats of Formation and Optimized Geometries[a]

	1[b]	**2**[c]	**3**	**4**[d]
point group	T	D_2	T_d	D_{2h}
ΔH_f, kcal mol^{-1}	81.2	74.5	136.6	90.7
$R(C_r{=}C_r)$, Å		1.381		1.357
$R(C_r{-}C_r)$, Å	1.534	1.557	1.520	1.534
$R(C_r{-}C_t)$, Å	1.501	1.520		
$R(C_t{-}C_m)$, Å	1.559	1.556–1.564		
$R(C{-}H)$, Å	1.108	1.108	1.063	1.071
$\theta(C_rC_tC_m)$, deg	110.4	110.8–112.6		
$\theta(C_tC_mH)$, deg	111.7	111.9		

[a] R, bond lengths; θ, bond angles; ϕ, dihedral angles. Indices for carbon atoms; r, ring atom; t, tertiary atom in butyl group; m, atom in methyl group. [b] For dihedral angles, see text. [c] $\theta(C_r{=}C_r{-}C_t)$, 136.5°; $\phi(C_r{=}C_r{-}C_r{=}C_r)$, 17.9°; $\phi(C_r{-}C_r{=}C_r{-}C_t)$, 157.8°. [d] $\theta(C_r{=}C_r{-}H)$, 138.1°.

The cyclobutadiene ring in **2** is calculated to be nonplanar, with a dihedral angle of 17.9° for the two double bonds. This puckering increases the nonbonding distances between the *tert*-butyl groups and thus stabilizes the system. When planarity is enforced during the optimization, the resulting structure is 11.1 kcal/mol higher in energy than the nonplanar one. The MNDO structure of **2** thus differs from the X-ray structure of the related, but sterically less hindered, methyl tri-*tert*-butyl[4]annulenecarboxylate which contains a planar cyclobutadiene ring.[6]

At the optimized geometries, the energy difference between the tetrahedrane and cyclobutadiene system (see Table I) is predicted to decrease from 45.9 to 6.7 kcal/mol when replacing the four hydrogen atoms by four *tert*-butyl groups. This shift of 39.2 kcal/mol[7] is undoubtedly due to steric effects since the *tert*-butyl groups occupy much more favorable positions in the tetrahedrane system. Based on previous experience,[8] the MNDO heat of formation of **4** is expected to be too low; the magnitude of the steric effect is believed to be somewhat overestimated, but of a reasonable order of magnitude.

The thermal rearrangement **3** → **4**, and the C_4H_4 potential surface in general, has recently been investigated both by semiempirical[9,10] and ab initio[11-13] methods. Since the rearrangement is "forbidden" thermally and involves a HOMO/LUMO crossing, a minimal 2 × 2 configuration interaction treatment (CI_0) is required for a correct description. The MNDO-CI_0 activation energy for this reaction is 15.2 kcal/mol. The transition state corresponds to a bicyclobutanediyl