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(14) At 200 °C the rate constants of the reactions (**6** → **9**)[6] and (**5** → **9**)[11] are 2.53×10^{-4} and 0.30 s^{-1}, respectively. At this temperature with a contact time of 1.5 s, **6** virtually does not rearrange (~0.04%).

(15) 1,3- as well as 1,4-cyclohexadiene is stable under the reaction conditions applied.

(16) For the sole simple example of a Bamford–Stevens reaction of the sodium salt of the tosylhydrazone of 2,3-di-*tert*-butyl-cyclopropanone see: Greene, F. D.; Camp, R. L.; Abegg, V. P.; Pierson, G. O. *Tetrahedron Lett.* **1973,** 4091.

Udo H. Brinker,* Lothar König
Abteilung für Chemie der Ruhr-Universität
4630 Bochum, West Germany

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Absolute Configuration of $(-)_D$-Tris(2,2′-bipyridine)cobalt(III)

Sir:

A direct determination of the absolute configuration of $(-)_D$-tris(2,2′-bipyridine)cobalt(III) complex ($(-)_D$-$[Co(bpy)_3]^{3+}$) presented here concludes a Δ configuration.

The absolute configuration of $[Co(bpy)_3]^{3+}$ has been controversial. The CD spectrum of the enantiomer of this particular complex exhibits two CD bands of opposite signs in the bipyridine (π,π^*) absorption region at ~32 000 cm^{-1}. An application of the exciton theory to the analysis of the CD bands of $(-)_D$-$[Co(bpy)_3]^{3+}$ yields a Δ configuration.[1-5] On the other hand, an alternative procedure, which should be well devised for the prediction of the absolute configuration of the coordinated ligands especially of those lacking the conjugated system, is based on an empirical analysis of both CD and absorption data of the (d,d*) ligand-field band and its application in a traditional way assuming the CD intensity-dominant E state predicts a Λ configuration.[6-8] In fact, Hawkins and coworkers assigned a Λ configuration to $(-)_D$-$[Co(bpy)_3]^{3+}$.[7]

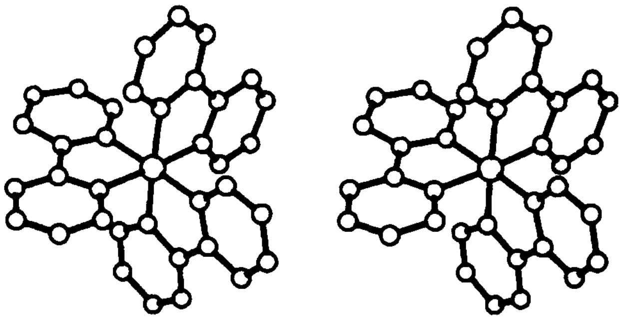

Figure 1. A stereoscopic view of $(-)_D$-$[Co(bpy)_3]^{3+}$.

The enantiomer used in the earlier stage of the present work was prepared by chlorine oxidation of trisbipyridinecobalt(II) $(+)_D$-bistartaratoantimonate(III) dispersed in carbon tetrachloride and deposited as crystals of $(-)_D$-$[Co(bpy)_3]$-$(ClO_4)_3 \cdot 2H_2O$. Several trials with these perchlorate crystals did not give sufficient structural information because of the pseudosymmetry in the tetragonal unit cell. The anion was replaced by mixing the aqueous solution of the perchlorate complex with that of potassium hexacyanoferrate(III). The CD spectrum did not vary significantly before and after the anion exchange.

The prismatic crystals of $(-)_D$-$[Co(bpy)_3][Fe(CN)_6] \cdot 8H_2O$ are triclinic with a = 12.174 (3), b = 16.742 (7), c = 10.651 (3) Å; α = 103.25 (3), β = 104.09 (2), γ = 94.71 (3)°; V = 2027 (1) $Å^3$; space group $P1$. The density measured by flotation is 1.46 g cm^{-3}, whereas the calculated density is 1.45 g cm^{-3} if the crystal is assumed to have two formula units in the unit cell. Intensity data up to $2\theta \leq 55°$ were collected on a Rigaku four-circle diffractometer with Mo Kα radiation monochromated by graphite. A total of 6348 independent reflections, ($|F_o| \geq 3\sigma(|F_o|)$), were obtained. The structure was solved by the heavy-atom method and refined by the block-diagonal least squares, the final R being 0.076.

The absolute configuration of the $(-)_D$-$[Co(bpy)_3]^{3+}$ ion was assigned to Δ by the anomalous dispersion technique. Figure 1 is a stereoscopic view of the cation along its pseudo-three-fold axis. Average Co–N and N–Co–N are 1.932 Å and 83.2°, respectively. The other bond distances and angles are in good agreement with those of $[Ni(bpy)_3]^{2+}$.[9,10]

Corresponding to the Λ configuration of $(+)_D$-$[Co(bpy)_3]^{3+}$ determined in the present work, a Λ configuration has been suggested for $(+)_D$-$[Co(phenanthroline)_3]^{3+}$ ($(+)_D$-$[Co(phen)_3]^{3+}$) on the basis of the sign of the optical rotation at the D line observed upon fast oxidation of the equilibrium enantiomeric mixture obtained in the presence of (S)-$(-)_D$-malic acid.[11]

The absolute configuration supports the conclusion of exciton splitting analysis of the CD spectra in the lowest ligand (π,π^*) transition. The same theory also correctly predicts the Λ configurations of $(+)_D$-$[Ni(bpy)_3]^{2+}$, $(+)_D$-$[Ni(phen)_3]^{2+}$, and $(-)_D$-$[Fe(phen)_3]^{2+}$ which were already established by X-ray studies.[10,12,13] On the basis of the CD in the lowest ligand (π,π^*) transition, the absolute configurations of $(-)_D$-$[Fe(bpy)_3]^{2+}$ and $(-)_D$-$[Fe(phen)_3]^{2+}$ are assigned as the Λ configuration as well as those of the $(+)_D$ isomers of the ruthenium(II) and osmium(II) analogues, whereas the sign of the CD spectra in the visible charge-transfer band is not conserved. In the case of Ni(II) complexes, sufficient empirical relationships between configuration and the CD spectra in the lowest (d,d*) ligand-field transition have not been obtained because of the difficulties of resolution of labile optical isomers.[14] It should be noted, however, that the sign of CD spectra in the lowest (d,d*) transition ($^3A_{2g} \rightarrow {}^3T_{2g}$ in O_h symmetry) exhibited by the Λ isomers, $(+)_D$-$[Ni(bpy)_3]^{2+}$ and $(+)_D$-$[Ni(phen)_3]^{2+}$, is consistently opposite to the sign observed in the corresponding transition ($^1A_{1g} \rightarrow {}^1T_{1g}$) of the Δ isomer $(-)_D$-$[Co(bpy)_3]^{3+}$.

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(15) Laboratory of Chemistry for Natural Products.
(16) Department of Chemistry.

Y. Ohashi,[15] K. Yanagi,[16] Y. Mitsuhashi[16]
K. Nagata,[16] Y. Kaizu[16]
Y. Sasada,[15] H. Kobayashi*[16]
Laboratory of Chemistry for Natural Products
Tokyo Institute of Technology
Midori-ku, Yokohama 227, Japan, and
Department of Chemistry, Tokyo Institute of Technology
O-okayama, Meguro-ku, Tokyo 152, Japan

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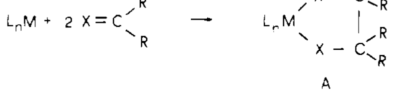
Reductive Coupling of Carbonyl or Imino Functional Groups by Dicarbonylbis(cyclopentadienyl)titanium(II): Model Reactions for Carbon Dioxide Dimerization and a Novel Metallacycle Formation

Sir:

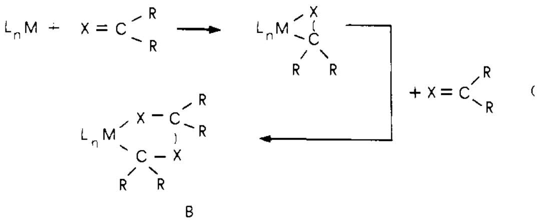
A new perspective on the utilization of transition metals in organic synthesis is represented by the reductive coupling of unsaturated functional groups other than C=C and C≡C[1] (eq 1) (where L_nM = low-valent transition metal complex undergoing oxidative addition reactions; X = O, NR).



(1)

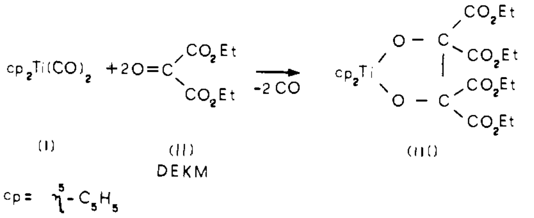
A

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 $cp_2Ti(CO)_2$ (I, cp = η^5-C_5H_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]



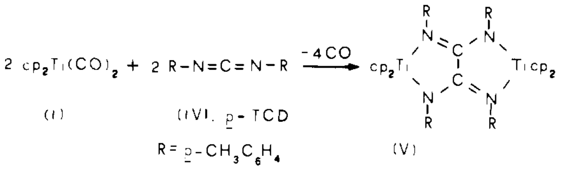
(2)

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. $C_{50}H_{48}N_4Ti_2$ (V): *M* = 800.8; triclinic; $a = 12.408\ (1)$, $b = 10.449\ (1)$, $c = 8.179\ (1)$ Å; $\alpha = 103.56\ (1)$, $\beta = 94.29\ (1)$, $\gamma = 94.23\ (1)°$; $Z = 1$; $d_{calcd} = 1.299$, $d_{obsd} = 1.31$ 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 ($\lambda = 1.54178$ A, $6° < 2\theta < 140°$) 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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