The X-ray crystal structure of II shows displacements of the tin atoms from the centroidal positions above the C_2B_3 faces, and the Lewis base is directly opposite the C–C(cage) bonds making rather severe bond angles (85–92°) with cage ligands. The average tin–carbon(cage) distance [2.646 (6) Å] is 0.267 Å longer than the tin–unique boron distance [2.379 (9) Å]. However, somewhat different bond distances were found in the structures of 1-Sn-$(C_{10}H_8N_2)$-2-(Me_3Si)-3-(R)-2,3-$C_2B_4H_4$ donor-acceptor complexes.[2,4] For example when R = Me (III),[4] the average Sn–C distance [2.818 (6) Å] is 0.459 Å longer than the Sn–B(unique) distance [2.359 (7) Å], whereas the difference between Sn–C [2.73 (1) Å] and Sn–B(unique) [2.37 (2) Å] distances is 0.36 Å when R = $SiMe_3$ (IV).[2] Surprisingly, the Sn–N distances of 2.639 (5) Å in the title compound II are significantly longer than those found in III [2.475 (4) Å][4] and IV [2.51 (1) Å].[2] Furthermore, the dihedral angles between the bipyrimidine rings and the carborane C_2B_3 faces [44.21 (3)°] in the bridged compound II are significantly higher than those between the bipyridine rings and C_2B_3 faces of the stannacarboranes in the nonbridged donor–acceptor complexes III [18.4 (2)°] and IV [26.8 (5)°]. Thus, the interaction between the orbitals of tin and aromatic ring nitrogens in II is weaker than those of III and IV. Consequently, the bridged donor–acceptor complex II in the present study is significantly less slip distorted than the nonbridged 2,2′-bipyridine complexes of the stannacarborane. The important features of the structure of II are the trans position of the two stannacarborane molecules with respect to the central 2,2′-bipyrimidine base (Figure 2) and their closo-geometries

The recent molecular orbital (MO) calculations of the Fenske–Hall type on the "experimental" geometries of the (2,2′-bipyridine)$SnB_4H_4(CER_3)_2$ (E = C, Si; R = H, Me) showed that the "slip distortion" is caused by an antibonding interaction in the HOMO between the tin's "lone pair" and the cage carbons of the carboranes.[13] From the tilt of the bipyrimidine rings in II with respect to the carborane ligands, that is, opposite the cage carbons, it is apparent that the bipyrimidine nitrogens are bonding with tin orbitals originally involved in π bonding with the carborane. As the tin–carborane π interactions become weaker, the main bonding interaction is with the tin σ orbital, and the complex is stabilized by an increased slippage of the tin away from the cage carbons. In this way, a change from η^5 to η^3 bonding is expected in the stannacarborane on complexing with bipyrimidine. This is further evidence of the predominance of σ interactions in the tin–carborane bonding in II. The geometry at tin in II suggests a localized "lone pair" exo to the cage and hence, according to Wades rules,[14] the apical tin is still a two-electron atom and the closo structure is maintained. The trans configuration of the stannacarboranes about the bipyrimidine molecule is not the one that would be favored on steric grounds; orbital effects contribute significantly. It is anticipated that going down from silicon to lead will increase not only the "slip distortion" but also the tilting as the "lone pair" orbital becomes more important.

Among group 14 heterocarboranes, the donor–acceptor complexes of the sila- and plumbacarboranes are not yet known. However, such an endeavor is currently underway in this laboratory.

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Registry No. I, 90388-43-5; II, 110374-95-3; 2,2′-$C_8H_6N_4$, 34671-83-5.

Supplementary Material Available: Tables of positional parameters for non-H atoms (Table 1), bond distances (Table 2), bond angles (Table 3), torsion angles (Table 4), thermal parameters (Table 5), positional parameters for H atoms (Table 6), and molecular planes (Table 7) (8 pages); a listing of observed and calculated structure factors (Table 8) (13 pages). Ordering information is given on any current masthead page.

(12) Crystallographic data: suitable crystals of II ($C_{24}H_{50}B_8Si_4Sn_2$) were grown by sublimation onto a glass surface. Crystals were sealed in 0.7-mm capillary tubes under dry argon. Data collection was carried out at −110 °C, using an upgraded Nicolet P$\bar{1}$ to P3F diffractometer, Mo Kα radiation. The space group is $P2_1/c$ with $a = 15.884$ (4) Å, $b = 9.841$ (3) Å, $c = 13.550$ (4) Å, $\beta = 104.71$ (2)°, $U = 2048.4$ (9) Å^3, $Z = 2$, and $d_{calcd} = 1.26$ g cm^{-3}. A total of 3481 reflections which measured $I > 3\sigma(I)$ were used for structure solution using direct methods (SHELXTL-Plus) and subsequent difference Fourier methods. The data were not corrected for absorption. Final full-matrix least-squares refinement (SHELXTL-Plus-Structure Determination Software Program; Nicolet Instrument Corp., 1986) converged to $R = 0.059$ and $R_w = 0.076$. All methyl H atoms were placed in calculated positions and not refined, the function minimized being $\sum w(|F_o| - |F_c|)^2$, the weight used being $w^{-1} = \sigma(F^2) + 0.013754F^2$, $(\Delta/\sigma)_{max} = 0.30$, and $\Delta\rho_{max} = 0.81$ e/Å^3. Scattering factors for C, H, B, N, Si, and Sn used were those stored in SHELXTL-Plus.

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The First Example of Photochemically Activated Carbon Dioxide Insertion into Transition-Metal–Carbon Bonds

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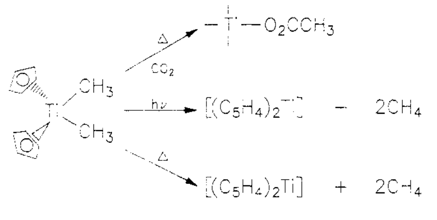
Summary: The photolysis of $Cp_2Ti(CH_3)_2$ (Cp = η^5-C_5H_5) (1) in the presence of CO_2 results in the insertion of CO_2 into one metal–carbon bond to form $Cp_2Ti(O_2CCH_3)CH_3$ (2).

$Cp_2Ti(CH_3)_2$ (1)[1] undergoes well-defined photolytic and thermal reactions:[2–6]



[†] NRC-NRL Research Associate.

(1) $Cp_2Ti(CH_3)_2$ was prepared by using a modification of Bestian's procedure: Clauss, K.; Bestian, H. *Justus Liebigs Ann. Chem.* **1962**, *654*, 8. Dry ethanol was used instead of using water to decompose the excess $LiCH_3$.

(2) (a) Rausch, M. D.; Boon, W. H.; Alt, H. G. *J. Organomet. Chem.* **1977**, *141*, 299. (b) Samuel, E.; Maillard, P.; Giannotti, C. *Ibid.* **1977**, *142*, 289. (c) Bamford, C. H.; Puddephatt, R. J.; Slater, D. M. *Ibid.* **1978**, *159*, C31.

(3) (a) Erskine, G. J.; Hartgerink, J.; Weinberg, E. L.; McCowan, J. D. *J. Organomet. Chem.* **1979**, *170*, 51. (b) Erskine, G. J.; Wilson, D. A.; McCowan, J. D. *Ibid.* **1976**, *114*, 119.

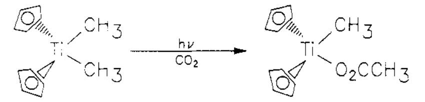
(4) Kolomnikov, I. S.; Lobeeva, T. S.; Vol'pin, M. E. *Zh. Obshch. Khim.* **1972**, *42*, 2232.

Table I. ^{1}H and ^{13}C NMR Spectral Data[a]

compd	group	^{1}H	^{13}C(^{1}H)
$Cp_2Ti(CH_3)_2$[b]	Cp	6.10	113.0
	CH_3	−0.14	45.5
$Cp_2Ti(O_2CCH_3)CH_3$[b]	Cp	6.14	114.1
		6.47	118.1[c]
	O_2CR		176.5
	RCH_3	1.66	23.0
	$TiCH_3$	0.79	43.1
$CpTi(CH_3)(OCH(CH_3)_2)_2$[d]	Cp	6.04	111.5
	$TiCH_3$	0.48	35.0
$CpTi(CH_3)(OCH_2CF_3)_2$[e]	Cp	6.24	114.3
	CH_3	0.82	46.4
$Ti(CH_3)(OCH(CH_3)_2)_3$[d]	$TiCH_3$	0.57	42.9

[a] All resonances are singlets. [b] Spectra were obtained on either a Bruker MSL 300 or Varian EM 390 spectrometer. Resonances are reported in parts per million relative to $CDCl_3$. [c] This resonance is due to minor product of the photochemical reaction. [d] Data from ref 12. [e] Data from ref 13.

Vol'pin et al. reported the insertion of CO_2 into titanium–methyl bonds at 80 °C in toluene to form the corresponding acetate complex and decomposition products. This thermal insertion reaction is not observed at room temperature.[4] We now report a new pathway near room temperature involving photochemical insertion of CO_2 into the titanium–methyl bond of 1.



This is the first example of a photochemically induced CO_2 insertion into transition-metal–carbon bonds.

Dilute pentane solutions of 1 and CO_2 were photolyzed for 24 h at 16 °C.[7] A yellow powder was obtained upon cooling the reaction solution to −20 °C. The ^{1}H NMR spectrum of the yellow product was equivalent to that reported for $Cp_2Ti(O_2CCH_3)CH_3$ (2) synthesized from 1 and acetic acid.[8] Elemental analyses, infrared spectra, and the molecular weight of the yellow product demonstrate that 2 is the photochemical product.[9] After 20 h of photolysis 80% of 1 reacted to insert CO_2 while 12% remained unreactive and 8% was not recovered. The high percentage of inserted product formed demonstrates a highly selective reaction pathway.

The methyl carbons bound to titanium in 1 and 2 show unusual ^{13}C NMR chemical shifts relative to the methyl proton shifts. The assignment of the titanium–methyl resonances of 1 and 2 were confirmed by selective heteronuclear NMR decoupling. While other metal–methyl complexes have been observed with methyl-carbon resonances near 0.0 ppm,[10] the methyl-carbon resonances in 1 and 2 show large downfield shifts in the ^{13}C NMR spectrum. However, the methyl-proton resonances of 1 and 2 display the usual upfield shift in the ^{1}H NMR spectrum (Table I). There is some precedence for large downfield shifts of σ-bonded carbons in ^{13}C NMR spectrometry (Table I).[11-13] The chemical shifts of these compounds may indicate an unusual polarization of the titanium–methyl bond, which could be an important requirement for the CO_2 insertion reaction.

The photolysis of 1 and CO_2 with a 350-nm light source[14] yields products other than 2,[15] indicating that no insertion reaction is observed and a different photochemical reaction has occurred. The formation of different products from different wavelengths of irradiation indicates that more than one photochemically activated reaction pathway exists for 1. Five photochemically induced reactions involving 1 are now known: (1) elimination of methane,[2] (2) polymerization,[2c] (3) insertion of acetylenes,[2a,5] (4) transmethylation[16] and (5) from this work, CO_2 insertion. A simple methyl migration does not occur during the photolysis of 1 in the presence of alkenes or acetylenes, since alkenes polymerize[2c] and acetylenes undergo an overall insertion.[2a,5] The CO_2 insertion cannot be compared directly with those of alkenes or acetylenes because of structural and reduction potential differences.[17] These differences imply that the CO_2 insertion involves a different mechanism.

The transmethylation and CO_2 insertion reactions are key steps to development of catalytic systems for the reduction of CO_2. However, the considerable interest in CO_2 insertion reactions in recent years has focussed on insertion into highly reactive or unstable metal–hydride and metal–carbon bonds.[18] These reactions generally lead to a mixture of products including decomposition products. This makes such systems less useful as potential catalysts for the reduction of CO_2. Photochemically activated CO_2 insertion reactions into transition-metal–hydride and –carbon bonds, on the other hand, offer the potential for clean reactions and for this reason show greater promise for the catalytic reduction of CO_2.

Acknowledgment. We are grateful to Dr. M. H. Rakowsky for the NMR data collection on the Bruker MSL 300.

Registry No. 1, 1271-66-5; 2, 86822-31-3.

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(5) Boon, W. H.; Rausch, M. D. *J. Chem. Soc., Chem. Commun.* **1977**, 397.

(6) One example of a photochemically activated CO_2 insertion into main group-metal–carbon bonds has been reported but appears to involve a different insertion mechanism. See: Cocolios, P.; Guilard, R.; Bayeul, D.; Lecomte, C. *Inorg. Chem.* **1985**, *24*, 2058.

(7) The solutions were irradiated with a 150-W GE tungsten lamp (300–700 nm source). Solutions were kept in a water bath at 16 °C during the irradiation to assure that no thermal insertion of CO_2 occurred even though no thermally induced insertion occurred at room temperature.

(8) Puddephatt, R. J.; Stalteri, M. A. *Organometallics* **1983**, *2*, 1400.

(9) Only the ^{1}H NMR spectral data were reported in ref 8, so here we report the complete characterization. The molecular weight of the yellow product was determined to be 226 g/mol by a vapor pressure lowering experiment (calculated mol wt for 2 is 252.17 g/mol). Elemental analyses were obtained by Schwartzkopf Microanalytical Laboratory, Inc. Calculated weight percents for $Cp_2Ti(O_2CCH_3)CH_3$ are 61.9% C, 6.4% H, and 19.0% Ti (found for yellow product 60.2% C, 6.3% H, and 18.8% Ti). Infrared spectrum of a KBr pellet was obtained on a Perkin-Elmer 1710 FTIR spectrometer. Strong carboxylate stretches were observed at 1642 and 1362 cm^{-1}. Additional peaks were observed at 3095 (w), 2956 (w), 2891 (w), 1642 (s), 1572 (w), 1444 (w), 1362 (s), 1298 (s), 1133 (w), 1116 (w), 1066 (w), 1018 (m), 943 (w), 851 (m), 812 (s), 664 (w), 633 (m), 600 (w), 505 (w), and 467 (w) cm^{-1}. The derivative methyl acetate was synthesized from the yellow product by using the method of Vol'pin (see ref 4). The presence of methyl acetate was determined by GC. Gas chromatograms were obtained on a Varian 3700 GC with a FID using a 50-m fused silica wall coated OD-101 capillary column.

(10) Mann, B. I.; Taylor, B. F. In *^{13}C NMR Data for Organometallic Compounds*; Maitlis, P. M., Stone, F. G. A., West, R. Eds.; Academic: London, 1981; Chapter 2.

(11) Sebald, A.; Fritz, P.; Wrackmeyer, B. *Spectrochim. Acta, Part A* **1985**, *41A*, 1405.

(12) Blandy, C.; Guerreiro, R.; Gervais, D. *J. Organomet. Chem.* **1977**, *128*, 415.

(13) Bert, M. B.; Gervais, D. *J. Organomet. Chem.* **1979**, *165*, 209.

(14) A Rayonet photochemical RPR-100 reactor was used with 350-nm fluorescent tubes or the tungsten lamp with a filter which passes light below 360 nm.

(15) The ^{13}C NMR spectrum contained broad resonances at 117.2 and 113.8 ppm and sharp resonances at 133.2, 132.3, 41.6, and 26.9 ppm. There is evidence for C—O or C═C stretches in the infrared although no ^{13}C carboxylate resonance is observed. There is no evidence for the formation of 2 from these spectra.

(16) Pankowski, M.; Samuel, E. *J. Organomet. Chem.* **1981**, *221*, C21.

(17) For example, alkenes and Alkynes are easily reduced by hydrogen and a Pd catalyst, whereas CO_2 is not reduced under such conditions.

(18) Darensbourg, D. J.; Kudaroski, R. A. *Adv. Organomet. Chem.* **1983**, *22*, 129 and references therein.