

1 could be low by as much as 17%. In general the spectrum of $\text{Mn}(\text{OH})^{2+}$ determined in this study is in good agreement with an earlier published spectrum of manganic pyrophosphate of pH 6.0.⁷

As is apparent from Figure 1, the spectrum of MnO_2^+ is quite different from the spectrum of $\text{Mn}(\text{OH})^{2+}$. With the exception of the small absorbance at 420 nm, it resembles the spectrum of O_2^- which has undergone a red shift due to complexing. Since in the present study MnO_2^+ was formed directly from O_2^- and Mn^{2+} and in absence of other oxidizing chemicals, we conclude that the superoxide radical is not capable of oxidizing Mn^{2+} to Mn^{3+} .

Preliminary kinetic studies of the MnO_2^+ and MnOH^{2+} species indicate that their decay mechanisms are very complex. For similar initial concentrations the observed ratio of overall half-lives of $\text{MnO}_2^+/\text{O}_2^-$ at pH 6.0 is 10. The decay of MnOH^{2+} which can be observed for up to 1 s under present experimental conditions is complicated by the formation of a precipitate.

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Novel Bonding Mode of Diphenylketene to a Transition Metal: a Metal Anchored Olefin System

Sir:

Diphenylketene has been regarded as an activated olefin in its interaction mode with a transition metal.^{1,2} Nevertheless,

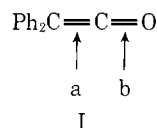


Table I. Bond Distances (Angstroms) and Bond Angles (Degrees)

Ti-C (cp)	2.410 (2) ^a	2.403 (2) ^a	O(1)-Ti-O(1')	67.7 (1)	Ti-O(1)	2.037 (2)
Ti-(cp)⊥	2.095 (4) ^a	2.088 (4) ^a	C(11)-Ti-O(1)	36.9 (1)	Ti-C(11)	2.099 (3)
C-C (cp)	1.401 (3) ^a	1.394 (3) ^a	Ti-O(1)-Ti'	116.0 (1)	Ti-O(1')	2.250 (3)
C-C (Ph)	1.393 (2) ^a	1.386 (2) ^a	Ti-O(1)-C(11)	74.1 (2)	O(1)-C(11)	1.311 (4)
cp(1)-Ti-cp(2)	131.2 (2)		O(1)-C(11)-C(12)	128.8 (3)	C(11)-C(12)	1.357 (4)
					C(12)-C(21)	1.460 (6)
					C(12)-C(31)	1.505 (6)

^a Values related to crystallographically nonequivalent cyclopentadienyl and phenyl groups.

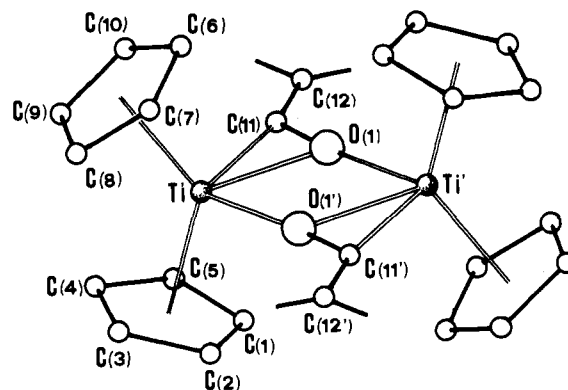
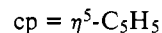
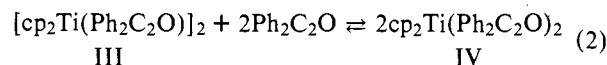
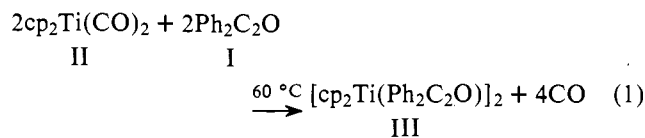


Figure 1. A view of the molecular structure of the dimer $[\text{cp}_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})]_2$, showing the atomic numbering scheme. The phenyl rings have been omitted for clarity.

two potential coordination sites (a and b) are, a priori, susceptible to the metal's attack. The a-bonding attachment of I to a Mn(I) complex² was recently confirmed by x-ray analysis, while interaction with C=O moiety is invoked as an intermediate in the metal-induced deoxygenation or decarbonylation of ketenes.³⁻⁶ The structure here reported shows that diphenylketene is $\eta^2\text{-C,C,O}$ bonded to the bis(η -cyclopentadienyl)titanium, $\text{Ti}(\text{cp})_2$, unit. This mode of attachment gives an anchored free C=C bond, highly affected by the metal. Until now, the π interaction of a ketonic C=O group was restricted to the complexes of hexafluoroacetone with d^{10} metals.⁷

It was reported that the reaction of $\text{cp}_2\text{Ti}(\text{CO})_2$ (II) with diphenylketene gives an orange-yellow monomeric complex, which was formulated as an olefin-like compound.⁸ Reaction between I and II must be, however, described by the following steps,⁹



giving III, orange-yellow,¹⁰ and IV,¹¹ black, crystalline solids, respectively. Regarding complex III, the dramatic absence of any C=O band above 1600 cm^{-1} (C=O is at 2093 cm^{-1} in free $\text{Ph}_2\text{C}_2\text{O}$), together with the observed C=O stretching in the range $1700\text{--}1800\text{ cm}^{-1}$ for $\text{M}(\text{C}=\text{C})$ coordinated diphenylketene,^{1,2} suggests that CO is involved in the metal-ketene interaction. An x-ray crystallographic study was required to prove the nature of the product. This was performed on $[\text{cp}_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})]_2 \cdot 2\text{THF}$ (THF = tetrahydrofuran). Crystal data: $\text{C}_{48}\text{H}_{40}\text{O}_2\text{Ti}_2 \cdot 2\text{C}_4\text{H}_8\text{O}$; $M = 889$; triclinic; $a = 9.990$ (1), $b = 11.058$ (2), $c = 10.820$ (2) Å; $\alpha = 73.86$ (2), $\beta = 94.98$ (2), $\gamma = 98.85$ (1)°; $Z = 1$; $d_{\text{calcd}} = 1.302\text{ g/cm}^3$; space group $P\bar{1}$. Intensity data were collected on an "on-line" single-crystal automated Siemens AED diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å, $6 < 2\theta <$

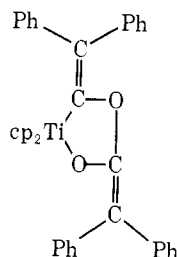


Figure 2.

140°) at a takeoff angle of 6°. The pulse height discriminator was set to accept 90% of the Cu K α peak. For intensities and background the "five-points technique"¹² was used. A total of 3545 reflections were considered observed [$I > 2\sigma(I)$] and used in the subsequent structure determination and refinement. The structure was solved by heavy-atom methods and refined by full-matrix least-squares techniques¹³ with anisotropic thermal parameters for all atoms, to give a discrepancy index $R = 0.069$.¹⁴ A view of the molecular structure of III is shown in Figure 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 atomic positions of THF, which is present as crystallization solvent, are poorly defined as is often the case in situations like this.

The molecular structure belongs to the symmetry point group C_i . The chemically interesting structural features of the molecule are (i) the compound consists of the dimeric centrosymmetric unit, $[\text{cp}_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})]_2$; (ii) cp ligands are π bonded to the titanium in a bent arrangement and Ti-O(1)-C(11)-O(1') define an orthogonal molecular plane to the plane containing the cp ring normals; (iii) the basic monomeric unit consists of η^2 -C,O bonded diphenylketene to the cp_2Ti moiety. Dimerization is achieved through an oxygen shared by two titanium atoms at nonequivalent bond distances (Ti-O(1) = 2.037 (2), O(1)-Ti' = 2.250 (3) Å). Ti-C(11) = 2.099 (3) and Ti-O(1) = 2.037 (2) bond distances are reminiscent of the η^2 -C,O-acyl bonded to titanium.¹⁵ C(11)-O(1) = 1.311 (4) Å distance is in the range of C(sp²)-O and compares well with the 1.32 (2) Å C-O distance in $(\text{PPh}_3)_2\text{Ni}(\text{CF}_3)_2\text{CO}$.¹⁶ The Ti-C(12) distance (3.415 (3) Å) rules out the possible interaction of the metal with the C=C unit of the diphenylketene, even if a suspected lengthening of the C(11)-C(12) = 1.357 (4) Å is observed.² The linearity of the C-C-O moiety of $\text{Ph}_2\text{C}_2\text{O}$ is lost by coordination to the titanium.

Coordinated diphenylketene in III undergoes an unusual C=C bond cleavage by the action of protic acids. Instead of the expected diphenylacetic acid, CO and a mixture of diphenylmethane and tetraphenylethane is obtained.¹⁷

Another aspect of the metal induced change on the reactivity of the coordinated diphenylketene is evident by the reaction of III with a further molecule of $\text{Ph}_2\text{C}_2\text{O}$ (reaction 2).⁹ This reaction has its parallel in the dimerization of diphenylketene. The reaction of a free diphenylketene on III is reversible⁹ and gives IV. The molecular weight deduced by x-ray analysis (566.56) shows that IV is monomeric even in the solid state. Analytical and NMR data are consistent with the reported formulation.¹¹ No carbonylic band above 1600 cm^{-1} can be found. The controlled hydrolysis with HCl gives cp_2TiCl_2 and the vinyl ester $\text{Ph}_2\text{C}=\text{CHOCOPh}_2$, in a quantitative yield.¹⁸ The results outlined above suggest for IV the structure indicated in Figure 2, as was confirmed by an x-ray analysis which is in progress.¹⁹

Reactions 1 and 2 can be recognized as related to the two steps of the dimerization of the C-O unit in $(\text{CF}_3)_2\text{CO}$ ²⁰ and CO_2 .²¹ The dimerization of CO_2 on Ir(I) complex gives a metallocycle very similar to that shown in Figure 2. Moreover, reaction between $\text{P}(\text{OC}_2\text{H}_5)_3$ and $\text{Ph}_2\text{C}_2\text{O}$, leading to the deoxygenation of the diphenylketene, gives an isolable adduct, $\text{P}(\text{OC}_2\text{H}_5)_3 \cdot (\text{Ph}_2\text{C}_2\text{O})_2$ with a proposed structure very similar

to that reported for IV.^{22,23}

The reactivity of the C=C and C=O bonds of the coordinated diphenylketene is being investigated.

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Supplementary Material Available: The final atomic parameters (Table 2 and 3), bond distances and angles (Table 4), and a complete listing of structure factor amplitude (37 pages). Ordering information is given on any current masthead page.

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- (10) Evolution of 2 mol of CO per titanium was gas volumetrically measured. Prepared from THF, III was obtained as solvated species. Anal. Calcd for $[\text{cp}_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})]_2 \cdot 2\text{C}_6\text{H}_6\text{O}$, $\text{C}_{58}\text{H}_{50}\text{O}_4\text{Ti}_2$: C, 75.67; H, 6.30; Ti, 10.81. Found: C, 74.75; H, 6.03; Ti, 11.03. ¹H NMR (THF-*d*₆ vs. Me₄Si) τ 4.44 (s, cp, 10 H), 3 (m, Ph, 10 H).
- (11) IV. Anal. Calcd for $\text{cp}_2\text{Ti}(\text{Ph}_2\text{C}_2\text{O})_2$, $\text{C}_{38}\text{H}_{30}\text{O}_2\text{Ti}$: C, 80.56; H, 5.30; Ti, 8.48. Found: C, 80.3; H, 5.3; Ti, 8.40. ¹H NMR (benzene-*d*₆ vs. Me₄Si) τ 4.32 (s, cp, 10 H), 3.0 (m, Ph, 20 H).
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- (17) Hydrolysis of III is carried out in THF with small amount of aqueous concentrated HCl. CO corresponds to 1 mol per titanium. The overall yield of Ph_2CH_2 (A) and $(\text{Ph}_2\text{CH})_2$ (B) is higher than 85%. The A:B ratio is practically fortuitous, the percentage of each one ranging from 10 to 40% for A, and 40 to 70% for B, for experiments carried out under same conditions. These results may indicate a free-radical-like evolution of an organic species originated from a homolytic Ti-C bond cleavage. Reference 7 reports as only identified product $(\text{Ph}_2\text{CH})_2$ in 53% yield.
- (18) $\text{Ph}_2\text{C}=\text{CHOCOPh}_2$: mp 94-95 °C; ¹H NMR (CCl₄ vs. Me₄Si) τ 5.12 (s, 1 H), 2.93 (m, 20 H), 2.48 (s, 1 H); mass spectrum m/e^+ 152, 167, 194, 196, 390; yield, over 70%; IR (Nujol mull) $\nu_{\text{C}=\text{O}}$ 1750 cm^{-1} . Anal. Calcd for $\text{C}_{28}\text{H}_{22}\text{O}_2$: C, 86.20; H, 5.64. Found: C, 85.71; H, 6.05.
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