

Table I^a

| PA ^b | Gly | Ala | Cys | Ser | Val | Asp | Leu | Thr | Ile | Phe | Met | Tyr | Asn | Pro | Glu | Trp | [Gln Lys] ^c | His | Arg |
|-----------------|-----|-----|-----|-----|------------------|------------------|-----|-----|-----|-----|-----|-----|-----|-----|------------------|------------------|------------------------|-----|-----|
| | Arg | | | | | | | | | | | | | | | | Arg | Arg | Arg |
| | His | | | | | | | | | | | | | | | | His | His | |
| | Lys | Lys | | Lys | | Lys | | | | Lys | | | | Lys | Lys ^d | Lys | | | |
| | Gln | | | | | | | | | Gln | Gln | | | | Gln | Gln ^d | Gln | | |
| | Trp | | | | | | | | | | | | | | Trp | Trp | | | |
| | Glu | Glu | | | | Glu | | | | Glu | | | | | Glu | Glu | | | |
| 218.4 | Pro | | | | Pro | | | | | Pro | Pro | Pro | Pro | | | | | | |
| | Asn | | | | | | | | | Asn | Asn | Asn | | | | | | | |
| | Tyr | | | | | | | | | Tyr | Tyr | | | | | | | | |
| | Met | | | | | | | | | Met | | | | | | | | | |
| 215.1 | Phe | Phe | | Phe | Phe | Phe | Phe | Phe | Phe | | | | | | | | | | |
| | Ile | | | Ile | Ile ^d | | | Ile | | | | | | | | | | | |
| | Thr | | | | | Thr | Thr | | | | | | | | | | | | |
| 214.5 | Leu | | | Leu | Leu | Leu ^d | | | | | | | | | | | | | |
| | Asp | Asp | Asp | Asp | Asp | | | | | | | | | | | | | | |
| 213.9 | Val | Val | Val | Val | | | | | | | | | | | | | | | |
| | Ser | Ser | Ser | | | | | | | | | | | | | | | | |
| | Cys | Cys | | | | | | | | | | | | | | | | | |
| 212.2 | Ala | | | | | | | | | | | | | | | | | | |
| 208.2 | Gly | | | | | | | | | | | | | | | | | | |

^a Each amino acid indicated to the right of the heavy line can be assigned to the most abundant ion in the MIKE spectrum of the cluster ion which contains the amino acid at the top of the column combined with that to the left in the row; e.g., decomposition of the cluster ion with the composition [Ser-Lys-H]⁺ yields primarily [Lys-H]⁺ and hence PA(Lys) > PA(Ser). ^b Values (in kcal/mol) from ref 1a. ^c Order is undetermined. See text. ^d Analyzed on the ZAB-3F.

of the positive charge. Charge-dipole interaction with the carboxylic acid group and for some of the amino acids, (e.g., Ser, Cys, Asp, and Asn) also with the side chain, may give some destabilization.⁶ For Arg, Lys, Gln, and Glu the protonated species fulfill the geometrical requirements for ring-formed structures which include basic sites in the side chain.⁷ In these cases an entropy effect is to be expected in proton exchange experiments.

In the protonated dimer the same interactions will be present, but owing to the charge dispersion each will be much weaker than in the protonated monomer. This is illustrated by the study on protonation reactions of trifunctional amines under equilibrium conditions.⁸ They show that when a proton is solvated by two of the basic sites on the amine, solvation by the third does not occur even when allowed by the geometry. A similar effect operating in the protonated amino acid dimer would mean that apart from solvating the proton with its most basic site each amino acid would have few conformational restraints.

Overall it appears that available experimental evidence supports the hypothesis that the entropy effect in the decomposition reaction of the protonated dimers can be ignored when establishing the order of amino acid PA's. It is also clear that positive evidence is needed. This can best be supplied by equilibrium measurements.

The order for Gln (MH⁺: 147.0699) and Lys (MH⁺: 147.1134) remains undetermined. Analysis of the decomposition of the cluster ion [Gln-Lys-H]⁺ demands high resolution for the separation of the cluster as well as for analysis of the fragments.

For Gly, Ala, Ser, Cys, and Thr the PA's have been calculated.⁹ The calculated values have the same magnitude as those obtained experimentally. For the groups Gly, Ala, and Cys, Ser, Thr the order is in agreement with the order presented here, but the overall order is not.

In order to determine proton affinities it has hitherto been necessary to evaporate a sample of the compound to be studied. This has prevented the study of compounds of high polarity. Just as desorption ionization methods have enabled the analysis of polar

compounds they should enable the study of their gas-phase chemistry.

Acknowledgment. Thomas Weiske and Helmut Schwarz, Technische Universität, Berlin, are gratefully acknowledged for their help with the analyses carried out on the ZAB-3F.

Registry No. H-Gly-OH, 56-40-6; H-Ala-OH, 56-41-7; H-Cys-OH, 52-90-4; H-Ser-OH, 56-45-1; H-Val-OH, 72-18-4; H-Asp-OH, 56-84-8; H-Leu-OH, 61-90-5; H-Thr-OH, 72-19-5; H-Ile-OH, 73-32-5; H-Phe-OH, 63-91-2; H-Met-OH, 63-68-3; H-Tyr-OH, 60-18-4; H-Asn-OH, 70-47-3; H-Pro-OH, 147-85-3; H-Glu-OH, 56-86-0; H-Trp-OH, 73-22-3; H-Gln-OH, 56-85-9; H-Lys-OH, 56-87-1; H-His-OH, 71-00-1; H-Arg-OH, 74-79-3.

Highly Reduced Organometallics. 19. ¹ Synthesis of Carbonyl Anions of Titanium(0) from Titanocene Dicarboxyl. The First Structural Characterization of a Carbonyl Hydride of Titanium, (C₅H₅)Ti(CO)₂(Me₂PCH₂CH₂PMe₂)H

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Reductive labilization of poor or nonacceptor ligands on transition-metal compounds has been demonstrated to be a versatile synthetic route to highly reduced anions and other organometallics in the past decade.² Jonas and his group have established that metallocenes of the first row transition metals are particularly useful in this regard. One or two cyclopentadienyl groups can often be selectively removed from metallocenes by reduction in the presence of a variety of neutral ligands to access totally new classes of organometallic materials.³

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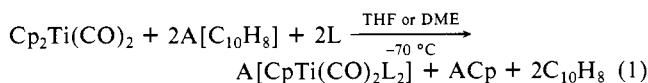
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(9) Wright, L. R.; Borkman, R. F. *J. Am. Chem. Soc.* **1980**, *102*, 6207. The calculated order is as follows: PA(Cys) < PA(Ser) < PA(Thr) < PA(Gly) < PA(Ala).

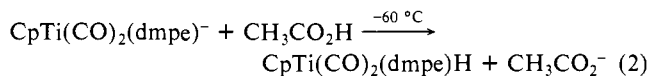
We now report that application of this synthetic methodology to the readily available titanocene dicarbonyl, $\text{Cp}_2\text{Ti}(\text{CO})_2$,⁴ provides an important new route to zerovalent titanium carbonyls, which are still extremely uncommon materials.¹ New anionic carbonyls of Ti(0) of the general formula $[\text{CpTi}(\text{CO})_2\text{L}_2]^-$ can be prepared according to the following equation, where A is an alkali metal, L is a neutral two electron donor, and THF = tetrahydrofuran and DME = 1,2-dimethoxyethane.



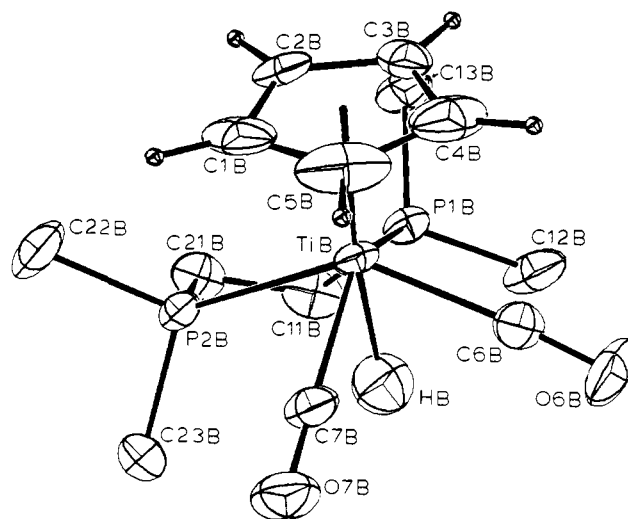
While potential ligands such as naphthalene, dienes, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$, and PMe_3 provide quite unstable adducts that have not been fully characterized, $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ (dmpe) yields an isolable anion $\text{CpTi}(\text{CO})_2(\text{dmpe})^-$, the initial example of a phosphine-substituted carbonyltitanate. More significantly, protonation of this extremely electron rich species yields the first carbonyl hydride of titanium, $\text{CpTi}(\text{CO})_2(\text{dmpe})\text{H}$. Since no terminal hydride of titanium had been structurally characterized previously,^{5,6} a single-crystal X-ray diffraction study on this material was carried out.

Dropwise addition of a THF solution of KC_{10}H_8 (2 equiv) at -20°C to a cold (-70°C) solution containing equimolar amounts of $\text{Cp}_2\text{Ti}(\text{CO})_2$ and dmpe in THF under an argon atmosphere provided deep red and thermally unstable solutions (dec $> -40^\circ\text{C}$). Nearly quantitative precipitation of KC_5H_5 (identified by NMR) occurred after the solution was stirred for 10 h at -70°C . After a low-temperature filtration, 1 equiv of cryptand 2.2.2⁷ was added which provided a thermally stable (20°C) red orange solution. Solvent was then removed in vacuo. Two recrystallizations of the residue from THF-ether gave dark red, thermally stable (dec $\geq 110^\circ\text{C}$) crystals of $[\text{K}(2.2.2)]^+[\text{CpTi}(\text{CO})_2(\text{dmpe})]^-$ (**1**) of satisfactory purity in 50% yield.⁸ Due to the poor solubility of **1**, definitive characterization of the anion in solution was provided by ^{13}C and ^{31}P NMR spectra of the 99% ^{13}C enriched anion as the Na^+ (**2**) and $[\text{Na}(2.2.1)]^+$ (**3**)⁷ salts.⁹ The carbonyl ^{13}C chemical shift of **2**, δ 320 ppm, is apparently the most downfield value reported to date for a carbonylmetalate.^{1,10} Upon addition of (2.2.1) to **2**, dramatic infrared and ^{13}C NMR spectral shifts occurred. These changes are indicative of substantial reduction of ion pairing between Na^+ and carbonyl oxygens of the anion by the cryptand,¹¹ and are accompanied by a considerable increase in the thermal stability of the anion in solution and in the solid state.¹²

Protonation of a cold (-60°C) solution of $\text{CpTi}(\text{CO})_2(\text{dmpe})^-$ in 1,2-dimethoxyethane with 1 equiv of acetic acid rapidly gave a deep red violet solution according to eq 2. After solvent removal



and three low-temperature fractional recrystallizations from toluene-pentane, a 15% yield (based on $\text{Cp}_2\text{Ti}(\text{CO})_2$) of deep violet $\text{CpTi}(\text{CO})_2(\text{dmpe})\text{H}$ (**4**) was obtained which provided satisfactory analytical data. In contrast to all previously known terminal



| Bonds (Å) | |
|-----------------|----------|
| TiB - HB | 1.74(6) |
| TiB - C6B | 2.001(6) |
| TiB - C7B | 2.029(6) |
| TiB - P1B | 2.505(2) |
| TiB - P2B | 2.520(2) |
| C6B - O6B | 1.171(7) |
| C7B - O7B | 1.152(7) |
| Ti-Cp centroid | 2.031(1) |
| Angles (°) | |
| TiB - C6B - O6B | 175.3(5) |
| TiB - C7B - O7B | 179.4(5) |
| C6B - Ti - HB | 62.2(20) |
| C7B - Ti - HB | 66.7(19) |
| P1B - Ti - HB | 68.3(20) |
| P2B - Ti - HB | 72.0(20) |
| P1B - Ti - P2B | 76.67(6) |

Figure 1. ORTEP drawing of $\text{C}_5\text{H}_5\text{Ti}(\text{CO})_2(\text{dmpe})\text{H}$, independent molecule B, showing the labeling scheme and selected bonds and angles. Thermal ellipsoids are drawn with 50% probability boundaries.

hydrides of group 4 elements, the ^1H NMR chemical shift of the hydride in this compound (δ -1.62 (t, $J_{\text{P-H}} = 57$ Hz) ppm) is upfield of the signal for tetramethylsilane.¹³ IR and ^{13}C NMR spectra of **4** in the respective carbonyl regions (1933 s, 1855 s cm^{-1} (toluene) and δ 267 ppm, t, $J_{\text{P-C}} = 9$ Hz (C_6D_6)) are similar to corresponding values obtained for $(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{CO})_2$; i.e., 1940, 1858 cm^{-1} (hexane)¹⁴ and δ 265 ppm (C_6D_6),¹⁵ respectively.

An X-ray structural characterization of the hydride revealed a unit cell containing two independent molecules of very similar structures.¹⁶ One of these is shown in Figure 1 along with selected interatomic distances and angles. The terminal hydride (Ti-H (av) = 1.75 (7) Å) resides nearly trans to the ring centroid in both molecules. On the basis that the Cp group occupies one coordination site, the titanium is approximately octahedral. Mean interatomic Ti-C(carbonyl), C-O, Ti-P, and Ti-Cp (centroid) distances are unexceptional and within the range of values previously observed in other titanium phosphines and carbonyls.^{1,17-20}

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(8) IR (THF) $\nu(\text{CO})$: 1725 s, 1647 s cm^{-1} . Anal. Calcd for **1**: C, 50.68; H, 7.82; N, 3.81. Found: C, 50.56; H, 7.37; N, 3.95.

(9) Selected spectroscopic data for **2** and **3**, respectively: IR (DME) $\nu(^{13}\text{C})$ 1613 s br, 1524 m br and 1680 s, 1596 s cm^{-1} ; NMR (DME, -10°C and -30°C) $^{13}\text{C}\{^1\text{H}\}$ δ 320 (1:2:1 t, $J_{\text{P-C}} = 18$ Hz) and 311 (t, $J_{\text{P-C}} = 16$ Hz); $^{31}\text{P}\{^1\text{H}\}$ δ +78 (t, $J_{\text{P-C}} = 18$ Hz) and +63 (t, $J_{\text{P-C}} = 16$ Hz) ppm.

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(16) The hydride formed orthorhombic crystals in the space group P_{bca} . Cell data: $a = 8.756$ (3) Å, $b = 24.686$ (20) Å, $c = 29.322$ (12) Å, $V = 6338$ (10) Å³, $Z = 16$, $R = 0.057$, $R_w = 0.052$, and GOF = 1.23 for a fit of 333 variables to 2995 observations. Supplementary Material contains complete details on the structural study.

The terminal Ti-H distance is similar to bridging Ti-H distances (1.7-1.8 Å) found in titanium(III) alu- or borohydrides.²¹

While the reaction chemistry of this and related hydrides²² promises to be interesting, extension of this study to zirconocene and hafnocene dicarbonyls will be especially desirable since zerovalent carbonyls of these elements are either extremely rare (Zr) or nonexistent (Hf).^{23,24}

Acknowledgment. Financial support for this work was generously provided by the National Science Foundation Grant CHE 85-06710 and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We are very grateful to Professor Doyle Britton for help with the crystal structure determination.

Supplementary Material Available: Details of the X-ray structural analysis, a drawing of independent molecule A of the unit cell, and tables of positional parameters and their esds, general temperature factor expressions, and bond lengths and angles for $C_5H_5Ti(CO)_2(dmpe)H$ (15 pages); tables of observed and calculated structure factors for $C_5H_5Ti(CO)_2(dmpe)H$ (12 pages). Ordering information is given on any current masthead page.

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Origin of Enhanced Axial Attack by Sterically Undemanding Nucleophiles on Cyclohexenones

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Small nucleophiles, such as lithium aluminum hydride (LAH), undergo predominantly axial nucleophilic additions to cyclohexanones² and this axial selectivity is substantially enhanced in 2-cyclohexenones.³⁻⁶ We have applied our recently developed computational model^{2a} to this problem and show that the torsional explanation of Felkin^{2c} quantitatively accounts for these phenomena.

Different explanations have been offered previously. Toromanoff concluded that axial attack on cyclohexenones is preferred

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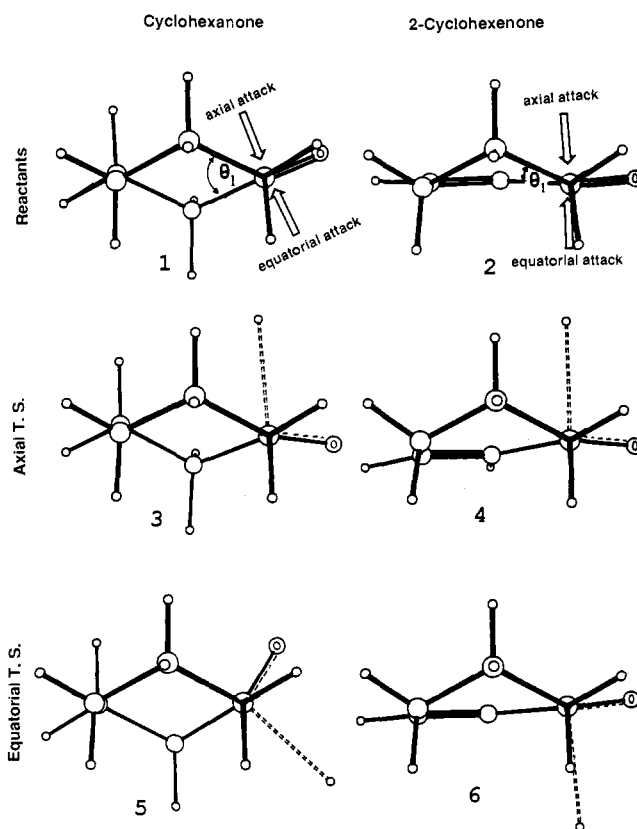


Figure 1. Newman projections along the C_2C_1 bonds for cyclohexanone, **1**, and 2-cyclohexenone, **2**, and for the transition structures for the axial and equatorial attack of hydride on cyclohexanone, **3** and **5**, and 2-cyclohexenone, **4** and **6**. The drawings are constructed with the modified MM2 model described in the text.

because this maintains continuous overlap of the forming bond with the π system.³ Baldwin proposed that the approach vector of nucleophiles on enones was different from saturated ketones and caused greater steric preference for axial attack.⁴

Alkynyllithium reagents typically give axial selectivities of about 6-8:1 with saturated ketones⁵ but greater than 20:1 with enones.⁵ Metalated acetonitriles show typical axial preferences with conformationally rigid cyclohexanones of 5-7:1 but greater than 20:1 with the corresponding enones.⁷

We have previously reported a modified MM2 model which reproduces ratios of attack of LAH upon the axial and equatorial positions of cyclohexanones.^{2a} For cyclohexanones, the only new parameters required define the torsional energies for rotation about the C_1C_2 bond. The V_2 torsional parameters for dihedral angles $O=C-C=C$ and $O=C-C_{sp^2}-H(C)$ are set to 2.0 mdyn/deg. This causes the enone to be approximately coplanar in transition states. When these parameters are reduced to zero, thus removing

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