a : n = 5 , b : n = 6

and gives some [6]metacyclophane as a byproduct.[4b] The rearrangement of **1a** to **3a** furnishes a chemical corroboration of the nature and the composition of **1a**.

One of the most fascinating conclusions is that the benzene ring retains its aromatic character with remarkable tenacity, in contrast to predictions based on theoretical calculations.[6a,7] The UV and especially the ^{1}H NMR spectra reveal an essentially delocalized, aromatic structure; the molecule does, however, pay a toll to strain in giving up another property traditionally connected with benzene-like aromaticity, i.e., stability.

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Registry No. 1a, 58634-37-0; **2a**, 53600-57-0; **3a**, 1075-16-7.

Acetylene Derivatives of Titanocene[†]
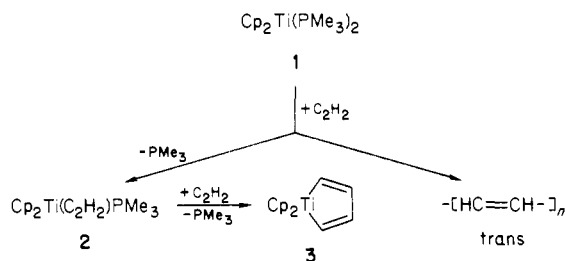
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Acetylene complexes of titanium have been proposed as key intermediates in the formation of polyacetylene [CH]$_x$.[1] At the present time, however, in spite of many attempts, no C_2H_2 derivatives of a group 4 transition metal could be prepared. The reason for this failure is the increased reactivity of the C_2H_2 hydrogens induced by the coordination of the alkyne to the metal. We now report evidence for the first C_2H_2 complex of titanocene and the first unsubstituted metallacyclopentadiene containing an early transition metal.

The highly reactive "titanocene" source $Cp_2Ti(PMe_3)_2$ (**1**) (Cp = η^5-cyclopentadienyl, Me = methyl)[2] reacts instantly with C_2H_2 in solution forming $Cp_2Ti(C_2H_2)PMe_3$ (**2**), the metallacycle $Cp_2TiC_4H_4$ (**3**), polyacetylene, and traces of benzene.

In a typical reaction to generate and characterize **2** in solution, 33.0 mg (0.1 mmol) of **1** were dissolved in 0.4 mL of cyclohexane-d_{12} and treated with the stoichiometric amount of C_2H_2 at 10 °C. The red-brown solution immediately turned purple with the formation of **2**. The ^{1}H NMR spectrum of **2** exhibits two broad doublets for the C_2H_2 ligand, resulting from coupling of the two nonequivalent C_2H_2 protons with the ^{31}P nucleus of the PMe$_3$ ligand [δ 8.82 (*J* = 9.0 Hz) and 6.99 (*J* = 5.4 Hz)], as confirmed by the ^{31}P-decoupled ^{1}H NMR spectrum.[3] These results imply a configuration in which the CC axis of the C_2H_2 ligand lies in the symmetry plane of a pseudotetrahedral molecule, analogous to that shown for $Cp_2Ti(C_2Ph_2)CO$[4] and Cp_2Ta-$(C_2H_4)H$[5] (Figure 1). In the IR spectrum of **2**, a band is observed at 1618 cm^{-1} (cyclohexane) that is indicative of a C-C double bond.[6]

On the basis of these spectroscopic data and in view of the absence of a C_2H_2 ligand rotation we formulate **2** as a titanacyclopropene derivative. This conclusion is supported by the reaction of **2** with hydrogen chloride, which yields ethylene and Cp_2TiCl_2. All attempts to isolate **2** as a solid have so far been unsuccessful. Removal of the solvent in vacuo yields a dark purple paramagnetic residue that is not identical with **2**.

Metallacycle **3** was obtained in a reaction of 2 mmol (0.66 g) of **1** in 20 mL of toluene with an excess of C_2H_2. Filtration of the resulting suspension, removal of the solvent in vacuo, and recrystallization of the residue from pentane afforded **3** as a light brown, relatively air- and light-sensitive powder.[7] In the ^{1}H NMR spectrum of **3** (CDCl$_3$, 20 °C), a sharp singlet can be observed for the Cp ligands at 6.18 ppm and an AA'BB' pattern for the four protons of the metallacyclic ring in the α- and β-positions (δ 6.30 (m) and 5.63 (m), respectively). These chemical shifts are consistent with the only other known C$_4$H$_4$ metallacycle, CpCo(PMe$_3$)C$_4$H$_4$.[8] In the ^{13}C NMR spectrum of **3** (CDCl$_3$, 20 °C), the Cp rings give rise to one signal at δ 113.0. The carbon atoms of the C$_4$H$_4$ moiety directly bonded to the metal are more strongly deshielded (198.5 ppm) than are the carbon atoms in the β-position (124.8 ppm).[9] This assignment is also supported by the different $^2J(C,H)$ long-range couplings of C$_\alpha$ and C$_\beta$.

In the mass spectrum of **3**, the molecular ion (*m/z* 230) is observed, as well as peaks derived from the fragmentation of this ion. The IR spectrum of **3** exhibits a ν(C=C) band at 1442 cm^{-1} (KBr), indicative of an olefinic double bond. The metallacyclic character of **3** is further established by its reaction with hydrogen chloride at -60 °C to yield mainly 1,3-butadiene and Cp_2TiCl_2, as identified by their ^{1}H and ^{13}C NMR spectra. The latter complex is also formed when chloroform solutions of **3** are kept at room temperature for a period of several days.

The insoluble black residue from the reaction of **1** and an excess of C_2H_2 shows IR bands characteristic for *trans*-polyacetylene.[1] Elemental analysis[10] of this material prepared under argon con-

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[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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(6) By comparison, the C=C stretching frequency for the metallacyclopropene complex Cp$_2$MoC$_2$H$_2$ is observed at 1613 cm^{-1}. (a) Tang Wong, K. L.; Thomas, J. L.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1974**, *96*, 3694. (b) Thomas, J. L. *Inorg. Chem.* **1978**, *17*, 1507.

(7) **3**: yield 250 mg, 55%; >45 °C dec. Anal. Calcd for C$_{14}$H$_{14}$Ti: C, 73.06; H, 6.13. Found: C, 71.31; H, 7.24. The reduction of Cp$_2$TiCl$_2$ with sodium in C$_2$H$_2$ atmosphere in toluene did not yield **3** but rather polyacetylene.

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(9) These conclusions are consistent with earlier studies on tetrasubstituted metallacyclopentadienes: Mattia, J.; Sikora, D. J.; Macomber, D. W.; Rausch, M. D.; Hickey, J. P.; Friesen, G. D.; Todd, L. J. *J. Organomet. Chem.* **1981**, *213*, 441.
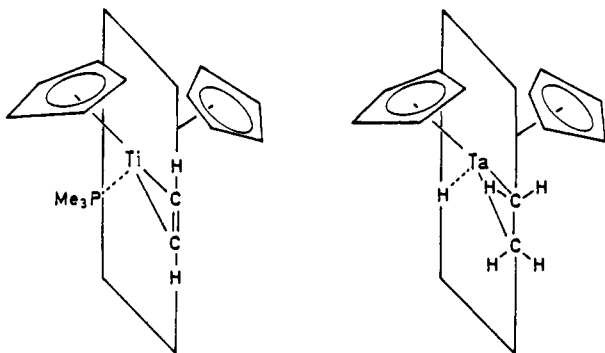
Figure 1. Configurations of Cp$_2$Ti(C$_2$H$_2$)PMe$_3$ and Cp$_2$Ta(C$_2$H$_4$)H.

firms the carbon hydrogen ratio of 1:1. The polymerization turnover rate under 1 bar of C$_2$H$_2$ pressure is approximately 120. The compressed polymer exhibits a characteristic metallic luster and shows a singlet signal in the EPR spectrum. It absorbs oxygen readily from the air up to 25% by weight and can be doped with iodine.

The reactivity of **1** with substituted alkynes has also been investigated. The reaction of methylacetylene and **1** followed by pentane extraction of the residue afforded the metallacycle Cp$_2$TiC$_4$Me$_2$H$_2$ (**4**).[11] This structural assignment is based upon ^{1}H and ^{13}C NMR data. Preliminary ^{1}H and ^{13}C NMR spectral data indicate that the other two possible isomers of **4** are also produced. Dimethylacetylene and **1** give the metallacycle Cp$_2$TiC$_4$Me$_4$ (**5**)[12] as the main product. Phenylacetylene and **1** form the alkyne complex Cp$_2$Ti(PhC$_2$H)PMe$_3$ (**6**)[13] and the metallacycle Cp$_2$TiC$_4$Ph$_2$H$_2$ (**7**).[14] Diphenylacetylene and **1** react
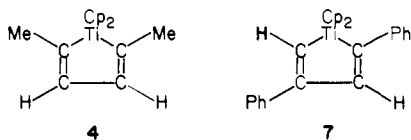
in an analogous manner producing Cp$_2$Ti(C$_2$Ph$_2$)PMe$_3$[15] and Cp$_2$TiC$_4$Ph$_4$.[16]

Further investigations concerning the reactivity of **2** and **3** as well as other alkyne derivatives of group 4 metals are in progress.

(10) **3**: Anal. Calcd for (CH)$_x$: C, 92.26; H, 7.74. Found: C, 90.38; H, 7.59; Ti, 0.90.

(11) **4**: ^{1}H NMR (CDCl$_3$) δ 6.10 (10 H), 5.37 (2 H), 1.60 (6 H); ^{13}C NMR (CDCl$_3$) δ 201.5 (C$_\alpha$), 115.2 (C$_\beta$), 112.0 (Cp), 27.1 (Me); MS, m/z 258 (M$^+$); IR ν(C=C) 1440 cm^{-1} (KBr).

(12) **5**: ^{1}H NMR (CDCl$_3$) δ 5.95 (10 H), 1.28 (6 H), 1.13 (6 H); ^{13}C NMR (CDCl$_3$) δ 192.1 (C$_\alpha$), 122.3 (C$_\beta$), 111.7 (Cp), 19.1, 14.0 (Me); MS, m/z 286 (M$^+$); IR ν(C=C) 1438 cm^{-1} (KBr).

(13) **6**: ^{1}H NMR (toluene-d_8) δ 7.13 (m, 5 H), 5.83 (br, 10 H), 0.93 (d, 5.4 Hz, 9 H); ^{31}P NMR δ 26.8; MS, m/z 354 [(M − 2H)$^+$]; IR ν(C=C) 1590 cm^{-1} (KBr).

(14) **7**: ^{1}H NMR (CDCl$_3$) δ 7.23 (m, 10 H), 6.24 (10 H); ^{13}C NMR (CDCl$_3$) δ 198.6 (PhC$_\alpha$), 196.7 (HC$_\alpha$) [^1J(C,H) = 140.7, ^3J(C,H) = 10.3 Hz], 147.0, 141.2, 127.9, 125.1 (Ph), 146.6, 141.2, 127.7, 124.7 (Ph), 130.1 (PhC$_\beta$), 128.7 (HC$_\beta$); MS, m/z 386 (M$^+$).

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Threshold Resonances in Electron Photodetachment Spectra. Structural Evidence for Dipole-Supported States

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The existence of a bound state arising from the interaction of a neutral dipole and an electron was first predicted by Fermi and Teller in 1947.[1] They calculated that for a nonrotating point dipole a critical value of 1.625 D is necessary for a bound state to exist. Additional calculations have examined the influence of finite-length and rotating dipole moments on the critical value.[2] In this paper we provide structural evidence for such "dipole-supported" states arising from the interaction of a dipolar molecule and an electron.

Experimental evidence for the existence of dipole-supported states is limited. Electron scattering experiments on polar molecules have been carried out and have been interpreted as involving such states.[3] It has recently been proposed that resonances observed in the threshold region for electron photodetachment from molecular negative ions correspond to transitions to dipole-supported states.[4] Resonances have been observed in the electron photodetachment spectra of enolate anions indicating the presence of an electronically excited state occurring at the threshold for electron photodetachment.[5] Quantum mechanical calculations have been carried out for acetaldehyde enolate and have indicated the presence of a low-lying, non-valence electronic state near the photodetachment threshold.[6] The assignment of these resonances to dipole-supported states is strengthened considerably by recent very high resolution (0.0007 cm^{-1}) electron photodetachment experiments on acetaldehyde.[7] These experiments show that in the excited state the higher rotational states are not bound and that the excited-state geometry is very similar to that of the neutral radical.

We report here a further test of this model, in which photodetachment cross sections were measured for a pair of ions for which the neutral dipolar core could be varied without substantially changing the electronic structure of the anions. In this experiment, resonances at the threshold of electron photodetachment due to dipole-bound electronic states should be present only for the anion with a critical dipole moment.

One such set of molecules is o- and p-benzoquinone (OBQ and PBQ, respectively, structures in Figure 1). The symmetrical PBQ has no dipole moment; the dipole moment of OBQ is approximately[8] 5.1 D. Both of these neutral molecules have positive electron affinities and both form stable negative ions. The negative ions have similar electronic structures,[9] and we would expect that the large dipole moment of OBQ should support a quasi-bound electronically excited state, while that of PBQ would not. An excited electronic state above the threshold energy will give rise to a resonance in the spectrum corresponding to an additional channel opening besides direct photodetachment.[10]

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