(4)°, is nearly linear; however, C(1)–C(2)–P is slightly bent, 166.6 (5)°. The P–C(2) bond, 1.683 (6) Å, is shorter than a P–C single bond and appears typical of resonance-stabilized phosphoylides.[12] The C(1)–C(2) distance, 1.221 (7) Å, is not significantly different from other metal–acetylide complexes where this distance ranges between 1.20 and 1.22 Å.[13,14] Similar features are also observed[8] for **4**. The Mn–C(1) bond length, 1.895 (5) Å, is longer than Mn–C double-bond distances of 1.68 (2) Å and 1.79 (2) Å in $Cp(OC)_2Mn{=}C{=}CHPh$[15] and $Cp(OC)_2Mn{=}C{=}C{=}CMe_2$,[16] respectively, but is shorter than the single-bond distance of 2.185 (11) Å determined for $(OC)_5MnCH_3$[17] by electron diffraction. It is also significantly shorter than 1.99 (1) Å observed[8] for the Mn–C bond in **4**. In **4** the phosphonium acetylide ligand is trans to carbonyl ligands, which are good π acceptors, while in **3** it is trans to a Cp ligand which competes poorly for metal π electrons. Consequently back-bonding into the acetylide ligand should be greater in **3** accounting for the shorter metal–carbon bond. Similarly, the Mn–carbonyl distances in **3** are also shorter than those in **4**, by about 0.10 Å. This is not an isolated phenomenon, and Mn–C bond lengths to ligands *trans* to carbonyls are typically 0.06–0.12 Å longer than the analogous distances in ligands trans to weak π acceptors.[18,19] The decrease in both the Mn–acetylide and Mn–carbonyl distances in **3** compared to **4** indicates that the phosphonium acetylide ligand is a good π acceptor. Thus, the Mn C bond in **3** probably should be ascribed partial double-bond character.

The conversion of **2** to **3** formally involves the elimination of Cp_3UOH, via the cleavage of the oxygen–carbon bond and the abstraction of a proton from the beta carbon atom.[20] Precedence for the reaction can be found in the very recently reported[11] reaction of a closely related silyl vinyl ether complex.

$$(CH_3C_5H_4)(OC)_2MnC(OSiMe_3)CHPMe_3 \rightarrow (CH_3C_5H_4)(OC)_2MnC{\equiv}CPMe_3 + Me_3SiOH$$

In both reactions C–O bond cleavage has been promoted by the attachment of an oxophilic group which presumably weakens the carbon–oxygen bond and activates it. The present case demonstrates that the attachment of an oxophilic metal ion, such as uranium, to an oxygen can also induce C–O bond cleavage. The ability of the uranium–carbon multiple bond to either deoxygenate or induce coupling[2] of coordinated carbon monoxide indicates the potential use of organouranium complexes as synthetic reagents and may have relevance to catalytic CO reduction processes.

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Supplementary Material Available: Table I, crystal, data collection, and reduction parameters, Table II, bond distances and angles for $Cp(OC)_2MnCCPMe_2Ph$, Table III, positional and thermal parameters for anisotropically refined atoms of $Cp(OC)_2MnCCPMe_2Ph$, Table IV, positional and thermal parameters for isotropically refined atoms of $Cp(OC)_2MnCCPMe_2Ph$, and Table V, observed and calculated structure factors for $Cp(OC)_2MnCCPMe_2Ph$ (11 pages). Ordering information is given on any current masthead page.

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(20) While Cp_3UOH has not yet been unambigously identified as a reaction product, a green-brown solid precipitates during the reaction. NMR spectra obtained during reactions run in THF-d_8 contain a peak at about –2.5 ppm. After filtration and drying under vacuum, the molecular ion observed in EI mass spectrum of this material is at *m/e* 882, which corresponds to the anhydride $(Cp_3U)_2O$. While Cp_3UOH has been mentioned in the secondary literature,[22] its characterization and properties have not been reported in the primary literature or in the habilitation thesis[23] where its synthesis is described. In deoxygenated water $Cp_3U(H_2O)_n^+$ is stable, however, in basic solution the system appears to be complicated by reactions of OH^- at the cyclopentadienide. In aqueous basic solutions of Cp_3UCl an incompletely characterized bright green precipitate, which is postulated to be an oxyhydroxide, forms.[24] Very recently an NMR resonance obtained during a controlled oxidation of Cp_3UR conducted in saturated C_6D_6 solutions at 27 °C has been tentatively assigned to $(Cp_3U)_2O$, –3.16 ppm. Upon addition of small amounts of water a new peak, tentatively assigned to Cp_3UOH, appears at –3.40 ppm.[25]

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Synthesis of 1,3-Metallatitanacyclobutanes of Group 4[†]

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Summary: The reaction of the 1,3-di-Grignard reagent $Cp_2Ti(CH_2MgBr)_2$ (**2**) with the metallocene dichlorides Cp_2MCl_2 (M = Ti, Zr, Hf) gave the 1,3-metallatitanacyclobutanes $Cp_2\overline{MCH_2TiCp_2C}H_2$ (M = Ti, **1a**; M = Zr, **1b**; M = Hf, **1c**, respectively).

Titanacyclobutanes continue to receive a high level of attention including their synthesis,[1] bonding aspects,[2] and

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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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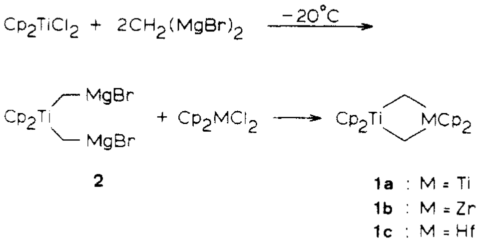
Table I. NMR Spectra of 1,3-Dimetallacyclobutanes 1

	^{1}H NMR[a]			^{13}C NMR[b]		
compd	Cp$_2$M	Cp$_2$Ti	CH$_2$	Cp$_2$M	Cp$_2$Ti	CH$_2$
1a[c]	6.23	6.23	8.72	112.1 [d, 172][d]	112.1 [d, 172][d]	235.8 [t, 125.2]
1b	6.2	6.22	7.63	110.1 [d, 171][d]	111.7 [d, 172][d]	205.7 [t, 124.5]
1c	6.15	6.25	6.26	109.3 [d, 172][d]	112.6 [d, 172][d]	193.3 [t, 120.9]

[a] δ in ppm; 90 MHz; C_6D_6 (C_6HD_5 as internal standard at 645 Hz; integrals in agreement with the number of protons). [b] δ in ppm [multiplicity; ^1J(C,H) in Hz]; 62.89 MHz; C_6D_6. [c] See also ref 4. [d] Additional long-range coupling leads to quasi-quintets with ^2J(C,H) $\approx$ ^3J(C,H) = 6 Hz.

Scheme I



intermediacy in catalytic processes.[3] In this context, 1,3-metallatitanacyclobutanes[1c–f,4] are of special interest because the replacement of a carbon atom by an additional metal may be expected to change the bonding situation, the ease of fragmentation to metal–carbene complexes such as Cp$_2$Ti=CH$_2$, the catalytic activity, etc. The only 1,3-metallatitanacyclobutane known so far is 1,1,3,3-tetracyclopentadienyl-1,3-dititanacyclobutane (Cp$_2$TiCH$_2$TiCp$_2$CH$_2$, **1a**), obtained by Ott and Grubbs[4] in the thermal decomposition of titanacyclobutanes.[5] On the basis of the recently developed bimetallic di-Grignard reagent Cp$_2$Ti(CH$_2$MgBr)$_2$ (**2**),[1d] we present here a new access not only to **1a** but also to other, mixed group 4 analogues Cp$_2$MCH$_2$TiCp$_2$CH$_2$ (**1b**, M = Zr; **1c**, M = Hf) (Scheme I).

In a typical experiment, dichlorodicyclopentadienyltitanium (Cp$_2$TiCl$_2$; 0.342 mmol) was converted to **2** by stirring in a sealed glass vessel for 1 hour at −20 °C with 2 molar equiv of bis(bromomagnesio)methane, CH$_2$(MgBr)$_2$[6] (0.684 mmol), in ether/benzene (1:1, 20 mL); **2** was obtained as a dark red, viscous precipitate in 40% yield.[1d] On addition of Cp$_2$MCl$_2$ (M = Ti, Zr, Hf; 0.274 mmol), followed by warming up to room temperature, the precipitate dissolved and yielded a solution of **1** which was purple-red in the case of **1a**[4] and brownish in the case of **1b** and **1c**. The isolation of **1** was achieved by evaporation of the solvent, extraction of the residue with toluene (10 mL), filtration, and concentration of the filtrate followed by crystallization at −80 °C; in this way, **1a** was obtained as dark purple crystals, **1b** as brown crystals, and **1c** as light brownish crystals in 33, 31, and 36% yield, respectively, relative to the Cp$_2$TiCl$_2$ used for the preparation of **2**. The new compounds were characterized by elemental analysis[7] and by their NMR spectra (Table I).

The data of Table I reveal some interesting trends which are, however, not fully understood at the moment. Most remarkable are the low field shifts of the protons and carbon nuclei of the methylene groups. While low field shifts of a much less dramatic degree have been observed in titanacyclobutanes bearing a group 14 atom at position 3,[1] the presence of two group 4 metals in the four-membered ring leads to values reminiscent of metal carbenes[8,9] and metal–carbene complexes.[2b,5,10] Theory[2a] predicts that the tendency to form such metal–carbene structures decreases for the higher elements, in line with the upfield shifts observed for **1a**, **1b**, and **1c**, respectively. The same trend would be expected on the basis of electronegativity considerations, although we feel that the electronegativity differences are not sufficient to explain the magnitude of the effects observed. Alternatively, low field shifts of bridging methylene groups have been connected to metal–metal bonding,[9] which results in a relatively acute M–C–M angle. Interestingly, the decrease of the carbon–proton coupling constant of the methylene group in the sequence **1a** → **1c** (Table I) would be in line with an increasing M–C–M angle, caused by increasing s character of the carbon to metal bond. A final distinction will only be possible if a crystal structure has been determined; unfortunately, the crystals obtained so far were not suitable for this purpose.

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Registry No. 1a, 79389-12-1; 1b, 96227-73-5; 1c, 96213-70-6; 2, 96213-71-7; Cp$_2$TiCl$_2$, 1271-19-8; Cp$_2$ZrCl$_2$, 1291-32-3; Cp$_2$HfCl$_2$, 12116-66-4; CH$_2$(MgBr)$_2$, 27329-47-1.

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Kinetic Control in Catalytic Olefin Isomerization. An Explanation for the Apparent Contrathermodynamic Isomerization of 3-Pentenenitrile[†]

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Summary: The isomerization of 3-pentenenitrile with homogeneous cationic nickel hydride or palladium catalysts is kinetically controlled, initially producing the terminal olefin 4-pentenenitrile in preference to the conjugated and thermodynamically favored isomer 2-pentenenitrile by ratios as high as 70:1.

[†] Contribution No. 3437.

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