Registry No. 1, 76831-03-3; 2, 86508-07-8; Rh, 7440-16-6; Mo, 7439-98-7.

Supplementary Material Available: Tables of atomic positional and thermal parameters and structure factors for $(C_5Me_5)(CH_3)\overline{Rh(\mu\text{-}PMe_2)_2Mo}(CO)_3I$ (11 pages). Ordering information is given on any current masthead page.

New 1,3-Diene Complexes of Zirconium and Hafnium: One-Step Conversion of the Butadiene Fragment with Carbon Monoxide to Cyclopentadienes under Mild Conditions

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Summary: Substituted cis-diene complexes Cp*M(diene)Cl (Cp* = η-$C_5(CH_3)_5$; M = Zr, Hf) were obtained by reduction of Cp^*MCl_3 with Na/Hg in the presence of trans-1,3-dienes. Exceptionally low ^{13}C–^1H coupling constants (138–141 Hz) of the terminal diene carbon atoms indicate a metallacyclo-3-pentene type of bonding for the diene–metal fragment. Reaction with carbon monoxide (1 atm, 25 °C) results in complete reduction of CO, splitting of the carbon oxygen bond, and formation of cyclopentadienes in which the carbon atom of the CO molecule is incorporated in the ring.

Our earlier work on group 4B diene complexes[2] and CO reduction with early transition-metal organic compounds[3] led us to investigate the synthesis and the reactivity toward carbon monoxide of complexes Cp*M(1,3-diene)Cl, **1**–**4** (**1**, M = Zr, 2-methyl-1,3-butadiene; **2**, M = Zr, 2,3-dimethyl-1,3-butadiene; **3**, M = Hf, 2-methyl-1,3-butadiene; **4**, M = Hf, 2,3-dimethyl-1,3-butadiene). The complexes were made by the reduction of Cp^*MCl_3 in THF with Na/Hg in the presence of the appropriate 1,3-diene and characterized by elemental analysis, IR, ^1H NMR, and ^{13}C NMR.[4,5]

The NMR spectra[5] allow conclusions with respect to the bonding of the diene ligand. In contrast to other group 4B complexes,[7] it is nonfluxional (**4** in toluene-d_8, −80 to +100 °C) over the temperature range studied. The small vicinal coupling constants $^3J_{HH}$ = 7.5 Hz in **1** and **3** clearly show that the ligands are in a cis conformation. For trans conformations much larger values ($^3J_{HH}$ = 12–16 Hz) are expected.[7] The coupling constants are smaller than those found for the related compound Cp_2Zr(*cis*-2-methyl-1,3-butadiene)[7a] but comparable with those reported for the tantallacyclopentane *cis*-1,3-butadiene complex $Cp^*\overline{TaCH_2CH_2CH_2CH_2}(C_4H_6)$.[8] The chemical shifts of the syn, anti, meso protons are comparable with the data reported for the complexes Cp_2Zr(cis-1,3-diene)[7a,c] and (η^8-C_8H_8)M(η^4-1,3-butadiene) (M = Zr, Hf,[7b] but there are remarkable differences. The meso protons in **1** and **3** are at extreme low-field positions (~5.5 ppm); the syn and anti protons are located at high-field positions (0.2–1.2 ppm), and their differences in chemical shift, $\Delta\delta$ (**1**, 0.7; **2**, 0.5; **3**, 0.9; **4**, 0.6 ppm), are among the smallest reported for η^4-1,3-diene complexes. Normally the shifts for the meso protons lie between 5.0 and 4.3 ppm, for the syn protons at about 3.5–1.8 ppm, and for the anti protons at 0.4–0.7 ppm, the difference in chemical shift $\Delta\delta$, varying between 4.1 and 2.2 ppm.[7]

In the ^{13}C NMR spectra[5] the resonances of the carbon atoms of the diene skeleton are found at 55–62 (terminal C) and at 119–134 ppm (internal C). The values are in the same range as reported for other group 4B 1,3-diene complexes[7] and are, as such, no indication for a specific bonding of the diene. The coupling constants, $^1J_{CH}$, clearly indicate a strong contribution of the metallacyclopentene structure. In compounds **1** and **3** the ^{13}C NMR spectrum shows for the CH group a doublet with $^1J_{CH}$ = 160–162 Hz. This value is what is expected for a sp^2-hybridized carbon atom.[9,10] The terminal carbons all have a triplet signal, with $^1J_{CH}$ values of 138–141 Hz. These are among the lowest coupling constants reported so far for 1,3-diene complexes and are close to the value of 125–130 Hz expected for a sp^3-carbon atom.[10]

On the basis of these NMR data, a strong contribution of a metallacyclo-3-pentene structure to the bonding of the diene ligand is evident; it could well be that the complexes

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(4) The compounds were made by the reduction of Cp^*MCl_3[2] (20 mmol) in THF (100 mL) with an excess of Na/Hg (0.5%) in the presene of a 50% excess of the 1,3-diene. After the solution was stirred for 24 h at room temperature, the solvent was removed under vacuum. Compounds **1** and **3** were obtained pure by extraction of the residue with hot toluene, concentration of the extracts, and subsequent cooling to −30 °C (yields 15 and 80%, respectively). Compounds **2** (yield 20%) and **4** (60%) were obtained by extraction of the crude product with pentane and subsequent sublimation of the extracts (110 °C (0.001 torr)). Anal. Calcd for **1**: C, 54.59; H, 7.03; Zr, 27.64; Cl, 10.74. Found: C, 53.76; H, 7.10; Zr, 27.21; Cl, 11.48. Calcd for **2**: C, 55.86; H, 7.32; Zr, 26.51; Cl, 10.30. Found: C, 55.68; H, 7.32; Zr, 26.89; Cl, 10.31. Calcd for **3**: C, 43.18; H, 5.56; Hf, 42.77; Cl, 8.49. Found: C, 42.90; H, 5.54; Hf, 43.00; Cl, 8.52. Calcd for **4**: C, 44.56; H, 5.84; Hf, 41.38; Cl, 8.25. Found: C, 44.50; H, 5.81; Hf, 41.55; Cl, 8.37. IR (Nujol; ν (cm^{-1})): all compounds show characteristic Cp* absorptions at about 2915 (m), 2870 (m), 1485 (s), 1425 (s), 1380 (s), 1070 (m), 1025 (s), and 800 (m). Vibrations characteristic for ν(CC) of complexed conjugated dienes are found between 1500 and 1530 cm^{-1} in agreement with data reported for other metal diene compounds.[6]

(5) ^1H NMR data (60 MHz, THF-d_8, 34 °C, δ) for the anti, syn, and meso protons of the diene ligands: **1**, H_{anti} 0.5 (m, 2 H), H_{syn} 1.2 (m, 2 H), H_{meso} 5.54 (t, J = 7.5 Hz, 1 H); **2**, H_{anti} 0.6 (d, J = 7.0 Hz, 2 H), H_{syn} 1.14 (d, J = 7.0 Hz, 2 H); **3** H_{anti} 0.3 (m, 2 H), H_{syn} 1.2 (m, 2 H), H_{meso} 5.55 (t, J = 7.5 Hz, 1 H); **4**, H_{anti} 0.24 (d, J = 8.2 Hz, 2 H), H_{syn} 0.84 (d, J = 8.2 Hz, 2 H). A detailed analysis of the spectra was not performed (see ref 7b,c). ^{13}C NMR data (50.3 MHz, THF-d_8, 25 °C, δ) for the carbon atoms of the diene group: **1**, terminal C 55.6 (t, J = 138 Hz), 60.5 (t, J = 138 Hz), internal C 119.2 (d, J = 162 Hz), 134.1 (s); **2**, terminal C 63.3 (t, J = 141 Hz), internal C 128.0 (s); **3**, terminal C 54.7 (t, J = 138 Hz), 59.6 (t, J = 138 Hz), internal C 118.5 (d, J = 160 Hz), 134.0 (s); **4**, terminal C 61.8 (t, J = 138 Hz), internal C 126.7 (s).

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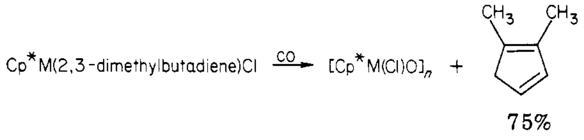
are in fact group 4B metallacyclo-3-pentenes. Additional support for this is found in the IR spectra, where an absorption at 1530–1550 cm^{-1} can be assigned to the double bond of the metallacyclo-3-pentene.[7c]

The chemistry of the compounds Cp*M(1,3-diene)Cl is very interesting. The chlorine atom can be easily substituted by organic groups R by treatment with appropriate Grignard or lithium reagents.[11] The coordinatively strongly unsaturated (14-electron) compounds react readily with donor ligands (e.g., THF or PR_3) to give 16-electron systems Cp*M(1,3-diene)(Cl)(L). Formation of 18-electron complexes Cp*M(1,3-diene)(Cl)$(L)_2$ was not observed.

With CO, adduct formation is the initial step,[12] but the adducts are unstable and react further in what is probably an intramolecular reaction of the carbonyl ligand with the coordinated diene.



M = Zr, Hf

The reaction proceeds under moderate conditions (1 atm of CO, 25 °C) and leads to complete reduction of the carbon monoxide molecule with incorporation of the carbon atom into the 4-position of the product 1,2-dimethyl-1,3-cyclopentadiene, as could be demonstrated by reaction with ^{13}C-enriched CO.[13] The oxygen atom ends up at the transition-metal atom, forming a complex of composition [Cp*M(O)Cl]$_n$,[15] which is most likely oligomeric. To the best of our knowledge this reaction is the first example of carbon monoxide reduction, with complete separation of the carbon–oxygen bond, on a mononuclear transition-metal species under mild conditions. Insertion of CO into several early transition-metal metallacycles has been observed, and normally cyclic ketones are formed directly or isolated after quenching.[16,17]

The closely related compounds Cp_2Zr(cis-diene) react with CO similarly with formation of dimethylcyclopentenone, and cleavage of the C–O bond is not observed.[18] The pentamethylcyclopentadienyl 1,3-diene complexes are unique in showing that the oxophilicity of early transition metals is so great that it can lead to split the CO molecule completely.

Further reactions of these types of complexes and the related compounds Cp*M(1,3-diene)R (R = alkyl, aryl) with CO, and isocyanides are under investigation at the moment.

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Registry No. 1, 87050-41-7; 2, 87050-42-8; 3, 87050-43-9; 4, 87050-44-0; Cp*ZrCl$_3$, 75181-07-6; Cp*HfCl$_3$, 75181-08-7; Cp*Hf(2,3-dimethylbutadiene)Me, 87050-45-1; Cp*Hf(2,3-dimethylbutadiene)Et, 87050-46-2; Cp*Hf(2,3-dimethylbutadiene)*neo*-pent, 87050-47-3; Cp*Hf(2,3-dimethylbutadiene)Ph, 87050-48-4; Cp*Hf(2,3-dimethylbutadiene)allyl, 87050-49-5; Cp*Hf(2,3-dimethylbutadiene)Cl(CO), 87050-50-8; [Cp*Hf(O)Cl]n, 87050-52-0; [Cp*Zr(O)Cl]n, 87050-54-2; CO, 630-08-0; 1,2-dimethyl-1,3-cyclopentadiene, 4784-86-5.

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(11) For 4 this substitution has been worked out in detail: Cp*Hf(2,3-dimethylbutadiene)R (R = Me, Et, neo-Pent, Ph, allyl) was prepared and characterized (analyses, ^{1}H NMR ^{13}C NMR, IR).

(12) The IR spectrum of a pentane solution of 4 showed, after admission of CO, a strong absorption at 2114 cm^{-1} due to Cp*Hf(2,3-dimethylbutadiene)Cl(CO). The absorption disappears quickly to give new absorptions at 1589 and 1630 cm^{-1} due to C–C stretching frequencies of free 1,2-dimethyl-1,3-cyclopentadiene.

(13) A solution of 2 or 4 (about 1 M) in benzene-d_6 was treated with CO (1 atm, 25 °C). After the uptake of CO had ceased, the reaction mixture was evaporated in vacuo and the volatile components were condensed into a cold trap (−78 °C). 1,2-Dimethyl-1,3-cyclopentadiene was identified (MS, ^{1}H NMR, ^{13}C NMR) by comparison with an authentic sample.[14] ^{13}C NMR (50.3 MHz, benzene-d_6, 34 °C, δ): 136.9 (d, $J = 160$ Hz, $CH_2CH{=}CH$), 135.6 (s, $C(CH_3)$), 134.7 (s, $C(CH_3)$), 129.4 (d, $J = 165$ Hz, $CH_2CH{=}CH$), 45.8 (t, $J = 124$ Hz, $CH_2CH{=}CH$), 13.1 (q, $J = 127$ Hz, $C(CH_3)$), and 12.6 (q, $J = 127$ Hz, $C(CH_3)$). With ^{13}C-enriched CO the intensity of the absorption at 129.4 ppm increased strongly, demonstrating the incorporation of ^{13}C at the 4-position of the cyclopentadiene.

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(15) After the solution was washed, the compound [Cp*Hf(O)Cl]$_n$ was isolated, as a white powder. Anal. Calcd: C, 32.89; H, 4.14; Hf, 48.87; Cl, 9.80. Found: C, 33.08; H, 4.19; Hf, 48.31; Cl, 9.71. ^{1}H NMR (60 MHz, $CDCl_3$, 34 °C, δ): 2.15(s).

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Silylene to Disilene and Disilene to Silylene Rearrangements[1]

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Summary: The silylene to disilene rearrangement was further confirmed by generating $Me_3SiMe_2SiMeSi$: from 3-methoxyundecamethylpentasilane to afford $Me_2Si{=}SiMe(SiMe_3)$. However, at the same time the reverse rearrangement from the latter disilene to the former disilanylsilylene was also demonstrated by generating $Me_2Si{=}SiMe(SiMe_3)$. Results of photochemically generated disilanylsilylene and silyldisilene were compared with those of thermal reactions.

Recently we have reported the first clear evidence of the silylene to disilene rearrangement by generating $Me_3SiMe_2SiMeSi$: (1) from the newly prepared precursor 2,3-benzo-1,4-diphenyl-7-methyl-7-(pentamethyldisilanyl)-7-silanorbornadiene (2).[2] The silylene 1 rearranges to $Me_2Si{=}SiMe(SiMe_3)$ (3) by the 1,2-trimethylsilyl shift. Although the mechanism of the thermal decomposition of 7-silanorbornadiene derivatives has been well established to give a sound basis for giving the silylene, it is desirable to generate the silylene by an alternative route in order to confirm the previous result. Thus we have synthesized 3-methoxyundecamethylpentasilane (4) and conducted its thermolysis (sealed tube, 300 °C, 7 h) in the hope to generate 1.

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