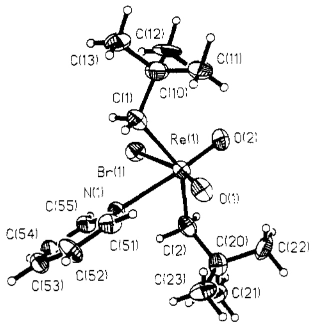

Figure 1. ORTEP plot of $ReO_2(CH_2CMe_3)_2Br(py)$ (**3a**) showing the atom-numbering scheme (50% probability level). Selected distances (Å) and angles (deg): Re(1)–Br(1), 2.680 (1); Re(1)–O(1), 1.696 (7); Re (1)–O(2), 1.680 (7); Re(1)–N(1), 2.396 (7); Br(1)–Re(1)–O(1), 165.6 (2); O(1)–Re(1)–O(2), 107.4 (3); O(1)–Re(1)–C(1), 95.6 (3); O(2)–Re(1)–C(1), 103.4 (4); O(1)–Re(1)–C(2), 100.0 (4); O(2)–Re(1)–C(2), 99.3 (4); Br(1)–Re(1)–N(1), 83.7 (2); O(2)–Re(1)–N(1), 170.7 (3); C(1)–Re(1)–N(1), 75.0 (3); C(2)–Re(1)–N(1), 78.8 (3).

a mixture of products is obtained which we have not yet been able to separate.

The structure of **3a** has been determined by an X-ray crystallography study; an ORTEP drawing of one of the two similar independent molecules in the unit cell is given in Figure 1.[8] One noteworthy strucural feature in **3a** is the bending of the neopentyl methylene groups away from the Re=O multiple bonds (C(1)–Re–C(2) = 147.1 (4)°). An analogous structural feature was also observed in the octahedral *cis*-dioxo *trans*-dialkyl compounds $MoO_2R_2(bpy)$ (R = Me, CH_2CMe_3, CH_2Ph).[9] In all of these complexes it is likely that the closed $RH_2C–M–CH_2R$ angles are due to electronic effects because the bending facilitates metal p_x–d_{xz} mixing (*xz* plane bisecting the O–M–O angle), which in turn enhances Re–O π bonding.[10]

The pyridine ligands in **3a–c** rapidly dissociate on the ^1H NMR time scale at 23 °C, but spectra recorded for the compounds at low temperatures (<−35 °C) are consistent with expectations based upon the solid-state structure of **3a**; e.g., **3c** reveals an AB quartet with coupling to ^{19}F ($^2J_{HH}$ = 12.1 Hz, $^3J_{H_aF}$ = 9.2 Hz, $^3J_{H_bF}$ = 13.8 Hz, $CH_aH_bCMe_3$) and a singlet (CH_2CMe_3) as well as five separate resonances assigned to the protons of coordinated pyridine.

In order to determine if substitution reactions can be carried out on the Re(VII) complexes without reduction of the metal center, we attempted the preparation of $ReO_2(CH_2CMe_3)_3$ (**4**)[1c] from **3a** and **3b**. Compound **3b** reacts with an excess of $Zn(CH_2CMe_3)_2$ (eq 5) to give **4** in

$$ReO_2(CH_2CMe_3)_2Cl(py) + Zn(CH_2CMe_3)_2 \xrightarrow[-5\ °C,\ 30\ min]{toluene} ReO_2(CH_2CMe_3)_3 + ZnCl(CH_2CMe_3) \quad (5)$$

79% yield and a small amount of **1**,[3] a product of reduction. Under similar conditions, reaction of **3a** with an excess of $Zn(CH_2CMe_3)_2$ generates **4** and **1** in 53% and 26% isolated yields, respectively, indicating, as expected, that the bromide complex is more easily reduced than the chloride.

We have shown that oxidation reactions can be used to prepare Re(VII) *cis*-ReO_2 complexes from Re(VI) $[Re(\mu\text{-}O)O(CH_2CMe_3)_2]_2$ in moderate to good yields. Similar oxidation reactions involving the Re(VI) dimers $[Re(\mu\text{-}O)O(R)_2]_2$ (R = Me,[11] CH_2SiMe_3,[1d] CH_2CMe_2Ph[3b]) should yield Re(VII) compounds analogous to **3a–c**. Additionally, reaction 5 shows that substitution of halide by alkyl can be accomplished with only a small amount of undesirable Re(VII) reduction. Substitutions of the halides with other types of ligands (e.g., alkoxides via trimethylalkoxysilane reagents) are therefore feasible. Further studies concerning the reactivity of **2** and **3a–c** are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Supplementary Material Available: Experimental procedures and spectroscopic data for all new compounds, procedure for the X-ray structure determination, complete tables of bond distances and angles, atomic coordinates, non-hydrogen atom anisotropic displacement parameters, a packing diagram, and an ORTEP plot of the other independent molecule in the unit cell (19 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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[8] Crystal data for $C_{15}H_{27}NO_2BrRe$ at −80 (1) °C: triclinic, space group $P\bar{1}$, a = 10.304 (3) Å, b = 12.360 (4) Å, c = 14.553 (4) Å, α = 90.72 (2)°, β = 93.77 (2)°, γ = 91.59 (2)°, Z = 4. A total of 5909 reflections were collected in the range 4° < 2θ < 45° (0,−k,−l to h,k,l). Of these, 4852 were unique reflections and 3897 with $F_0 > 4\sigma(F_o)$ were used in the structure solution. $R(F)$ = 0.0364; $R_w(F)$ = 0.0409.

[9] Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Robinson, P. R.; Schlemper, E. O. *Organometallics* **1982**, *1*, 44. Schrauzer, G. N.; Hughes, L. A.; Strampach, N.; Ross, F.; Ross, D.; Schlemper, E. O. *Organometallics* **1983**, *2*, 481. Schrauzer, G. N.; Hughes, L. A.; Schlemper, E. O.; Ross, F.; Ross, D. *Organometallics* **1983**, *2*, 1163.

[10] See Figure 15.4 on p 292 and its accompanying discussion in the following reference: Albright, T. A. Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.

[11] Hoffman, D. M.; Wierda, D. A., unpublished results.

Selective Formation of Alkenylcyclopentadienyl Substituents by Means of Olefin/Butadiene Coupling at Zirconium

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Summary: Coupling of a Cp-bonded (Cp = cyclopentadienyl) substituent with a C_4H_6 unit at zirconium is observed by reacting $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)_2ZrCl_2$ (**5**) with the (butadiene)magnesium reagent **6**. Treatment of the resulting metallacyclic π-allyl-type coupling product **8** with stoichiometric gaseous HCl yields the mixed Cp-substituted metallocene dihalide (Cp-allyl) $[\eta^5\text{-}C_5H_4(CH_2)_4CH{=}CHCH_3]ZrCl_2$ (**9**). Repetition of this reaction sequence cleany converts **9** into $[\eta^5\text{-}C_5H_4(CH_2)_4CH{=}CHCH_3]_2ZrCl_2$ (**11**). The *trans*-5-heptenylcyclopentadienyl substituent is prepared regio- and stereoselectively by the CC coupling/HCl addition reaction at the early-transition-metal center.

Substituted η-cyclopentadienyl ligands are gaining ever increasing importance in organometallic chemistry; e.g., using various new Cp-substituted metal complexes has led to very interesting developments of novel catalyst systems recently.[1] An increasing number of synthetic entries to

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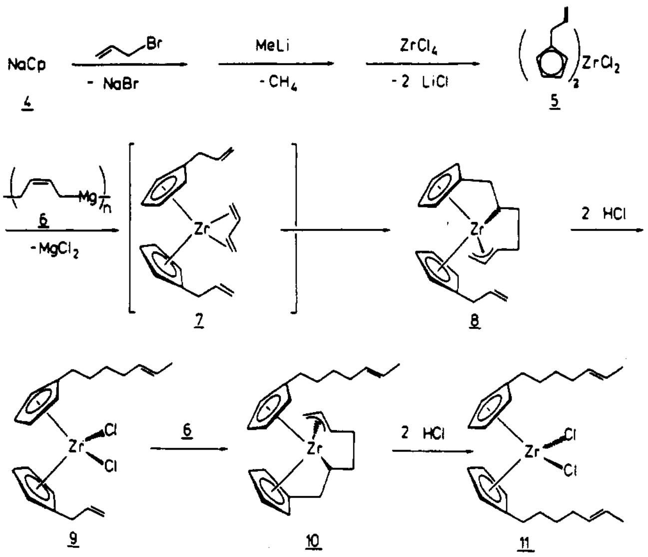
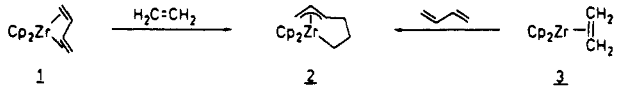
[1] (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 3241. (b) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Cesarotti, E.; Ugo, R.; Kagan, H. B. *Angew. Chem.* **1979**, *91*, 842. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 779. (d) Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* **1981**, *12*, 63. (e) Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983**, *105*, 3893. (f) Faller, J. W.; Chao, K.-H. *Organometallics* **1984**, *3*, 927. (g) Paquette, L. A.; McKinney, J. A.; McLaughlin, M. L.; Rheingold, A. L. *Tetrahedron Lett.* **1986**, 5599. (h) Haltermann, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1987**, *109*, 8105.

0276-7333/88/2307-2070$01.50/0

Scheme I



RCp ligands has become known which rely on selectively introducing substituents at various stages during the process of constructing the five-membered ring system.[2] It seemed to be less fashionable to apply a simple series of substitution and carbon–carbon coupling reactions to build up substituents attached to cyclopentadienyl moieties, although this can sometimes be done very easily.[3] We report here an example, where an intramolecular variation of coupling an olefin with a butadiene ligand at a group IV transition-metal center has been used successfully to very selectively elongate Cp-bonded allyl substituents by a chain of four carbon atoms. Starting from **1** or **3**, butadiene and ethylene have been coupled at the Cp_2Zr unit to give **2**.[4] In order to develop this into an intramolecular coupling reaction, we have prepared $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)_2ZrCl_2$ (**5**) via the route indicated[5] which was in turn treated with 1 equivalent of the (butadiene)magnesium reagent **6**.[6] The expected (η^4-butadiene)Zr(CpR)$_2$ complex **7**[7] is not stable under the reaction conditions applied. Immediate selective intramolecular carbon–carbon coupling reaction occurs between the conjugated diene ligand and the olefinic functionality of one Cp-bonded allyl group to yield the (π-allyl)metallocene complex **8**.[8a] Its reaction with a stoichiometric amount of gaseous HCl at ambient temperature gives a high yield of the metallocene dichloride **9**.[8b]



This reaction sequence has been repeated starting from **9**. Selective carbon–carbon coupling of the remaining allyl group occurs upon reaction with the butadiene dianion equivalent **6**. The resulting π-allyl metallocene complex was not characterized but was subjected to the subsequent HCl addition reaction. The exclusively formed metallocene dichloride **11** containing two $(\eta^5\text{-}C_5H_4(CH_2)_4CH{=}CHCH_3)$ ligands bonded to zirconium was isolated in 42% yield based on **9**.[8c]

The **5** → **9** → **11** reaction sequence is remarkably regio- and stereoselective. Not unexpected is the favored formation of the syn-substituted π-allyl metallocene complex resulting from butadiene/alkene ligand coupling at zirconium.[9] Its stereochemical information is retained upon

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(8) (a) **8**. ^{1}H NMR (C_6D_6): 2,5–7-η-heptenetriyl substituent, δ 3.40, 2.25 (2 m, 2 H, CpCH_2CH(Zr)), –0.05 (m, 1 H, CpCH$_2$*CH*(Zr)), 2.60, 2.70 (2 m, 2 H, CH(Zr)CH_2CH$_2$), 1.75, 2.35 (2 m, 2 H, CH(Zr)CH$_2$$CH_2$), 3.96 (m, 1 H, CH$_2$*CH*CHCH$_2$), 5.95 (m, 1 H, CH$_2$CH*CH*CH$_2$), 1.33, 2.05 (2 m, 2 H, CHCHCH_2); 2-propen-1-yl, δ 2.91 (m, 2 H, CH_2CH=), 5.65–5.90 (m, 1 H, *CH*=CH$_2$), 5.90 (m, 2 H, CH=CH_2); cyclopentadienyl, δ 4.28, 4.82, 5.1–5.4 (8 m, 8 H). ^{13}C NMR (C_6D_6, $^1J_{CH}$ in Hz): 2,5–7-η-heptenetriyl C(1)–C(7), δ 27.8 (t, 127), 5.4 (d, 128), 52.0 (t, 121), 34.0 (t, 127), 104.4 (d, 146), 124.2 (d, 147), 37.8 (dd, 146, 150); 2-propen-1-yl, δ 34.6 (t, 127, *C*H$_2$CH=CH$_2$), 115.2 (t, 156, CH=*C*H$_2$), 138.0 (d, 153, *C*H=CH$_2$); cyclopentadienyl, δ 96.2 (d, 170), 99.6 (d, 170), 103.0 (d), 104.8 (d), 105.1 (d), 105.2 (d), 105.5 (d), 106.3 (d), 101.9 (s), 118.9 (s). (b) **9**. A sample of 2.30 g (6.18 mmol) of **5** in 300 mL of toluene was added to 1.38 g (6.20 mmol) of solid butadiene–magnesium ($C_4H_6Mg{\cdot}2THF$) (**6**) at –78 °C. The mixture was warmed up to ambient temperature over 12 h and filtered. Gaseous HCl (280 mL) (12.5 mmol) was added via syringe. Stirring for 10 min and stripping yielded 1.80 g (69%) of **9** (≥95% pure by ^{1}H NMR). ^{1}H NMR ($CDCl_3$): *trans*-5-hepten-1-yl, δ 2.61 (t, 2 H, CpCH_2CH$_2$), 1.30–1.57 (2 m, each 2 H, CpCH$_2$$CH_2$$CH_2CH_2$), 1.91–2.01 (m, 2 H, CH$_2$$CH_2$CH=CH), 5.36–5.41 (m, 2 H, CH$_2$*CH*=*CH*CH$_3$), 1.62 (m, 5 H, CH=CHCH_3); 2-propen-1-yl, δ 3.39 (m, 2 H, CH_2CH=CH$_2$), 5.00–5.10 (m, 2 H, CH=CH_2), 5.79–6.00 (m, 1 H, *CH*=CH$_2$); cyclopentadienyl, δ 6.19, 6.29 (2 m, 8 H). ^{13}C NMR ($CDCl_3$, $^1J_{CH}$ in Hz): *trans*-5-hepten-1-yl, δ 17.9 (q, 125, =CH*C*H$_3$), 124.9 (d, 151, CH=*C*HCH$_3$), 131.1 (d, 151, CH$_2$*C*H=CHCH$_3$), 29.1 (t, 127, CH$_2$), 30.0 (t, 127, CH$_2$), 30.1 (t, 127, CH$_2$), 32.2 (t, 124, CH$_2$); 2-propen-1-yl, δ 34.2 (t, 127, *C*H$_2$CH=CH$_2$), 116.6 (t, 155, CH=*C*H$_2$), 135.9 (d, 153, *C*H=CH$_2$); cyclopentadienyl, δ 112.3 (d, 173), 112.5 (d, 173), 116.5 (d, 173), 116.7 (d, 173), 132.5 (s), 135.1 (s). IR (KBr): 1638 (C=C), 992 (oop, C, H), 913 (oop, =CH$_2$), 965 cm^{-1} (oop, 1,2 trans substitution). High-resolution mass spectrum, *m/e* (70 eV): calcd ($C_{20}H_{26}Cl_2Zr$), 426.0453; obsd, 426.0463. (c) **11**: prepared analogously to **9**. ^{1}H NMR ($CDCl_3$): *trans*-5-hepten-1-yl, δ 2.60 (t, 4 H, CpCH_2CH$_2$), 1.30–1.58 (2 m, each 4 H, CpCH$_2$$CH_2$$CH_2CH_2$), 1.90–2.00 (m, 4 H, CH$_2$$CH_2$CH=CH), 5.35–5.41 (m, 4 H, CH$_2$*CH*=*CHCH*$_3$), 1.61 (m, 6 H, CH=CHCH_3); cyclopentadienyl, δ 6.18, 6.27 (2 m, 4 H). ^{13}C NMR ($CDCl_3$, $^1J_{CH}$ in Hz): *trans*-5-hepten-1-yl, δ 17.9 (q, 125, =CH*C*H$_3$), 125.0 (d, 151, CH=*C*HCH$_3$), 131.1 (d, 152, CH$_2$*C*H=CHCH$_3$), 29.1 (t, 127, CH$_2$), 30.0 (t, 128, CH$_2$), 30.1 (t, 128, CH$_2$), 32.3 (t, 125, CH$_2$); cyclopentadienyl, δ 112.3 (d, 174), 116.7 (d, 172), 135.0 (s). IR (KBr): 965 (oop, 1, 2 trans substitution). High-resolution mass spectrum, *m/e* (70 eV) calcd ($C_{24}H_{34}Cl_2Zr$), 482.1076; obsd, 482.1085.

quenching with hydrochloric acid. Protonation occurs exclusively at the CH_2 terminus of the π-allyl group of **8**. The trans stereochemistry of the resulting $CH_2CH{=}CH{-}CH_3$ portion of the newly formed Cp substituent is evident from its typical IR and ^{13}C NMR features.[8b] The favored butadiene/allyl rather than butadiene/alkenyl coupling starting from **9** may be due to steric reasons. Syn substitution of the endocyclic π-allyl functionality in **10** probably determines that a second chemically equivalent *trans*-5-hepten-1-yl Cp substituent is also formed selectively upon treatment with HCl. Interesting new metallocene complexes are expected to become available by subsequently modifying the alkene RCp functionalities introduced by this novel method.

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Registry No. **5**, 85500-11-4; **6**, 83995-88-4; **8**, 115677-38-8; **9**, 115677-39-9; **11**, 115677-40-2.

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A New, General Route to (μ-Bis(carbene))ditungsten Complexes: X-ray Crystal Structure of $(CO)_5W\{C(OCH_3)CH_2[\overline{CH(CH_2)_3C}(CH_2CH{=}CH_2)]C(OCH_3)\}W(CO)_5$

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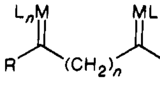
Summary: α-Lithio carbene anions $(CO)_5W[C(OCH_3)CR^1R^2]^-Li^+$ (**2**) react with α,β-unsaturated carbene complexes $(CO)_5W[C(OCH_3)C(R^4){=}CHR^3]$ (**3**) to produce the intermediate α-lithio (μ-bis(carbene))ditungsten anions $(CO)_5W[C(OCH_3)C(R^1)(R^2)CH(R^3)C(R^4)C(OCH_3)]W(CO)_5^-Li^+$ (**4**), which were subsequently quenched with electrophilic reagents (E–X = $CH_3OSO_2CF_3$, $CH_2{=}CHCH_2Br$, $PhCH_2Br$, Me_3SiCl, HCl) to afford good yields of the desired (μ-bis(carbene))ditungsten complexes $(CO)_5W[C(OCH_3)C(R^1)(R^2)CH(R^3)C(R^4)(R^5)C(OCH_3)]W(CO)_5$ (**5**). Complex **5j** ($R^1 = R^2 = H$; R^3, $R^4 = (-CH_2-)_3$; $R^5 = CH_2CH{=}CH_2$), which was the only diastereomer formed, was characterized by X-ray crystallography and showed the two large tungsten carbene fragments to be on the same side of the cyclopentane ring.

Transition-metal carbene complexes are ubiquitous throughout organometallic chemistry because of their involvement in many catalytic and stoichiometric processes.[1] Unlike the more common transition-metal carbene complexes comprised of *one* carbene fragment bonded to a *single* transition metal, (μ-bis(carbene))dimetallic complexes are relatively rare. This interesting group of complexes consists wholly of homodimetallic derivatives of chromium,[2] molybdenum,[2] tungsten,[2] manganese,[3] rhenium,[4] and iron.[5] For some of these complexes the μ-bis(carbene) ligands can be considered to be derivatives of the parent μ-bis(alkylidene) systems represented by structure **1** (n = 1, 2, 3, etc.). To our knowledge the only derivatives of **1** are dichromium ($n = 2$,[2f] $n = 3$,[2c] $n = 4$[2k]), ditungsten ($n = 2$,[2f] $n = 4$[2k]), dimanganese ($n = 4$),[3a,b] and diiron ($n = 1$)[5] complexes. Furthermore, a closely related ditungsten derivative of **1**, $(CO)_5W[C(OCH_2CH_3)(CH_2)_9CH{=}CH(CH_2)_9C(OCH_2CH_3)]W(CO)_5$, has recently been reported.[2l] None of these compounds, however, possess the simple parent structure **1**.



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We now report a new, general route to (μ-bis(carbene))ditungsten complexes **5**, which have the general structure represented by **1** (M = W, $L_n = (CO)_5$, R = OCH_3, $n = 3$), the X-ray crystal structure of one of these compounds (**5j**), and some preliminary findings on their reactivity. Our approach to the synthesis of complexes **5** involved the conjugate addition of substituted α-lithio carbene anions (**2**) (obtained by treating the corresponding carbene complexes with n-BuLi at −78 °C)[2c,6] to various α,β-unsaturated tungsten carbene complexes (**3**) (Scheme I). The resulting α-lithio (μ-bis(carbene))ditungsten anions **4** were then quenched with various electrophilic reagents (E–X)[6a,c,d,i] to afford good yields of the desired compounds **5** (Table I).[7] Although the overall process outlined in Scheme I was previously proposed to explain

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