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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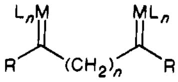
Summary: α-Lithio carbene anions $(CO)_5W[C(OCH_3)CR^1R^2]^-Li^+$ (**2**) react with α,β-unsaturated carbene complexes $(CO)_5W[C(OCH_3)C(R^4){=}CHR^3]$ (**3**) to produce the intermediate α-lithio (μ-bis(carbene))ditungsten anions $(CO)_5W[C(OCH_3)C(R^1)(R^2)CH(R^3)C(R^4)C(OCH_3)]W(CO)_5^-Li^+$ (**4**), 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**, $(CO)_5W[C(OCH_2CH_3)(CH_2)_9$-$CH{=}CH(CH_2)_9C(OCH_2CH_3)]W(CO)_5$, has recently been reported.[2l] None of these compounds, however, possess the simple parent structure **1**.



1

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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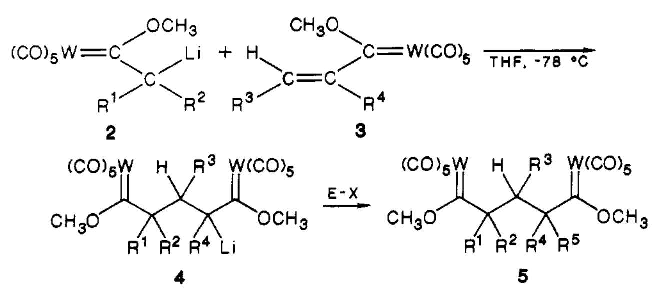
Table I. Yields of Complexes 5 Prepared According to Scheme I

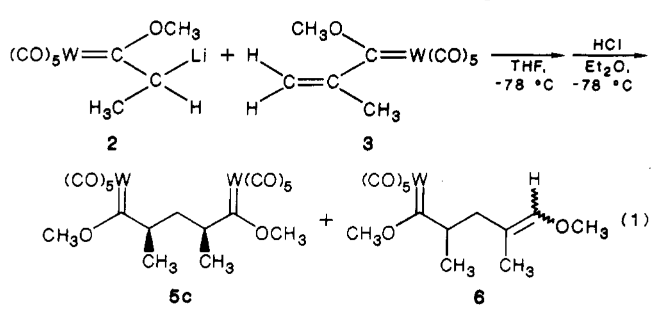
5	R^1	R^2	R^3	R^4	R^5	E-X	% yield
a	H	H	H	H	H	Me_3SiCl	52
b	H	H	H	CH_3	H	Me_3SiCl	57
c	H	CH_3	H	CH_3	H	Me_3SiCl	58
d	H	H	CH_3	CH_3	$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Br$	73
e	H	n-C_3H_7	H	CH_3	$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Br$	72
f	H	n-C_3H_7	H	CH_3	$PhCH_2$	$PhCH_2Br$	66
g	CH_3	CH_3	H	CH_3	CH_3	$CH_3OSO_2CF_3$	60
h	H	H	$(-CH_2-)_3$		H	Me_3SiCl	62
i	H	CH_3	$(-CH_2-)_3$		$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Br$	78
j	H	H	$(-CH_2-)_3$		$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Br$	74
k	H	H	$(-CH_2-)_4$		$CH_2CH{=}CH_2$	$CH_2{=}CHCH_2Br$	72
l	H	H	$(-CH_2-)_6$		H	HCl	71

Scheme I



the formation of a single (μ-bis(carbene))dichromium complex,[2c] the yields were generally lower than those prepared by our method (Table I). Furthermore, the generality of this new method has not been exploited until now.

Our initial investigations at converting anions **4** to products **5** involved by using reagents known to react with α-lithio carbene anions.[6a,c,d,i] Whereas $CF_3SO_3CH_3$, $CH_2{=}CHCH_2Br$, and $PhCH_2Br$ worked satisfactorily, anhydrous HCl in ether usually gave lower yields of **5** because of vinyl ether formation. For example, upon reacting **2** ($R^1 = CH_3$, $R^2 = H$) with **3** ($R^3 = H$, $R^4 = CH_3$) followed by quenching with HCl/ether resulted in the formation of **5c** (43%), as expected, and the vinyl ether derivative **6** (30%) (eq 1). Complex **6** presumably arises by protonation of



(1)

4c at tungsten followed by reductive elimination and loss of a $W(CO)_5$ fragment. Moreover, complex **6** was formed as a 6:1 mixture of E and Z isomers as determined by a two-dimensional NOESY experiment.[8] We subsequently found when anions **4** were quenched with Me_3SiCl instead of HCl that the **5**:vinyl ether ratio increased such that moderate yields of complexes **5** were obtained (Table I). What may be occurring in the conversion of **4** to **5**, when E-X is Me_3SiCl, is that α-trimethylsilyl (μ-bis(carbene))ditungsten derivatives **5** ($R^5 = SiMe_3$) are formed as intermediates that subsequently undergo protodesilylation upon chromatographic purification to **5** (R^5 = H).[9] We were also able to use this apparent hydrolytic sensitivity of α-(trimethylsilyl)alkyl Fischer-type carbene complexes in the preparation of the parent (μ-bis(carbene))ditungsten compound **5a** (R^1-R^5 = H). Thus, attempts to add $(CO)_5W[C(OCH_3)CH_2]^-Li^+$ (**2**, $R^1 = R^2 = H$) to $(CO)_5W[C(OCH_3)CH{=}CH_2]$ (**3**, $R^3 = R^4 = H$) led only to polymerization of **3** ($R^3 = R^4 = H$).[11] We found, however, that **2** ($R^1 = R^2 = H$) cleanly added to $(CO)_5W[C(OCH_3)C(SiMe_3){=}CH_2]$[12] (**3**, R^3 = H, $R^4 = SiMe_3$) followed by

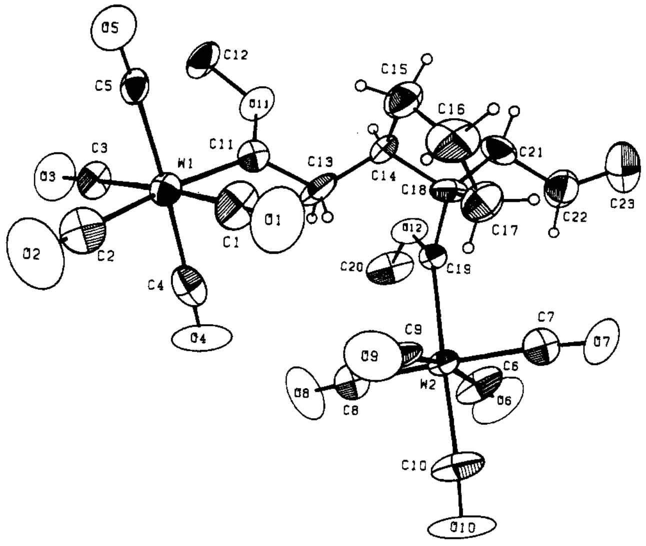


Figure 1. Molecular structure and atom-labeling scheme for **5j** with the atoms represented by their 50% probability ellipsoids for thermal motion.

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[7] All new compounds were characterized by ^1H NMR (400.1 MHz) and ^{13}C NMR (100.6 MHz) spectroscopy and gave satisfactory combustion analyses. The detailed experimental and spectroscopic information will be presented in a future publication.

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[9] To our knowledge $(CO)_5W[C(NMe_2)CH_2SiMe_3]$ is the only characterized α-(trimethylsilyl)alkyl Fischer-type carbene complex, which in contrast to complexes **5** ($R^5 = SiMe_3$), is stable to protodesilylation on silica gel.[10a] Moreover, the protodesilylations of monomeric α-(trimethylsilyl)alkyl tungsten carbene complexes have previously been reported.[10b] **Note added in proof**: We are indebted to Professor Ulrich Schubert for bringing to our attention the existence of the compound $(CO)_5Cr[C(OC_2H_5)CH_2SiMe_3]$.[10c]

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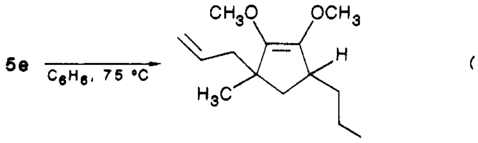
addition of Me_3SiCl and purification on silica gel to give **5a** in 52% yield. A possible intermediate in the formation of **5a**, which we did not attempt to isolate nor detect, would be **5** (R^1–R^3 = H, R^4 = R^5 = $SiMe_3$).

Whenever possible (**5c–f,h–l**) the reactions described in Scheme I proceeded in a highly stereoselective manner with the formation of complexes **5** as one major diastereomer. For example, *meso*-**5c** (eq 1) was formed diastereoselectively (>90%, as determined by ^1H NMR spectroscopy)[13] in the reaction between **2** (R^1 = CH_3, R^2 = H) and **3** (R^3 = H, R^4 = CH_3) and Me_3SiCl as the electrophilic quenching agent. Moreover, a single-crystal X-ray structure of **5j** (Figure 1) clearly revealed that this isomer, which was the only one formed, had the two large tungsten carbene fragments on the same side of cyclopentane ring. No doubt, **5j** arises by $CH_2{=}CHCH_2Br$ adding to the sterically less hindered side of **4j**.[14]

The solid-state structure of **5j** (Figure 1) contains two $(CO)_5W$ fragments bridged by a μ-1,5-bis(pentylidene) ligand.[15] To our knowledge compound **5j** is only the second (μ-bis(carbene))ditungsten complex that has been characterized by X-ray crystallography.[2k] The structural features associated with the $(CO)_5W$–carbene portions of **5j** are similar and are typical of other Fischer-type pentacarbonyl tungsten carbene complexes.[2k,l,16] For example, the W(1)–C(11) and W(2)–C(19) carbene bond distances of 2.10 (2) and 2.16 (2) Å, respectively, are similar to distances in other tungsten carbene complexes in which an alkoxy group and a carbon are directly bonded to the carbene carbon. The two tungsten carbene fragments have different orientations with respect to the cyclopentane ring; the angle between the respective mean planes through C(12), O(11), C(11), W(1), C(13) and C(20), O(12), C(19), W(2), C(18) is 83.1°.

Initial studies on the reactivity of these (μ-bis(carbene))ditungsten complexes **5** have revealed an interesting intramolecular carbene–carbene coupling reaction (eq 2).[17]



(2)

7

Thus, heating a solution of **5e** in benzene for 3 h cleanly produced the 1,2-dimethoxycyclopentene derivative **7** in 90% yield. The organometallic products formed in this reaction, as determined by an $^{13}C\{^1H\}$ NMR experiment conducted in C_6D_6, were $W(CO)_6$ and $(\eta^6\text{-}C_6D_6)W(CO)_3$.[18] The formation of **7** is significant, in that, the parent compound 1,2-dimethoxycyclopentene appears to be unknown;[20] furthermore, a new, general route to highly substituted five-membered carbacycles could be developed starting with complexes **5**.[21]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

Registry No. **2** (R^1 = R^2 = H), 115677-70-8; **2** (R^1 = H, R^2 = CH_3), 115677-71-9; **2** (R^1 = H, R^2 = n-C_3H_7), 115677-72-0; **2** (R^1 = R^2 = CH_3), 115677-73-1; **3** (R^3 = R^4 = H), 83801-34-7; **3** (R^3 = H, R^4 = CH_3), 108104-17-2; **3** (R^3 = R^4 = CH_3), 115792-67-1; **3** (R^3, R^4 = $(CH_2)_3$), 111772-18-0; **3** (R^3, R^4 = $(CH_2)_4$), 111772-19-1; 3 (R^3, R^4 = $(CH_2)_6$), 111772-20-4; **5a**, 115677-58-2; **5b**, 115677-59-3; **5c**, 115677-60-6; **5d**, 115677-61-7; **5e**, 115677-62-8; **5f**, 115677-63-9; **5g**, 115677-64-0; **5h**, 115677-65-1; **5i**, 115677-66-2; **5j**, 115677-67-3; **5k**, 115677-68-4; **5l**, 115677-69-5; Me_3SiCl, 75-77-4; $CH_2{=}CHCH_2Br$, 106-95-6; $PhCH_2Br$, 100-39-0; $CH_3OSO_2CF_3$, 333-27-7.

Supplementary Material Available: Spectral and analytical data for new compounds, particulars of data collection, and tables of bond distances and angles, positional and thermal parameters, and least-squares planes results for **5j** (12 pages); a listing of observed and calculated structure factor amplitudes for **5j** (6 pages). Ordering information is given on any current masthead page.

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(12) Macomber, D. W.; Liang, M.; Rogers, R. D. *Organometallics* **1988**, *7*, 416.

(13) ^1H NMR of *meso*-**5c** ($CDCl_3$): δ 4.58 (s, 6 H), 4.02 (sextet, J = 6.7 Hz, 2 H), 1.95 (dt, J = 13.9, 6.9 Hz, 1 H), 1.12 (dt, J = 13.8, 7.0 Hz, 1 H), 1.06 (d, J = 6.7 Hz, 6 H).

(14) We are currently investigating the origins of this observed diastereoselectivity and will report these findings in a more complete form at a later date.

(15) Complex **5j** crystallizes in the centric *Pbca* space group with cell constants (at 20 °C) a = 11.931 (6) Å, b = 14.404 (8) Å, c = 31.496 (9) Å, and D_{calcd} = 2.10 g cm^{-3} for Z = 8 (Mo Kα, λ = 0.71073 Å). Data were collected on a Enraf-Nonius CAD4 diffractometer. Least-squares refinement based on 2868 observed reflections led to a final R value of 0.064 (314 parameters varied in the final cycles). All but the methyl (C(12), C(20)) and C(23) hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 $Å^2$. All non-hydrogen atoms except C(2), C(7), C(18), and C(11) were refined with anisotropic thermal parameters.

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(18) $^{13}C\{^1H\}$ NMR (C_6D_6): $W(CO)_6$, δ 191.11; $(\eta^6\text{-}C_6D_6)W(CO)_3$, δ 215.73, 89.04 (t).[19]

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Chemistry of the 17-Electron Compound $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]$

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Summary: The compound $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]_2$ has a very weak metal-metal bond and dissociates extensively in solution. The resulting monomer $[(\eta^5\text{-}C_5Me_5)Cr(CO)_3]$ takes part in a variety of reactions characteristic of 17-electron compounds.

The compound $[(\eta^5\text{-}C_5H_5)Cr(CO)_3]_2$ (I) is unusual among 18-electron, dimeric metal carbonyls in that it has a very weak metal–metal bond and dissociates thermally in solution to an extent of about 10%.[1] We have utilized this fact to study the chemistry of the monomeric $[(\eta^5\text{-}C_5H_5)\text{-}Cr(CO)_3]$ (II),[2] with which I is in facile equilibrium, veri-

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