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Synthesis and Structures of (μ-Bis(carbene))dimetal Complexes of Chromium and Tungsten

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Treatment of the α-lithio carbene anions $(CO)_5M^1[C(X^1R)C(R^1)(R^2)]Li$ (**1**) (M^1 = Cr, W; X^1R = OCH_3, OCH_2Ph, OCH_2CH_2Ph, $N(CH_3)_2$; R^1, R^2 = H, CH_3, *n*-C_3H_7, $Si(CH_3)_3$) with the α,β-unsaturated carbene complexes $(CO)_5M^2[C(X^2R)C(R^4){=}CHR^3]$ (**2**) (M^2 = Cr, W; X^2R = OCH_3, OCH_2Ph, $N(CH_3)_2$; R^3, R^4 = H, CH_3, $Si(CH_3)_3$, $(-CH_2-)_3$, $(-CH_2-)_4$, $(-CH_2-)_6$) produced the intermediate α-lithio (μ-bis(carbene))dimetal anions $\{(CO)_5M^1[C(X^1R)C(R^1)(R^2)CH(R^3)C(R^4)C(X^2R)]M^2(CO)_5\}Li$ (**3**), which were subsequently quenched with various electrophilic reagents E–X (E–X = $CH_3OSO_2CF_3$, $CH_2{=}CHCH_2Br$, $PhCH{=}CHCH_2Br$, $PhCH_2Br$, $(CH_3)_3SiCl$, HCl) to afford the (μ-bis(carbene))dimetal complexes $(CO)_5M^1[C(X^1R)C(R^1)(R^2)CH(R^3)C(R^4)(R^5)C(X^2R)]M^2(CO)_5$ (**4a–z**) (R^1 = H, CH_3, $CH_2CH{=}CH_2$, $CH_2CH{=}CHPh$, CH_2Ph) in 46–78% yields. Along with the desired (μ-bis(carbene))dimetal complexes (**4**) were produced small amounts of the vinyl ether derivatives $(CO)_5M^1[C(X^1R)C(R^1)(R^2)CH(R^3)C(R^4){=}CH(OCH_3)]$ (**5**). Complexes **4c–f,h,j–l,r–t,w,x**, which each have two asymmetric carbon centers, were produced as one major diasteromer. Complexes **4j** ($M^1 = M^2$ = W; $X^1R = X^2R$ = OCH_3; $R^1 = R^2$ = H; R^3, R^4 = $(-CH_2-)_3$; R^5 = $CH_2CH{=}CH_2$), **4s** (M^1 = Cr, M^2 = W, $X^1R = X^2R$ = OCH_3, $R^1 = R^3 = R^5$ = H, $R^2 = R^4$ = CH_3), and **4x** ($M^1 = M^2$ = W; X^1R = $N(CH_3)_2$; X^2R = OCH_3; $R^1 = R^2$ = H; R^3, R^4 = $(-CH_2-)_3$; R^5 = $CH_2CH{=}CH_2$) were also characterized by single-crystal X-ray diffraction methods. Complex **4s** crystallizes in the centric *Pbca* space group with cell constants a = 14.083 (7) Å, b = 18.032 (3) Å, c = 19.380 (5) Å, and D_{calcd} = 1.81 g cm^{-3} for Z = 8. Least-squares refinement based on 2471 independent observed [$F_o \geq 5\sigma(F_o)$] reflections led to a final conventional R value of 0.044. Complexes **4j** and **4x**, which differ only in the heteroatom substituent X^1R, crystallize in the centric *Pbca* space group with cell constants 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 and monoclinic $P2_1/c$ space group with cell constants a = 13.931 (3) Å, b = 12.729 (2) Å, c = 16.032 (2) Å, β = 93.47 (2)°, and D_{calcd} = 2.03 g cm^{-3} for Z = 4, respectively. Both were refined via least squares, **4j** to a conventional R value of 0.064 based on 2868 independent observed [$F_o \geq 5\sigma(F_o)$] reflections and **4x** to 0.028 (based on 4037 reflections).

Introduction

Transition-metal carbene complexes composed of one carbene ligand bonded to a single transition-metal fragment (i.e. monometallic terminal carbene complexes) have been studied extensively[1] since the seminal discoveries of $(CO)_5W[C(OCH_3)R]$ (R = CH_3, C_6H_5) by Fischer and Massböl.[2] These complexes were prepared by treating $W(CO)_6$ with CH_3Li and C_6H_5Li, respectively, followed by protonation of the resulting metal acylate with dilute acid and finally O-alkylation with diazomethane. It was rapidly recognized by Fischer and co-workers, as well as several other research groups, that this method could be extended to prepare may other transition-metal carbene complexes by using other organolithium reagents, metal carbonyl systems, and alkylating agents. The terms "heteroatom-stabilized" or "Fischer" carbene complexes are commonly used today to describe this class of carbene complexes whose structures[3] are similar, in that they consist of a low-valent transition metal, usually with carbonyl ligands, and a carbene ligand having at least one heteroatom substituent (e.g. OR, NR, SR, SeR) bonded directly to the carbene carbon. Much of the considerable current interest in studying Fischer carbene complexes stems from their wide-spread use as reagents in organic synthesis.[4]

Given the extensive chemistry of monometallic terminal Fischer carbene complexes,[1,4] it might be envisioned that the (μ-bis(carbene))dimetal analogues, which consist of two carbene ligands (similar or dissimilar) bonded to two transition-metal fragments (similar or dissimilar), could exhibit reactivities that are equally extensive and interesting. Although several (μ-bis(carbene))homodimetal complexes of chromium,[5] molybdenum,[5] tungsten,[5] man-

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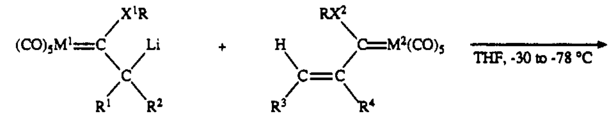
Table I. Yields of Complexes 4a–z Prepared According to Scheme I

	reactants			products										yield	
entry	1	2	EX	4	M^1	M^2	X^{1}R	X^{2}R	R^1	R^2	R^3	R^4	R^5	g	%
1[a]	a	a	$(CH_3)_3SiCl$	a	W	W	OCH_3	OCH_3	H	H	H	H	H	1.20	52
2	a	b	$(CH_3)_3SiCl$	b	W	W	OCH_3	OCH_3	H	H	H	CH_3	H	1.35	57
3[b]	c	b	$(CH_3)_3SiCl$	c	W	W	OCH_3	OCH_3	H	CH_3	H	CH_3	H	1.41	58
4	a	d	$CH_2{=}CHCH_2Br$	d	W	W	OCH_3	OCH_3	H	H	CH_3	CH_3	$CH_2CH{=}CH_2$	1.84	73
5	e	b	$CH_2{=}CHCH_2Br$	e	W	W	OCH_3	OCH_3	H	n-C_3H_7	H	CH_3	$CH_2CH{=}CH_2$	1.89	72
6	e	b	$PhCH_2Br$	f	W	W	OCH_3	OCH_3	H	n-C_3H_7	H	CH_3	CH_2Ph	1.83	66
7	g	b	$CH_3OSO_2CF_3$	g	W	W	OCH_3	OCH_3	CH_3	CH_3	H	CH_3	CH_3	1.51	60
8	a	h	$(CH_3)_3SiCl$	h	W	W	OCH_3	OCH_3	H	H	$(\text{-}CH_2\text{-})_3$		H	1.52	62
9[c]	c	h	$CH_2{=}CHCH_2Br$	i	W	W	OCH_3	OCH_3	H	CH_3	$(\text{-}CH_2\text{-})_3$		$CH_2CH{=}CH_2$	2.04	78
10	a	h	$CH_2{=}CHCH_2Br$	j	W	W	OCH_3	OCH_3	H	H	$(\text{-}CH_2\text{-})_3$		$CH_2CH{=}CH_2$	1.90	74
11	a	k	$CH_2{=}CHCH_2Br$	k	W	W	OCH_3	OCH_3	H	H	$(\text{-}CH_2\text{-})_4$		$CH_2CH{=}CH_2$	1.88	72
12[d]	a	l	HCl	l	W	W	OCH_3	OCH_3	H	H	$(\text{-}CH_2\text{-})_6$		H	1.83	71
13	m	b	$CH_2{=}CHCH_2Br$	m	W	W	OCH_2Ph	OCH_3	H	H	H	CH_3	$CH_2CH{=}CH_2$	0.40	55
14	n	b	$CH_2{=}CHCH_2Br$	n	W	W	OCH_2CH_2Ph	OCH_3	H	H	H	CH_3	$CH_2CH{=}CH_2$	0.37	50
15	m	o	$CH_2{=}CHCH_2Br$	o	W	W	OCH_2Ph	OCH_2Ph	H	H	H	CH_3	$CH_2CH{=}CH_2$	3.17	65
16[e]	p	p	$(CH_3)_3SiCl$	p	Cr	Cr	OCH_3	OCH_3	H	H	H	H	H	1.03	50
17[f]	p	q	$(CH_3)_3SiCl$	q	Cr	Cr	OCH_3	OCH_3	H	H	H	CH_3	H	1.03	49
18[g]	p	r	$CH_2{=}CHCH_2Br$	r	Cr	Cr	OCH_3	OCH_3	H	H	$(\text{-}CH_2\text{-})_3$		$CH_2CH{=}CH_2$	1.19	50
19	s	b	$(CH_3)_3SiCl$	s	Cr	W	OCH_3	OCH_3	H	CH_3	H	CH_3	H	1.48	55
20	t	b	$CH_2{=}CHCH_2Br$	t	Cr	W	OCH_3	OCH_3	H	n-C_3H_7	H	CH_3	$CH_2CH{=}CH_2$	1.72	58
21[h]	u	a		u	W	W	$N(CH_3)_2$	OCH_3	H	H	H	H	H	0.58	58
22	u	b	$CH_2{=}CHCH_2Br$	v	W	W	$N(CH_3)_2$	OCH_3	H	H	H	CH_3	$CH_2CH{=}CH_2$	4.08	77
23	w	b	$CH_2{=}CHCH_2Br$	w	W	W	$N(CH_3)_2$	OCH_3	H	$Si(CH_3)_3$	H	CH_3	$CH_2CH{=}CH_2$	0.54	47
24	u	h	$CH_2{=}CHCH_2Br$	x	W	W	$N(CH_3)_2$	OCH_3	H	H	$(\text{-}CH_2\text{-})_3$		$CH_2CH{=}CH_2$	2.20	74
25	u	b	$PhCH{=}CHCH_2Br$	y	W	W	$N(CH_3)_2$	OCH_3	H	H	H	CH_3	$CH_2CH{=}CHPh$	3.15	63
26	u	z	$(CH_3)_3SiCl$	z	W	W	$N(CH_3)_2$	$N(CH_3)_2$	H	H	H	H	H	0.48	46

[a] Besides **4a**, the rearranged α-trimethylsilylated vinyl ether derivative (*E*)-$(CO)_5W[C(OCH_3)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$ (**8**) was isolated in varying amounts.[42] [b] Besides **4c**, the vinyl ether derivative **5c** was was obtained in 16% yield; see Experimental Section for details. [c] The reaction mixture was stirred at −60 °C for 5 h after the addition of **2h** to **1c**. [d] The reaction mixture was stirred at −35 °C for 3 h then −5 °C for 24 h after the addition of **2l** to **1a**. [e] The reaction mixture was stirred at −78 °C for 3 h after the addition of **2q** to **1p**. [f] The reaction mixture was stirred at −78 °C for 3 h after the addition of **2q** to **1p**. [g] The reaction mixture was stirred at −60 °C for 3 h after the addition of **2r** to **1p**. [h] No electrophilic quenching agent was used; see Experimental Section for details. Furthermore, besides **4u**, the rearranged α-trimethylsilylated vinyl ether derivative (*E*)-$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH{=}C(OCH_3)Si(CH_3)_3]$ (**9**) was isolated in varying amounts.[42]

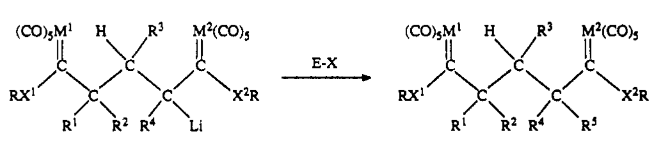
ganese,[6] rhenium,[7] and iron[8] have been prepared and characterized, their chemistry has only recently been investigated.[5n] Furthermore, we have recently communicated a new, general route to Fischer (μ-bis(carbene))ditungsten complexes,[9] and preliminary studies reveal that simple thermal decomposition of these complexes leads to a series of highly substituted cyclopentene derivatives.[10]

Scheme I



1	M^1	X^{1}R	R^1	R^2
a	W	OCH_3	H	H
c	W	OCH_3	H	CH_3
e	W	OCH_3	H	n-C_3H_7
g	W	OCH_3	CH_3	CH_3
m	W	OCH_2Ph	H	H
n	W	OCH_2CH_2Ph	H	H
p	Cr	OCH_3	H	H
s	Cr	OCH_3	H	CH_3
t	Cr	OCH_3	H	n-C_3H_7
u	W	$N(CH_3)_2$	H	H
w	W	$N(CH_3)_2$	H	$Si(CH_3)_3$

2	M^2	X^{2}R	R^3	R^4
a	W	OCH_3	H	$Si(CH_3)_3$
b	W	OCH_3	H	CH_3
d	W	OCH_3	CH_3	CH_3
h	W	OCH_3	$(\text{-}CH_2\text{-})_3$	
k	W	OCH_3	$(\text{-}CH_2\text{-})_4$	
l	W	OCH_3	$(\text{-}CH_2\text{-})_6$	
o	W	OCH_2Ph	H	CH_3
p	Cr	OCH_3	H	$Si(CH_3)_3$
q	Cr	OCH_3	H	CH_3
r	Cr	OCH_3	$(\text{-}CH_2\text{-})_3$	
z	W	$N(CH_3)_2$	H	H



3

4a-z

Since our initial report, which described the synthesis of complexes **4a–l**, we have extended the method to prepare (μ-bis(alkoxycarbene))ditungsten complexes (**4m–o**), (μ-bis(alkoxycarbene))dichromium complexes (**4p–r**), (μ-bis(alkoxycarbene))chromiumtungsten complexes (**4s,t**), (μ-bis(alkoxyaminocarbene))ditungsten complexes (**4u–y**),

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and a (μ-bis(aminocarbene))ditungsten complex (**4z**). This article describes experimental details for the preparation of all the (μ-bis(carbene))dimetal complexes (**4a–z**) and the X-ray crystal structures of **4j**, **4s**, and **4x**.

Results and Discussion

Our approach to the synthesis of complexes **4a–z** involved the conjugate addition of α-lithio carbene anions (**1**) (obtained by treating the corresponding alkylcarbene complexes with *n*-BuLi at −78 °C)[5c,11,12] to α,β-unsaturated carbene complexes (**2**) (Scheme I). The resulting α-lithio (μ-bis(carbene))dimetal anions (**3**) were then quenched with various electrophilic reagents (E–X)[11a,c,d,i,12] to afford good yields of the desired compounds **4** (Table I). To our knowledge, the reactions of carbene anions (i.e. **1**) with α,β-unsaturated carbene complexes (i.e. **2**) have been previously described in only two reports.[5c,13] In each case, however, either the carbene anion or the α,β-unsaturated carbene complex was generated in situ under the reaction conditions. Moreover, the synthesis of (μ-bis(carbene))dimetal complexes by the conjugate addition of α-lithio carbene anions to α,β-unsaturated carbene complexes (Scheme I) has only recently been developed into a general method.[9]

Although the process outlined in Scheme I proved to be quite general, there were, however, structural limitations (i.e. substituents R^1–R^4) observed for both the α-lithio carbene anions (**1**) and the α,β-unsaturated carbene complexes (**2**). For example, attempts to synthesize the parent (μ-bis(carbene))dimetal complexes **4a**, **4p**, and **4u** from the respective anions **1a**, **1p**, and **1u** and the vinylcarbene complexes $(CO)_5M^2[C(OCH_3)CH{=}CH_2]$ (**2**, M^2 = Cr, W; $R^3 = R^4 = H$)[14] led only to polymer formation.[15] To successfully synthesize these compounds (**4a**, **4p**, and **4u**) and prevent polymer formation, it was necessary to use complexes **2a** or **2p**, which have $R^4 = Si(CH_3)_3$. The trimethylsilyl group (R^4) in complexes **2a** and **2p** serves both to hinder their anionic polymerization, apparently because of steric factors[13] and, then once the (μ-bis(carbene))dimetal derivatives are formed, easily undergo protodesilylation (vide infra) to the desired complexes **4a**, **4p**, and **4u**. In contrast to $(CO)_5M^2[C(OCH_3)CH{=}CH_2]$ (M^2 = Cr, W), it was found that the dimethylamino analogue $(CO)_5W[C(N(CH_3)_2)CH{=}CH_2]$ (**2z**)[12] did not undergo polymerization upon its treatment with the α-lithio carbene anion **1u**.[16] Instead, the addition of **1u** to **2z**, followed by $(CH_3)_3SiCl$ as the electrophilic quenching reagent, afforded the (μ-bis(aminocarbene))ditungsten complex (**4z**) in 46% yield.[18]

It was also observed that as the number of substituents (R^1 and R^2) increased on the α-lithio carbene anions (**1**, $X^1R = OCH_3$) that their reactivities toward a given α,β-unsaturated carbene complex (**2**) decreased. This observed reactivity trend: $(CO)_5M^1[C(OCH_3)CH_2]Li > (CO)_5M^1[C(OCH_3)CH(R^1)]Li > (CO)_5M^1[C(OCH_3)C(R^1)(R^2)]Li$, which is no doubt due to steric factors, generally manifested itself, in the reactions between **1** and **2**, as longer reaction times and/or higher reaction temperatures (i.e. >−78 °C). Likewise, a similar, although more pronounced, reactivity trend was observed for **1** ($X^1R = N(CH_3)_2$). For example, whereas **1u** and **1w** underwent reactions with the α,β-unsaturated carbene complexes **2**, other more highly substituted α-lithio aminocarbene anions, such as the secondary anion $(CO)_5W[C(N(CH_3)_2)CH(CH_3)Li$, did not. This finding is consistent with the observed reactivity of these as well as other primary and secondary α-lithio aminocarbene anions with aldehydes,[12] $(CH_3)_3SiCl$,[12] and alkyl halides.[17] Furthermore, the reluctance of **2z** to undergo anionic initiated polymerization (vide supra), which would propagate by a secondary α-lithio aminocarbene anion, is yet another example of the diminished reactivity of α-lithio aminocarbene anions upon increasing substitution (i.e. R^1 and R^2).

As far as the reactivities of the α,β-unsaturated complexes **2** are concerned, they behave similarly to other (organic) Michael acceptors.[11e,19] For example, we have observed that substitution at the terminal carbon in complexes **2** (i.e. R^3) lowers their reactivities toward a given α-lithio carbene anion (**1**). Furthermore, it was found that only complexes **2** having the *E* configuration about the C=C double bond underwent reactions with anions **1**. For example, whereas (*E*)-$(CO)_5W[C(OCH_3)C(CH_3){=}CH(CH_3)]$ (**2d**) readily reacts with **1a**, we have not found, as yet, conditions in which the *Z* isomer of **2d** will react.

Our initial investigations at converting the α-lithio (μ-bis(carbene))dimetal anions (**3**) to products **4** (Scheme I) involved using reagents known to react with monomeric α-lithio carbene anions.[11a,c,d,i,12] Whereas $CH_3OSO_2CF_3$, $CH_2{=}CHCH_2Br$, $PhCH{=}CHCH_2Br$, and $PhCH_2Br$ worked satisfactorily in most cases, anhydrous HCl in diethyl ether usually gave lower yields of complexes **4**. This latter result was found to be due to competitive formation of the vinyl ether derivatives $(CO)_5M[C(X^1R)C(R^1)(R^2)CH(R^3)C(R^4){=}CH(OCH_3)]$ (**5**). Although the vinyl ether derivatives (**5**) were routinely observed[20] when HCl was employed, they were rarely, if ever, isolated and characterized. However, in one such example of isolation and characterization, treatment of **1c** with **2b**, followed by quenching with HCl in diethyl ether, resulted in the formation of **4c** (43%), as expected, and the vinyl ether derivative **5c** (30%) (eq 1). Complex **5c** may arise by protonation of the vinyl W–C bond[21] in **3c** with loss of a $W(CO)_5$ fragment. On the other hand, protonation at the α-lithio carbon in **3c**, of course, leads to **4c**. Moreover, the ratio of *E* and *Z* isomers in complex **5c**, as determined by a two-dimensional NOESY experiment,[22] was 6:1.

We subsequently found when anions **3** were quenched with $(CH_3)_3SiCl$ instead of HCl that the ratio of complexes **4** to **5** always increased. For example, repeating the re-

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[11] (a) Casey, C. P.; Boggs, R. A.; Anderson, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 8947. (b) Casey, C. P.; Anderson, R. L. *Ibid.* **1974**, *96*, 1230. (c) Casey, C. P.; Anderson, R. L. *J. Organomet. Chem.* **1974**, *73*, C28. (d) Casey, C. P.; Brunsvold, W. R. *Ibid.* **1976**, *118*, 309. (e) Casey, C. P.; Brunsvold, W. R.; Scheck, D. M. *Inorg. Chem.* **1977**, *16*, 3059. (f) Rudler-Chauvin, M.; Rudler, H. *J. Organomet. Chem.* **1981**, *212*, 203. (g) Wulff, W. D.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503. (h) Alverez-Toledano, C.; Parlier, A.; Rose-Munch, F.; Rudler, H.; Daran, J. C.; Knobler, C.; Jeannin, Y. *J. Organomet. Chem.* **1987**, *323*, 371. (i) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263.

[12] Macomber, D. W.; Madhukar, P.; Rogers, R. D. *Organometallics* **1989**, *8*, 1275.

[13] Macomber, D. W.; Hung, M. H. *J. Organomet. Chem.* **1989**, *366*, 147.

[14] Macomber, D. W.; Liang, M.; Madhukar, P.; Verma, A. G. *J. Organomet. Chem.* **1989**, *361*, 187 and references therein.

[15] Macomber, D. W.; Hung, M. H.; Liang, M.; Verma, A. G.; Madhukar, P. *Macromolecules* **1988**, *21*, 1187.

[16] For that matter, **2z** could not be made to undergo polymerization under a variety of conditions (anionic or free radical).[17]

[17] Macomber, D. W.; Madhukar, P. Unpublished findings.

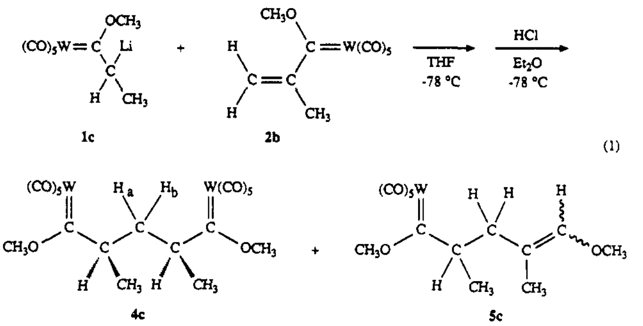
[18] A series of (μ-bis(aminocarbene))dichromium complexes have been prepared by Fischer and co-workers by treating (alkoxycarbene)chromium complexes with various diamines.[5a]

[19] Bergmann, E. D.; Ginsberg, D.; Pappo, R. *Org. React.* **1959**, *10*, 179.

[20] The vinyl ether derivatives **5**, which are in most cases more polar than the corresponding (μ-bis(carbene))dimetal complexes (**4**), could be separated from complexes **4** through column chromatography on silica gel.

[21] Reference 1, p 251.

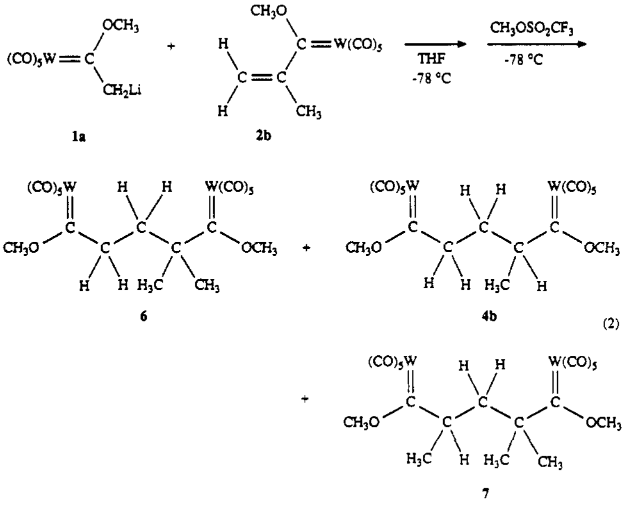
[22] Bösch, C.; Kumar, A.; Baumann, R.; Ernst, R. R.; Wüthrich, K. *J. Magn. Reson.* **1981**, *42*, 159.



(1)

action outlined in eq 1, but with $(CH_3)_3SiCl$ in place of HCl, resulted in the formation of **4c** (58%) and **5c** (16%). The proton source in the conversions of complexes **3** to **4** (Scheme I), when E–X is $(CH_3)_3SiCl$ (entries 1–3, 8, 16, 17, 19, 26 in Table I) is not presently known. We previously proposed[9] that α-trimethylsilyl (μ-bis(carbene))dimetal derivatives **4** ($R^5 = Si(CH_3)_3$) were formed as intermediates, which subsequently underwent protodesilylation[23] to complexes **4** ($R^5 = H$) upon chromatographic purification.[24] Although monomeric α-(trimethylsilyl)alkyl Fischer carbene complexes have been prepared[12,23] or proposed as intermediates in reactions,[26] we have not, as yet, been successful in isolating the proposed intermediates **4** ($R^5 = Si(CH_3)_3$). Furthermore, when monomeric α-lithio carbene anions $(CO)_5M[C(OCH_3)CH_2Li]$ (**1a**, M = W; **1p**, M = Cr) were treated with $(CH_3)_3SiCl$, under the same conditions described in Scheme I, the expected α-(trimethylsilyl)alkylcarbene complexes $(CO)_5M[C(OCH_3)CH_2Si(CH_3)_3]$ (M = Cr, W) were not obtained. The products from this reaction, which are both sensitive to temperature and silica gel chromatography, have not been characterized. Taken altogether, the above findings suggest that α-trimethylsilyl (μ-bis(carbene)dimetal derivatives **4** ($R^5 = Si(CH_3)_3$) are not intermediates in the conversions of **3** to **4**.

It was also found, when $CH_3OSO_2CF_3$ was employed as the electrophilic quenching agent, that dialkylation[5c,11c,d,e,i] of anions **3** occurred in several cases. In one example, treatment of **1a** with **2b**, followed by 1 equiv of $CH_3OSO_2CF_3$, resulted in the formation of complexes **6**, **4b**, and **7** (eq 2) in the approximate respective ratios of 2:1:1.



(2)

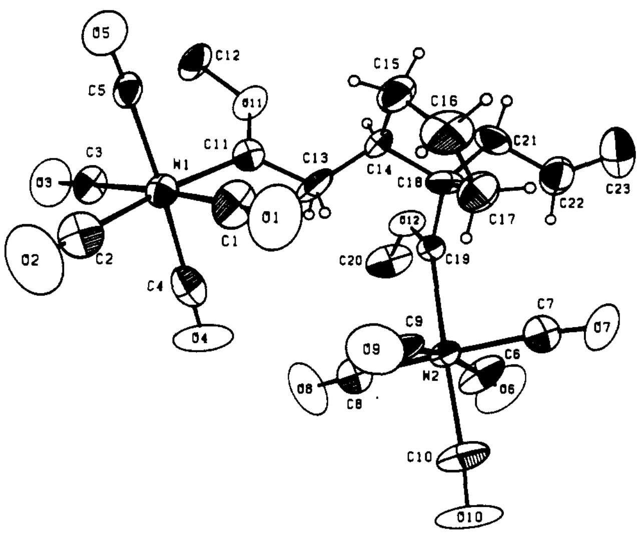


Figure 1. Molecular structure and atom-labeling scheme for **4j** with the atoms represented by their 50% probability ellipsoids for thermal motion.

Complexes **6**, **4b**, and **7** could not be separated by chromatography, and therefore, their structural assignments and relative ratios of formation were determined only by ^1H NMR spectroscopy.

Complexes **4a–z** were all isolated as yellow or yellow-orange crystalline solids, except **4f**, **4m** , **4n**, **4w**, and **4y**, which were obtained as yellow-orange oils. The structures of compounds (**4a–z**) were easily assigned through spectroscopic (^1H and ^{13}C NMR) (Table II) and analytical (Table III) methods. It was also observed that the (μ-bis(alkoxycarbene))dimetal complexes (**4a–t**) exhibited the following thermal stability trend: $M^1 = M^2 = W$ (**4a–o**) > $M^1 = Cr$, $M^2 = W$ (**4s,t**) > $M^1 = M^2 = Cr$ (**4p–r**). Moreover, all the (μ-bis(carbene))ditungsten complexes containing a dimethylamino heteroatom group (i.e. $X^1R = N(CH_3)_2$, **4u–y**) exhibited greater thermal stability than their alkoxy counterparts (i.e. $X^1R = OCH_3$, OCH_2Ph, OCH_2CH_2Ph; **4a–o**). These two observations are consistent with similar findings for monomeric Fischer carbene complexes.[27]

In the reactions described in Scheme I, complexes **4c–f,h,j–l,r–t,w,x**, which each have two asymmetric carbon centers, were always formed as one major diastereomer. We believe the generation of these two new asymmetric centers in complexes **4** is a result of a diastereoselective quenching[28] of anions **3** with the electrophilic reagents E–X. The formation of one diastereomer for the cyclic compounds **4h,j–l,r,x** is probably due to steric factors, wherein reagents E–X attack the respective anions **3h,j–l,r,x** from the sterically less hindered side. This process, which is illustrated for the reaction of anions **3j** and **3x** with $CH_2{=}CHCH_2Br$ in eq 3, results in the formation of complexes **4j** and **4x**, respectively. Moreover, the stereochemical assignments of complexes **4j** and **4x** were confirmed by X-ray crystallography (vide infra).

The molecular structures and atom-labeling schemes for complexes **4j** and **4x** are presented in Figures 1 and 2, respectively, whereas selected bond distances and angles for these two structures are summarized in Table IV. The overall structures of **4j** and **4x**, which both have the two

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[23] Connor, J. A.; Jones, E. M. *J. Organomet. Chem.* **1973**, *60*, 77.

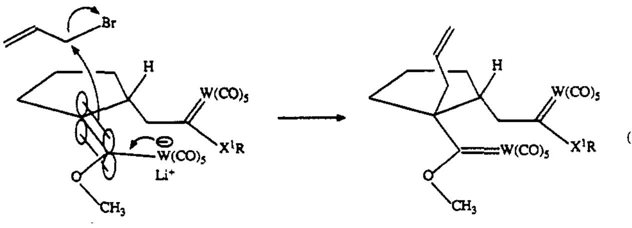
[24] Another possible proton source, as suggested by a referee, would be the ring opening of THF by $(CH_3)_3SiCl$. Although the ring opening of THF with $(CH_3)_3SiCl$ can occur under very severe conditions to generate protons,[25] it seems an unlikely possibility under the reaction conditions described in Scheme I.

[25] Kawakami, Y.; Yamashita, Y. *Synth. Commun.* **1982**, *12*, 253.

[26] Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1986**, 514.

[27] (a) Reference 1, p 6. (b) Fischer, E. O.; Leupold M. *Chem. Ber.* **1972**, *105*, 599.

[28] For examples of related diastereoselective alkylations of stabilized carbanions, see: (a) Mulzer, J.; Chucholowski, A.; Lammer, O.; Jibril, I.; Huttner, G. *J. Chem. Soc., Chem. Commun.* **1983**, 869. (b) Nógrádi, M. *Stereoselective Synthesis*; VCH: Weinheim, 1987; pp 244–248.



(3)

3j $X^1R = OCH_3$
3x $X^1R = N(CH_3)_2$

4j $X^1R = OCH_3$
4x $X^1R = N(CH_3)_2$

large tungsten carbene fragments on the same side of the cyclopentane ring, are almost identical and differ only in the heteroatom substituent (X^1R). The W–C(alkoxycarbene) distances in **4j** (W(1)–C(11), 2.10 (2) Å; W(2)–C(19), 2.16 (2) Å and in **4x** (W(2)–C(18), 2.180 (6) Å) are similar to each other and are typical of other (alkoxycarbene)tungsten structures;[5h,29] this includes the only other structurally characterized (μ-bis(carbene))ditungsten complex *o*-$(CO)_5W[C(OC_2H_5)CH_2C_6H_4CH_2C(OC_2H_5)]W(CO)_5$.[51] Likewise, the W–C(aminocarbene) distance (W(1)–C(11)) of 2.274 (6) Å in **4x** is also typical of (aminocarbene)tungsten structures.[12,30] The longer W–C(carbene) distances associated with aminocarbene fragments (i.e. **4x**, W(1)–C(11)) as compared to alkoxycarbene fragments (i.e. **4j**, W(1)–C(11) and W(2)–C(19) and **4x**, W(2)–C(18)) is widely recognized and has been ascribed to the better π-donating ability of an amino group over an alkoxy group.[31] The bond angles about the carbene carbons in **4j** (C(11), C(19)) and in **4x** (C(11), C(18)) are also similar to other (alkoxycarbene)tungsten and (aminocarbene)tungsten complexes. The only striking structural difference between complexes **4j** and **4x** is the orientations of the tungsten carbene fragments with respect to the cyclopentane rings. For example, 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° for **4j**, whereas for the corresponding planes in **4x**, C(12), C(11), W(1), N and C(17), C(18), W(2), O(11), it is 59.6°.

The acyclic (μ-bis(carbene))dimetal complexes **4c–f,s,t,w** were also formed as one major diastereomer in the reactions described in Scheme I. For example, *meso*-**4c** (eq 1) was formed diastereoselectively (>90%), as determined by ¹H NMR spectroscopy, in the reaction between **1c** and **2b** and $(CH_3)_3SiCl$ as the electrophilic quenching reagent. The meso stereochemistry of **4c** was easily established by ¹H NMR spectroscopy;[32] the diastereotopic protons H_a and H_b each appeared as clean doublets of triplets at 400 MHz. It was also found that complex **4s**, which is the heterodimetallic analogue of **4c** (i.e. M = Cr instead of W), was formed exclusively as the meso isomer. The structural assignment of **4s** as the meso isomer was confirmed by X-ray crystallography.

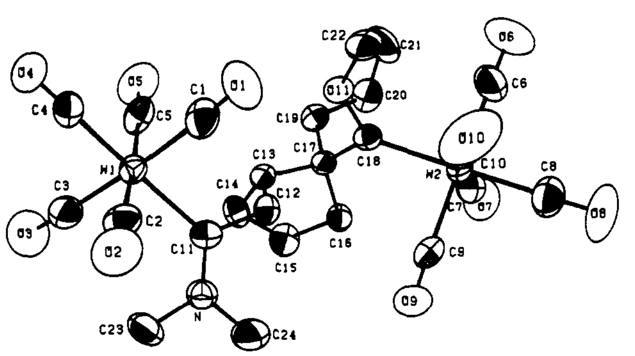


Figure 2. Molecular structure and atom-labeling scheme for **4x** with the atoms represented by their 50% probability ellipsoids for thermal motion.

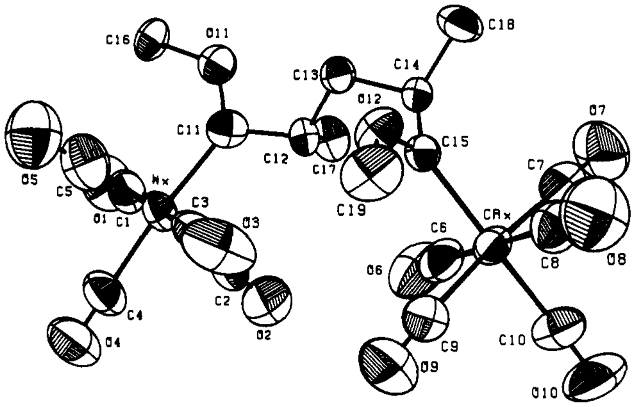


Figure 3. Molecular structure and atom-labeling scheme for **4s** with the atoms represented by their 50% probability ellipsoids for thermal motion.

The molecular structure and atom-labeling scheme for *meso*-**4s**, which is the first structurally characterized (μ-bis(carbene))heterodimetal complex, is presented in Figure 3, whereas bond distances and angles are summarized in Table IV. Although the metal positions (W and Cr) are disordered in this structure (see Experimental Section for refinement details), it is still evident (Figure 3) that complex **4s** possesses the meso stereochemistry. Moreover, the torsion angles associated with the carbon chain, which contains the two asymmetric carbons C(12) and C(14), are quite similar. For example, the torsion angles of the C(13)–C(12) bond are C(14)–C(13)–C(12)–C(11) = 164.6° and C(14)–C(13)–C(12)–C(17) = −77.3°, whereas for the C(13)–C(14) bond they are C(12)–C(13)–C(14)–C(15) = −72.7° and C(12)–C(13)–C(14)–C(18) = 168.7°.

Experimental Section

General Data. All reactions were conducted under an inert argon or nitrogen atmosphere. Hexane, methylene chloride, and chlorotrimethylsilane were distilled from CaH_2 under nitrogen. Diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Flash chromatography[33] was conducted on E. Merck silica gel 60 (40–63 μm). The starting (alkylcarbene)chromium and (alkylcarbene)tungsten complexes $(CO)_5W[C(OCH_3)CH_3]$,[34] $(CO)_5W[C(OCH_3)CH_2CH_3]$,[34] $(CO)_5Cr[C(OCH_3)CH_3]$,[35] $(CO)_5W[C(N(CH_3)_2)CH_3]$,[12] and $(CO)_5W[C(N(CH_3)_2)CH_2Si(CH_3)_3]$[12] were prepared according to literature procedures. $(CO)_5W[C(OCH_3)CH_2CH_2CH_2CH_3]$ and $(CO)_5Cr$-

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[29] (a) Daran, J.; Jeannin, Y. *Acta Crystallogr.* **1980**, *B36*, 1392. (b) Fischer, E. O.; Gammel F. J.; Besenhard, J. O.; Frank, A.; Neugebauer, D. *J. Organomet. Chem.* **1980**, *191*, 261. (c) Toledano, C. A.; Levisalles, J.; Rudler, M.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Organomet. Chem.* **1982**, *228*, C7. (d) Toledano, C. A.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 547. (e) Parlier, A.; Rudler, M.; Rudler, H.; Daran, J. C. *J. Organomet. Chem.* **1987**, *323*, 353. (f) Toledano, C. A.; Parlier, A.; Rudler, H.; Rudler, M.; Daran, J. C.; Knobler, C.; Jeannin, Y. *Ibid.* **1987**, *328*, 357. (g) Macomber, D. W.; Liang, M.; Rogers, R. D. Unpublished results

[30] (a) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417. (b) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *Ibid.* **1984**, *106*, 3754. (c) Parlier, A.; Rudler, H.; Daran, J. C.; Alvarez, C.; Delgado Reyes, F. *J. Organomet. Chem.* **1987**, *327*, 339. (d) Dötz, K. H.; Noack, R.; Müller, G. *J. Chem. Soc., Chem. Commun.* **1988**, 302.

[31] Reference 1, pp 74–111.

[32] Bovey, F. A. *Chain Structure and Conformation of Macromolecules*; Academic: New York, 1982; pp 44–46.

[33] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

[34] Macomber, D. W. *Organometallics* **1984**, *3*, 1589 and references therein.

[35] Hegedus, J. S.; McGuire, M. A.; Schultze, L. M. *Org. Synth.* **1987**, *65*, 140.

Table II. ^{1}H and ^{13}C{^{1}H} NMR Spectral Data for Complexes 4a–z

4	^{1}H NMR^a chemical shifts, δ (multiplicity, coupling constant(s) in Hz, relative intensity)	^{13}C{^{1}H} NMR^a chemical shifts, δ
a	4.60 (s, 6 H), 3.18 (t, 8, 4 H), 1.72 (p, 7, 2 H)	335.35, 203.00, 197.11, 70.53, 63.58, 22.66
b	4.59 (s, 3 H), 4.58 (s, 3 H), 4.06 (sextet, 7, 1 H), 3.21 (m, 2 H), 1.78 (m, 1 H), 1.44 (m, 1 H), 1.01 (d, 7, 3 H)	341.00, 335.11, 203.00, 197.11, 70.76, 70.51, 66.09, 62.56, 29.43, 16.47
c	4.58 (s, 6 H), 4.02 (sextet, 6.7, 2 H), 1.95 (dt, 13.9, 6.9, 1 H), 1.12 (dt, 13.8, 7.0, 1 H), 1.06 (d, 6.7, 6 H)	341.08, 202.70, 197.11, 70.84, 65.00, 36.05, 17.60
d	5.48 (m, 1 H), 4.90 (m, 2 H), 4.81 (s, 3 H), 4.63 (s, 3 H), 3.54 (dd, 18, 10, 1 H), 2.79 (m, 1 H), 2.55 (dd, 18, 4, 1 H), 2.42 (dd, 18, 8, 1 H), 2.08 (dd, 18, 8, 1 H), 1.64 (s, 3 H), 0.80 (d, 7 3 H)	353.76, 337.32, 203.02, 202.05, 197.50, 197.19, 133.48, 118.17, 70.85, 70.47, 67.05, 66.53, 43.67, 39.89, 23.38, 15.22
e	5.58 (m, 1 H), 5.03 (m, 2 H), 4.75 (s, 3 H), 4.61 (s, 3 H), 3.94 (p, 6, 1 H), 2.25 (dd, 14, 7, 1 H) 2.04 (dd, 13, 8, 1 H), 1.87 (dd, 14, 8, 1 H), 1.76 (dd, 14, 6, 1 H), 1.63 (s, 3 H), 1.49–1.32 (m, 4 H), 0.88 (t, 8, 3 H)	349.73, 341.16, 202.29, 201.68, 197.59, 197.28, 132.79, 118.91, 70.61, 70.52, 69.33, 64.31, 46.39, 41.00, 36.64, 26.83, 21.43, 14.61
f	7.25 (m, 3 H), 7.00 (m, 2 H), 4.68 (s, 3 H), 4.55 (s, 3 H), 3.92 (m, 1 H), 2.85 (d, 14, 1 H), 2.52 (d, 14, 1 H), 1.87 (dd, 14, 8, 1 H), 1.76 (dd, 14, 5, 1 H), 1.63 (s, 3 H), 1.49–1.32 (m, 4 H) 0.88 (t, 8, 3 H)	350.28, 341.78, 222.43, 216.21, 201.74, 197.47, 136.16, 130.65, 128.06, 126.83, 70.25, 68.01, 67.97, 65.04, 48.08, 41.63, 37.10, 26.85, 21.41, 14.65
g	4.75 (s, 6 H), 2.30 (s, 2 H), 1.18 (s, 12 H)	348.70, 201.49, 197.57, 70.82, 61.95, 51.08, 30.76
h	4.64 (s, 3 H), 4.62 (s, 3 H), 3.37 (dd, 18, 8, 1 H), 3.15 (dd, 18, 6, 1 H), 2.13 (m, 1 H), 1.90–1.28 (m, 6 H)	342.80, 334.98, 203.23, 202.93, 197.32, 197.25, 74.68, 70.73, 70.33, 66.58, 42.69, 32.69, 30.00, 24.23
i	5.70 (m, 1 H), 5.02 (m, 2 H), 4.87 (s, 3 H), 4.57 (s, 3 H), 4.14 (m, 1 H), 2.56 (m, 3 H), 2.26 (m, 2 H), 1.81–1.60 (m, 4 H), 0.83 (d, 8, 3 H)	351.58, 340.72, 202.03, 201.88, 197.38, 197.15, 133.42, 118.34, 76.53, 70.59, 70.29, 66.40, 49.30, 45.73, 38.73, 25.57, 22.51, 12.69
j	5.67 (m, 1 H), 5.02 (m, 2 H), 4.79 (s, 3 H), 4.63 (s, 3 H), 3.37 (m, 1 H), 2.72 (m, 2 H), 2.61 (m, 1 H), 2.38 (m, 1 H), 2.31 (m, 1 H), 2.19 (m, 1 H), 1.95 (m, 1 H), 1.78 (m, 2 H), 1.32 (m, 1 H)	353.50, 336.97, 202.88, 202.56, 197.38, 197.18, 133.37, 118.14, 76.59, 70.47, 70.40, 65.64, 47.30, 43.76, 35.63, 28.17, 20.70
k	5.57 (m, 1 H), 5.01 (m, 2 H), 4.84 (s, 3 H), 4.63 (s, 3 H), 3.78 (m, 1 H), 2.78 (m, 1 H), 2.52 (m, 3 H), 2.29 (m, 2 H), 1.76 (m, 1 H), 1.53 (m, 5 H)	357.83, 337.15, 202.68, 202.60, 197.51, 197.19, 133.04, 118.05, 70.81, 70.50, 65.53, 63.65, 40.58, 40.42, 32.40, 25.69, 21.98, 19.72
l	4.64 (s, 6 H), 4.00 (m, 1 H), 3.66 (dd, 15, 7, 1 H), 2.68 (m, 2 H), 1.65–1.25 (m, 12 H)	342.08, 337.51, 202.87, 202.67, 197.26, 197.19, 75.65, 70.85, 70.44, 69.14, 39.52, 29.33, 27.10, 26.85, 26.32, 25.42, 24.92
m	7.45 (m, 5 H), 5.80 (s, 2 H), 5.57 (m, 1 H), 5.03 (m, 2 H), 4.71 (s, 3 H), 3.08 (t, 8, 2 H), 2.40 (dd, 13, 8, 1 H), 2.14 (dd, 13, 8, 1 H), 1.90 (m, 1 H), 1.60 (m, 1 H), 1.53 (s, 3 H)	351.78, 332.97, 202.84, 201.92, 197.37, 197.08, 133.74, 133.08, 129.35, 128.99, 128.42, 118.64, 86.38, 70.39, 63.66, 60.38, 45.30, 36.41, 26.54
n	7.22–7.38 (m, 5 H), 5.55 (m, 1 H), 5.10 (m, 2 H), 5.00 (m, 2 H), 4.72 (s, 3 H), 3.22 (t, 7, 2 H), 3.10 (m, 2 H), 2.37 (dd, 13, 7, 1 H), 2.11 (dd, 13, 7, 1 H), 1.82 (m, 1 H), 1.53 (s, 3 H), 1.45 (m, 1 H)	351.88, 332.98, 202.86, 201.88, 197.37, 197.07, 136.65, 133.09, 128.87, 128.79, 127.07, 118.61, 84.48, 70.92, 63.60, 60.23, 45.45, 36.35, 35.49, 26.84
o	7.50–7.30 (m, 10 H), 5.95 (d, 12, 1 H), 5.89 (d, 12, 1 H), 5.77 (s, 2 H), 5.54 (m, 1 H), 4.93 (m, 2 H), 3.20 (m, 1 H), 3.00 (m, 1 H), 2.36 (dd, 13, 8, 1 H), 2.10 (dd, 13, 8, 1 H), 1.89 (m, 1 H), 1.63 (m, 1 H), 1.55 (s, 3 H)	348.84, 332.57, 202.84, 201.85, 197.43, 197.05, 133.69, 133.42, 129.48, 129.28, 129.05, 128.97, 128.78, 128.31, 87.16, 86.63, 63.67, 60.41, 45.17, 36.53, 26.49
p^b	3.96 (s, 6 H), 2.85 (p, 7, 4 H), 1.25 (p, 7, 2 H)	361.67, 224.50, 216.58, 67.26, 61.40, 22.51
q^c	4.79 (s, 3 H), 4.77 (s, 3 H), 4.03 (sextet, 7, 1 H), 3.29 (m, 2 H), 1.72 (m, 1 H), 1.35 (m, 1 H), 0.99 (d, 7, 3 H)	366.84, 361.44, 223.13, 216.56, 216.51, 67.61, 67.20, 64.33, 60.38, 29.56, 16.34
r	5.61 (m, 1 H), 5.01 (m, 2 H), 4.97 (s, 3 H), 4.80 (s, 3 H), 3.51 (dd, 15, 12, 1 H), 2.90 (m, 1 H), 2.72 (d, 15, 1 H), 2.63 (m, 1 H), 2.42 (m, 1 H), 2.33 (dd, 13, 7, 1 H), 2.15 (dd, 13, 7, 1 H), 1.96 (m, 1 H), 1.73 (m, 2 H), 1.23 (m, 1 H)	378.89, 363.53, 222.94, 222.84, 216.37, 216.27, 133.40, 118.05, 67.84, 67.72, 64.25, 47.39, 34.41, 28.19, 20.91
s^b	4.01 (s, 3 H), 3.92 (m, 2 H), 3.86 (s, 3 H), 1.68 (m, 2 H), 0.81 (d, 7, 3 H), 0.77 (d, 7, 3 H)	366.45, 340.94, 223.01, 216.48, 202.90, 197.34, 70.44, 67.75, 64.67, 63.33, 36.16, 17.57, 17.38
t^b	5.46 (m, 1 H), 4.94 (m, 2 H), 4.12 (s, 3 H), 4.09 (s, 3 H), 4.03 (m, 1 H), 2.09 (m, 1 H), 1.87 (m, 1 H), 1.68 (m, 2 H), 1.58 (s, 3 H), 1.32–1.10 (m, 4 H), 0.85 (t, 7, 3 H)	366.99, 349.64, 222.78, 216.65, 201.98, 197.94, 132.90, 118.97, 70.11, 68.19, 67.60, 64.42, 46.61, 41.20, 36.98, 26.73, 21.71, 14.72
u	4.63 (s, 3 H), 3.78 (s, 3 H), 3.32 (t, 8, 2 H), 3.29 (s, 3 H), 3.14 (t, 8, 2 H), 1.64 (p, 8, 2 H)	334.66, 258.39, 202.92, 202.77, 198.80, 197.08, 70.55, 63.75, 56.04, 52.90, 40.74, 21.51
v	5.63 (m, 1 H), 5.05 (m, 2 H), 4.81 (s, 3 H), 3.79 (s, 3 H), 3.28 (s, 3 H), 3.07 (m, 1 H), 2.95 (m, 1 H), 2.49 (dd, 13, 7, 1 H), 2.17 (dd, 13, 7, 1 H), 1.92 (m, 1 H), 1.73 (s, 3 H), 1.42 (m, 1 H)	352.06, 259.47, 202.40, 201.82, 198.85, 197.39, 133.00, 118.79, 70.95, 63.98, 56.22, 48.88, 45.76, 40.67, 35.11, 27.08
w	5.47 (m, 1 H), 5.04 (m, 2 H), 4.76 (s, 3 H), 3.77 (s, 3 H), 4.01 (dd, 8, 3, 1 H), 3.28 (s, 3 H), 2.46 (d, 7, 2 H), 2.16 (dd, 14, 3, 1 H), 2.07 (dd, 14, 8, 1 H), 1.47 (s, 3 H), 0.28 (s, 9 H)	350.01, 267.22, 201.47, 199.87, 198.85, 133.14, 118.58, 71.09, 66.03, 56.28, 55.30, 45.22, 43.76, 40.69, 25.43, 0.65
x	5.72 (m, 1 H), 5.03 (dd, 17, 10, 2 H), 4.80 (s, 3 H), 3.86 (s, 3 H), 3.34 (s, 3 H), 3.05 (m, 1 H), 2.93 (t, 12, 1 H), 2.79 (m, 1 H), 2.62 (dd, 12, 4, 1 H), 2.44 (dd, 13, 7, 1 H), 2.25 (dd, 13, 7, 1 H), 1.86 (m, 3 H), 1.11 (m, 1 H)	353.08, 260.55, 202.41, 202.20, 198.99, 197.53, 133.23, 118.25, 77.15, 70.61, 56.98, 51.80, 49.23, 43.70, 42.61, 36.27, 26.59, 21.34
y	7.31–7.21 (m, 5 H), 6.35 (d, 15.7, 1 H), 6.04 (m, 1 H), 4.82 (s, 3 H), 3.79 (s, 3 H), 3.27 (s, 3 H), 3.10 (m, 1 H), 2.97 (m, 1 H), 2.61 (dd, 13.7, 7.2, 1 H), 2.35 (dd, 13.6, 7.3, 1 H), 2.05 (m, 1 H), 1.80 (s, 3 H), 1.45 (m, 1 H)	352.06, 259.19, 202.40, 201.81, 198.85, 197.31, 136.88, 133.84, 128.52, 127.40, 126.05, 124.42, 70.93, 64.64, 56.14, 48.91, 45.17, 40.64, 35.14, 27.16
z	3.79 (s, 3 H), 3.35 (s, 3 H), 3.26 (t, 8, 4 H), 1.55 (p, 8, 2 H)	257.08, 202.44, 198.99, 56.19, 53.43, 41.11, 19.93

^{a} CDCl$_3$ solvent with (CH$_3$)$_4$Si as internal standard, except where noted. ^{b} C$_6$D$_6$ solvent for both ^{1}H and ^{13}C NMR spectroscopy. ^{c} CDCl$_3$ solvent for ^{1}H NMR spectroscopy, C$_6$D$_6$ solvent for ^{13}C NMR spectroscopy.

[C(OCH$_3$)CH$_2$CH$_2$CH$_2$CH$_3$] were prepared, according to standard procedures,[34,35] by treating W(CO)$_6$ and Cr(CO)$_6$ with *n*-BuLi (Aldrich Chemical Co.), respectively, followed by methylation with trimethyloxonium tetrafluoroborate. (CO)$_5$W[C(OCH$_3$)CH(CH$_3$)$_2$] was prepared by two successive alkylations of (CO)$_5$W[C(OCH$_3$)CH$_3$] using *n*-BuLi followed by CH$_3$OSO$_2$CF$_3$ (Aldrich Chemical Co.). (CO)$_5$Cr[C(OCH$_3$)CH$_2$CH$_3$][11i] was prepared according to the procedure developed for the tungsten analogue (CO)$_5$W[C(OCH$_3$)CH$_2$CH$_3$].[34] (CO)$_5$W[C(O)CH$_3$]$^-$N(CH$_3$)$_4$$^+$ was prepared in 91% yield according to the literature procedure.[36] Complexes **2a**, **2b**,[30d] **2d**, **2h**,[37] **2k**, and **2l** were prepared according

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Table III. Physical and Analytical Data for Complexes 4a–z

		anal. data (calcd)			
4	mp, °C	mol formula	% C	% H	% N
a	85 dec	$C_{17}H_{12}O_{12}W_2$	26.46 (26.31)	1.58 (1.56)	
b	48 dec	$C_{18}H_{14}O_{12}W_2$	27.39 (27.36)	1.77 (1.79)	
c	88 dec	$C_{19}H_{16}O_{12}W_2$	28.52 (28.38)	1.90 (2.01)	
d	75 dec	$C_{22}H_{20}O_{12}W_2$	31.22 (31.30)	2.23 (2.39)	
e	63 dec	$C_{24}H_{24}O_{12}W_2$	33.01 (33.05)	2.80 (2.77)	
f[b]	*a*	$C_{28}H_{33}O_{12}W_2$	37.54 (36.47)	3.07 (2.48)	
g	*c*	$C_{21}H_{20}O_{12}W_2$	30.09 (30.31)	2.40 (2.42)	
h	*c*	$C_{20}H_{16}O_{12}W_2$	29.52 (29.44)	1.94 (1.98)	
i	*c*	$C_{24}H_{22}O_{12}W_2$	33.18 (33.13)	2.68 (2.55)	
j	*c*	$C_{23}H_{20}O_{12}W_2$	32.18 (32.27)	2.42 (2.35)	
k	*c*	$C_{24}H_{22}O_{12}W_2$	33.17 (33.13)	2.44 (2.55)	
l	*c*	$C_{22}H_{22}O_{12}W_2$	32.01 (32.19)	2.66 (2.59)	
m	*a*	$C_{27}H_{22}O_{12}W_2$	35.53 (35.79)	2.33 (2.45)	
n	*a*	$C_{28}H_{24}O_{12}W_2$	36.72 (36.55)	2.53 (2.63)	
o	97	$C_{33}H_{26}O_{12}W_2$	40.28 (40.35)	2.67 (2.66)	
p[d]	75 dec	$C_{17}H_{12}Cr_2O_{12}$	40.56 (39.86)	2.41 (2.36)	
q	*c*	$C_{18}H_{14}Cr_2O_{12}$	41.18 (41.08)	2.57 (2.68)	
r	79 dec	$C_{23}H_{20}Cr_2O_{12}$	46.67 (46.63)	3.28 (3.40)	
s	80 dec	$C_{19}H_{16}CrO_{12}W$	33.67 (33.95)	2.49 (2.40)	
t[d]	*c*	$C_{24}H_{24}CrO_{12}W$	40.04 (38.94)	3.58 (3.27)	
u	87–88	$C_{18}H_{15}NO_{11}W_2$	27.54 (27.40)	1.87 (1.92)	1.72 (1.78)
v	84–85	$C_{22}H_{21}NO_{11}W_2$	31.24 (31.34)	2.66 (2.51)	1.64 (1.66)
w[b]	*a*	$C_{25}H_{29}NO_{11}SiW_2$	33.99 (32.81)	3.33 (3.19)	1.62 (1.53)
x	141 dec	$C_{24}H_{23}NO_{11}W_2$	33.11 (33.17)	2.67 (2.67)	1.65 (1.61)
y	*a*	$C_{28}H_{25}NO_{11}W_2$	36.75 (36.58)	2.65 (2.74)	1.49 (1.52)
z	146 dec	$C_{19}H_{18}N_2O_{10}W_2$	28.51 (28.45)	2.21 (2.26)	3.38 (3.50)

[a] Liquid. [b] The carbon and hydrogen analyses exceed the acceptable limits because attempted distillation led to decomposition and attempted low-temperature crystallization was unsuccessful. [c] Not determined. [d] Moderately thermally sensitive.

Table IV. Selected Bond Lengths (Å) and Angles (deg) for 4j, 4x, and 4s

bond distances		bond angles	
		4j	
W(1)–C(11)	2.10 (2)	W(1)–C(11)–O(11)	128 (1)
W(2)–C(19)	2.16 (2)	W(1)–C(11)–C(13)	129 (2)
O(11)–C(11)	1.42 (2)	O(11)–C(11)–C(13)	103 (2)
O(12)–C(19)	1.34 (2)	W(2)–C(19)–O(12)	128 (1)
C(11)–C(13)	1.43 (3)	W(2)–C(19)–C(18)	131 (1)
C(18)–C(19)	1.58 (3)	O(12)–C(19)–C(18)	102 (1)
		4x	
W(1)–C(11)	2.274 (6)	W(1)–C(11)–N	126.6 (5)
W(2)–C(18)	2.180 (6)	W(1)–C(11)–C(12)	118.7 (4)
N–C(11)	1.333 (6)	N–C(11)–C(12)	114.4 (6)
O(11)–C(18)	1.326 (6)	W(2)–C(18)–O(11)	128.2 (4)
C(11)–C(12)	1.520 (8)	W(2)–C(18)–C(17)	129.2 (4)
C(17)–C(18)	1.547 (7)	O(11)–C(18)–C(17)	102.5 (5)
C(12)–C(13)	1.540 (7)		
		4s	
W_x–C(11)	2.12 (1)	W_x–C(11)–O(11)	131.5 (8)
O(11)–C(11)	1.34 (1)	W_x–C(11)–C(12)	122.5 (8)
C(11)–C(12)	1.54 (1)	O(11)–C(11)–C(12)	106.0 (9)
Cr_x–C(15)	2.09 (1)	Cr_x–C(15)–O(12)	131.0 (7)
O(12)–C(15)	1.31 (1)	Cr_x–C(15)–C(14)	122.1 (7)
C(14)–C(15)	1.54 (1)	O(12)–C(15)–C(14)	106.9 (8)
C(12)–C(13)	1.58 (1)		
C(13)–C(14)	1.56 (1)		

to literature procedures.[38] Complex **2p** was prepared according to a procedure developed for the tungsten analogue **2a**,[38] starting from 1-bromo-1-(trimethylsilyl)ethylene.[39] Complexes **2q**,[40] **2r**,[37,38] and **2z**[12] were prepared according to literature procedures.

^1H and ^{13}C NMR spectra were recorded on a Bruker WM-400 instrument operating at 400.1 and 100.6 MHz, respectively. Elemental analyses were performed by Microlytics, South Deerfield, MA.

X-ray Data Collection, Structure Determination, and Refinement for Compound 4j. A yellow-orange transparent crystal of the title compound was mounted on a pin and transferred to the goniometer. The space group was determined to be centric *Pbca* from the systematic absences. A summary of data collection parameters is given in Table V.

The hydrogen atoms (except those bonded to C(12), C(20), and C(23)) 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. The eight remaining hydrogen atoms could not be located nor refined as rigid groups and were therefore not included in the final refinement. Carbon atoms C(2), C(7), C(8), and C(11) could not be refined anisotropically. Refinement of the other non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.064$ and $R_w = 0.066$. The final values of the positional parameters are provided in the supplementary material.

X-ray Data Collection, Structure Determination, and Refinement for Compound 4s. A yellow single crystal of the title compound was mounted in a thin-walled glass capillary under argon and transferred to the goniometer. The space group was determined to be centric *Pbca* from the systematic absences. A summary of data collection parameters is given in Table V.

The heavy-atom positions were located by utilizing the direct-methods program MULTAN.[41] It was immediately obvious that the metal positions were disordered, each unique site in the molecule occupied by a certain percentage of both Cr and W. Site W was determined to be 67% W and 33% Cr, site Cr was 67% Cr and 33% W. The metal sites were refined as such, and the occupancy factor was determined by refinement such that the total occupancy of each site and the total occupancy of each metal was 100%. As a result, the CO positions have high thermal parameters (a consequence of small differences in M–C bonding parameters for the two metals).

Least-squares refinement with the disorder model and isotropic thermal parameters led to $R = 0.083$. Due to the disorder, the hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.044$ and $R_w = 0.044$. The final values of the positional parameters are provided in the supplementary material.

X-ray Data Collection, Structure Determination, and Refinement for Compound 4x. A transparent yellow crystal of the title compound was mounted in a thin-walled glass capillary and transferred to the goniometer. The space group was determined to be the centric $P2_1/c$ from the systematic absences. A summary of data collection parameters is given in Table V.

Least-squares refinement with isotropic thermal parameters led to $R = 0.061$. The geometrically constrained 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. The methyl hydrogen atoms were refined as rigid groups with C–H fixed at 0.95 Å. The remaining hydrogen atoms were not included

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Table V. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	4j	**4s**	**4x**
color/shape	yellow-orange/parallelepiped	yellow/parallelepiped	yellow/parallelepiped
mol wt	856.1	672.17	896.1
space group	*Pcba*	*Pbca*	$P2_1/c$
temp, °C	20	20	20
cell constants[a]			
a, Å	11.931 (6)	14.083 (7)	13.931 (3)
b, Å	14.404 (8)	18.032 (3)	12.729 (2)
c, Å	31.496 (9)	19.380 (5)	16.032 (2)
β, deg			93.47 (2)
cell vol, Å^3	5412.7	4921.4	2838
formula units/unit cell	8	8	4
D(calcd), g cm^{-3}	2.10	1.81	2.03
μ(calcd), cm^{-1}	81.8	49.4	78.0
diffractometer/scan	Enraf-Nonius CAD-4/θ–2θ	Enraf-Nonius CAD-4/θ–2θ	Enraf-Nonius CAD-4/θ–2θ
λ(Mo Kα radiatn, graphite monochromator), Å	0.71073	0.71073	0.71073
range of rel transm factors	61%/94%	62%/100%	75%/100%
max cryst dimens, mm	0.15 × 0.20 × 0.38	0.25 × 0.28 × 0.40	0.13 × 0.20 × 0.40
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
standard reflcns	10,0,0; 060; 0,0,22	600; 080; 0,0,14	11,0,0; 0,10,0; 008
decay of stds	±2.4%	±4%	±2%
reflcns measd	5279	4784	5437
2θ range, deg	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
range of *hkl*	+14,+17,+37	+16,+21,+23	+16,+15,±19
reflcns obsd $[F_o \ge 5\sigma(F_o)]$[b]	2868	2471	4037
computer programs[c]	SHELX[43]	SHELX[43]	SHELX[43]
struct soln	heavy-atom techniques	MULTAN[41]	MULTAN[41]
no. of params varied	314	299	352
weights	$[\sigma(F_o)^2 + 0.00009F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00005F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00005F_o^2]^{-1}$
GOF	1.67	0.89	0.79
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.064	0.044	0.028
R_w	0.066	0.044	0.027
largest feature final diff map, e/Å^{-3}	2–3, ripple peaks near W(1), W(2)	0.8	0.5

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 16°$ (**4j**) and 20° (**4s**, **4x**). [b] Corrections: Lorentz–polarization and absorption (empirical, ψ scan). [c] Neutral-scattering factors and anomalous dispersion corrections from ref 44.

in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of $R = 0.028$ and $R_w = 0.027$. The final values of the positional parameters are provided in the supplementary material.

General Procedure for the Preparation of Complexes 4a–l. To a stirred solution of the appropriate (alkylcarbene)tungsten complex (3.0 mmol) in 30 mL of THF, which had been cooled to −78 °C, was added a precooled (−78 °C) solution of 2.5 M *n*-BuLi/hexane (1.2 mL, 3.0 mmol) in 5 mL of THF over a 10-min period. After the addition was complete, the solution was stirred at −78 °C for 1 h. Into this solution was added the appropriate α,β-unsaturated carbene complex **2** (3.0 mmol) in 5 mL of THF over the course of 20 min. The reaction mixture was stirred at −78 °C for 1 h, except where noted in Table I, and then quenched with a precooled (−78 °C) solution of the appropriate electrophilic reagent (E–X, Table I) (3.0 mmol) in 3 mL of THF. The resulting mixture was stirred for an additional 10 min, then warmed to 25 °C and diluted with 200 mL of hexane, and then passed through a column (30 × 3 cm) of silica gel. The column was then washed with an additional 500 mL of 10% methylene chloride/hexane and the solvent removed under vacuum. The resulting residue was chromatographed on silica gel by using 1% methylene chloride/hexane as the eluent. The fractions showing a single TLC spot and having an R_f value of ca. 0.3 (10% methylene chloride/hexane) were combined, and the solvent was removed under vacuum to afford the corresponding complex **4**. Crystallization from 5% methylene chloride/hexane at −5 °C gave complexes **4a–l** as yellow to yellow-orange crystals, except **4f**, which was obtained as a yellow-orange liquid.

$(CO)_5W[C(OCH_3)CH(CH_3)CH_2CH(CH_3)C(OCH_3)]W(CO)_5$ (4c) and $(CO)_5W[C(OCH_3)CH(CH_3)CH_2C(CH_3){=}CH(OCH_3)]$ (5c). Using $(CO)_5W[C(OCH_3)CH_2CH_3]$ (1.20 g), complex **2b** (1.23 g), and as the electrophilic quenching agent, chlorotrimethylsilane (0.38 mL), in the general procedure described above, afforded **4c** (1.41 g, 58%). Further elution of the column, after the isolation of **4c**, with 5% methylene chloride/hexane and removal of the solvent under vacuum afforded **5c** (0.21 g, 16%) as a 6:1 mixture of E and Z isomers: orange liquid; ^{1}H NMR of the major isomer (*E*)-**5c** ($CDCl_3$) δ 5.76 (br s, 1 H), 4.50 (s, 3 H), 4.12 (m, 1 H), 3.56 (s, 3 H), 2.17 (dd, J = 14, 5 Hz, 1 H), 1.69 (dd, J = 14, 9 Hz, 1 H), 1.60 (s, 3 H), 0.90 (d, J = 9 Hz, 3 H); $^{13}C\{^1H\}$ NMR of (*E*)-**5c** ($CDCl_3$) δ 342.73, 203.15, 197.31, 144.18, 110.88, 70.55, 65.93, 59.32, 37.05, 15.63, 13.04. Anal. Calcd for $C_{14}H_{16}O_7W$: C, 35.02; H, 3.36. Found: C, 35.15; H, 3.49. For comparison, the reaction was performed exactly as described above, except 1 M HCl/diethyl ether (3.0 mL, 3.0 mmol) was used to quench the reaction instead of chlorotrimethylsilane. This modification afforded **4c** (1.05 g, 43%) and **5c** (0.42 g, 30%) as a mixture of isomers.

Reaction of 1a with 2b followed by $CH_3OSO_2CF_3$. Using $(CO)_5W[C(OCH_3)CH_3]$ (1.15 g), complex **2b** (1.23 g), and as the electrophilic quenching agent, methyl trifluoromethanesulfonate (0.34 mL), in the general procedure described above, afforded 1.62 g of a 2:1:1 mixture of complexes **6**, **4b**, and **7**. ^{1}H NMR of **6** ($CDCl_3$): δ 4.75 (s, 3 H), 4.58 (s, 3 H), 3.05 (m, 2 H), 1.76 (m, 2 H), 1.32 (s, 6 H). ^{1}H NMR of **7** ($CDCl_3$): δ 4.72 (s, 3 H), 4.61 (s, 3 H), 3.51 (m, 1 H), 1.73 (m, 2 H), 1.43 (s, 3 H), 1.15 (s, 3 H), 0.89 (d, 3 H).

$(CO)_5W[C(OCH_2Ph)CH_3]$. To a stirred solution of $(CO)_5W[C(O)CH_3]^-N(CH_3)_4^+$ (0.90 g, 2.0 mmol) in methylene chloride (90 mL) at −35 °C was added acetyl chloride (190 μL, 2.7 mmol). The mixture was stirred at −35 °C for 5 min, and then benzyl alcohol (1.40 mL, 13.5 mmol) was added with continued stirring at −30 °C for 2 h. The mixture was warmed to 25 °C and the solution concentrated to half of its original volume under vacuum, and then 10% methylene chloride/hexane (40 mL) was added. The resulting yellow solution was then passed through a short column of silica gel by using 10% methylene chloride/hexane as the eluent. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum amount of 10% methylene chloride/hexane and then transferred to a column of silica gel. Eluting the column with hexane and removal of the solvent under vacuum afforded $(CO)_5W[C(OCH_2Ph)CH_3]$ (0.65 g, 70%): yellow crystals; mp 69.5 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.45 (m, 5 H), 5.81 (s, 2 H), 2.93 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 331.02, 203.50, 197.23, 133.87, 129.31, 128.97, 128.55, 86.15, 52.35. Anal. Calcd for $C_{14}H_{10}O_6W$: C, 36.71; H, 2.20. Found: C, 36.58; H, 2.08.

$(CO)_5W[C(OCH_2CH_2Ph)CH_3]$. To a stirred solution of $(CO)_5W[C(O)CH_3]^-N(CH_3)_4^+$ (0.90 g, 2.0 mmol) in methylene chloride (90 mL) at -35 °C was added acetyl chloride (190 μL, 2.7 mmol). The mixture was stirred at -35 °C for 5 min, and then 2-phenylethanol (1.61 mL, 13.5 mmol) was added with continued stirring at -30 °C for 2 h. The mixture was warmed to 25 °C and the solution concentrated to half of its original volume under vacuum, and then 10% methylene chloride/hexane (40 mL) was added. The resulting yellow solution was then passed through a short column of silica gel by using 10% methylene chloride/hexane as the eluent. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum amount of 10% methylene chloride/hexane and then transferred to a column of silica gel. Eluting the column with hexane and removal of the solvent under vacuum afforded $(CO)_5W[C(OCH_2CH_2Ph)CH_3]$ (0.61 g, 65%): unstable yellow oil; ^1H NMR ($CDCl_3$) δ 7.20–7.40 (m, 5 H), 4.98 (br s, 2 H), 3.28 (t, J = 7 Hz, 2 H), 2.86 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 330.92, 203.40, 197.22, 136.55, 128.84, 128.79, 127.05, 84.49, 52.17, 35.57.

General Procedure for the Preparation of Complexes 4m and 4n. To a stirred solution of $(CO)_5W[C(OCH_2Ph)CH_3]$ (0.37 g, 0.8 mmol) or $(CO)_5W[C(OCH_2CH_2Ph)CH_3]$ (0.38 g, 0.8 mmol) in 10 mL of THF at -78 °C was added 2.5 M *n*-BuLi/hexane (0.36 mL, 0.9 mmol) dropwise. The reaction mixture was then stirred at -78 °C for 20 min followed by the addition of a solution of complex **2b** (0.36 g, 0.9 mmol) in 10 mL of THF. After stirring at -78 °C for 2 h, the reaction mixture was quenched with allyl bromide (0.30 mL, 3.5 mmol) and then stirred for an additional 20 min at -78 °C. The solution was warmed to 25 °C and concentrated to half of its original volume under vacuum, and then 10% methylene chloride/hexane (30 mL) was added. This solution was then passed through a short column of silica gel by using methylene chloride (100 mL) as the eluent. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum amount of 10% methylene chloride/hexane and then transferred to a column of silica gel. Eluting the column first with hexane separated the unreacted starting materials $(CO)_5W[C(OCH_2Ph)CH_3]$ and **2b** or $(CO)_5W[C(OCH_2CH_2Ph)CH_3]$ and **2b**; then, eluting with 5% methylene chloride/hexane afforded complexes **4m** or **4n** as yellow-orange oils.

$(CO)_5W[C(O)C(CH_3){=}CH_2]^-N(CH_3)_4^+$. To a stirred suspension of finely cut lithium (0.168 g, 24.0 mmol) in 40 mL of diethyl ether was added 2-bromopropene (1.06 mL, 12.0 mmol) in 10 mL of diethyl ether at such a rate as to maintain gentle reflux. After the addition was complete, the mixture was refluxed for 4 h. After cooling to 25 °C, the solution was transferred, over the course of 30 min, through a cannula to a suspension of $W(CO)_6$ (3.52 g, 10.0 mmol) in 150 mL of diethyl ether. The reaction mixture was then stirred for 1 h, and the solvent was removed under vacuum. The resulting residue was dissolved in a minimum of nitrogen-saturated water and then filtered under an atmosphere of nitrogen. To the filtrate was added tetramethylammonium bromide (4.60 g, 30.0 mmol), and then the resulting precipitate was collected and dried under vacuum. The product was purified by dissolving it in a minimum amount of methylene chloride, drying the solution over magnesium sulfate followed by filtration, and precipitation with hexane. The process was repeated two more times followed by drying under vacuum to afford the title compound (3.50 g, 75%): orange solid; ^1H NMR (CD_3COCD_3) δ 5.33 (br s, 1 H), 5.19 (br s, 1 H), 3.46 (s, 12 H), 1.53 (s, 3 H); $^{13}C\{^1H\}$ NMR (CD_3COCD_3) δ 278.79, 208.97, 205.11, 163.68, 116.66, 56.04, 16.96. Anal. Calcd for $C_{13}H_{17}NO_6W$: C, 33.42; H, 3.67; N, 2.99. Found: C, 31.28; H, 3.80; N, 3.25.

$(CO)_5W[C(OCH_2Ph)C(CH_3){=}CH_2]$ (2o). To a stirred solution of $(CO)_5W[C(O)C(CH_3){=}CH_2]^-N(CH_3)_4^+$ (2.00 g, 4.3 mmol) in methylene chloride (270 mL) at -60 °C was added acetyl chloride (405 μL, 5.7 mmol). The mixture was stirred at -55 °C for 5 min, and then benzyl alcohol (2.7 mL, 26.0 mmol) was added with continued stirring at -55 °C for 20 min. The solution was then warmed to -45 °C and stirred for 2 h. The mixture was warmed to 25 °C and the solution concentrated to half of its original volume under vacuum and then 10% methylene chloride/hexane (100 mL) was added. The resulting red solution was then passed through a short column of silica gel by using 10% methylene chloride/hexane as the eluent. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum amount of hexane and then transferred to a column of silica gel. Eluting the column with hexane and removal of the solvent under vacuum afforded **2o** (1.76 g, 85%): dark red crystals; mp 48 °C; ^1H NMR ($CDCl_3$) δ 7.44 (br s, 5 H), 5.84 (s, 2 H), 5.49 (br s, 1 H), 5.42 (br s, 1 H), 1.89 (s, 3 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 324.99, 203.28, 197.33, 160.52, 134.13, 129.17, 128.97, 128.22, 121.43, 85.09, 19.47. Anal. Calcd for $C_{16}H_{12}O_6W$: C, 39.69; H, 2.50. Found: C, 39.60; H, 2.43.

$(CO)_5W[C(OCH_2Ph)CH_2CH_2C(CH_3)(CH_2CH{=}CH_2)C(OCH_2Ph)]W(CO)_5$ (4o). To a stirred solution of $(CO)_5W[C(OCH_2Ph)CH_3]$ (2.31 g, 5.0 mmol) in 30 mL of THF at -78 °C was added 2.5 M *n*-BuLi/hexane (2.2 mL, 5.5 mmol) dropwise. The reaction mixture was then stirred at -78 °C for 30 min followed by the addition of a solution of complex **2o** (1.76 g, 3.6 mmol) in 20 mL of THF. After stirring at -78 °C for 2 h, the reaction mixture was quenched with allyl bromide (2.0 mL, 23.0 mmol) and then stirred for an additional 20 min at -78 °C. The solution was warmed to 25 °C and concentrated to half of its original volume under vacuum, and then 10% methylene chloride/hexane (50 mL) was added. This solution was then passed through a short column of silica gel by using methylene chloride (300 mL) as the eluent. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum amount of hexane and then transferred to a column of silica gel. Eluting the column first with hexane separated the unreacted starting complex $(CO)_5W[C(OCH_2Ph)CH_3]$ (0.65 g); then, eluting with 5% methylene chloride/hexane afforded **4o** (3.17 g, 65%) as orange cubes.

General Procedure for the Preparation of Complexes 4p–t. To a stirred solution of the appropriate (alkylcarbene)chromium complex (4.0 mmol) in 30 mL of THF, which has been cooled to -78 °C, was added a precooled (-78 °C) solution of 2.5 M *n*-BuLi/hexane (1.6 mL, 4.0 mmol) in 5 mL of THF over a 10-min period. After the addition was complete, the solution was stirred at -78 °C for 1 h. Into this solution was added the appropriate α,β-unsaturated carbene complex (**2**) (4.0 mmol) in 10 mL of THF over the course of 20 min. The reaction mixture was stirred at -78 °C for 1 h, except where noted (Table I), and the quenched with a precooled (-78 °C) solution of the appropriate electrophilic reagent (E–X, Table I) (4.0 mmol) in 3 mL of THF. The resulting mixture was stirred for an additional 10 min, then warmed to 25 °C and diluted with 200 mL of hexane, and then passed through a column (30 × 3 cm) of silica gel. The column was washed with an additional 500 mL of 10% methylene chloride/hexane and the solvent removed under vacuum. The resulting residue was chromatographed on silica gel by using 1% methylene chloride/hexane as the eluent. The fractions showing a single TLC spot and having an R_f value of ca. 0.3 (10% methylene chloride/hexane) were combined, and the solvent was removed under vacuum to give complexes **4p–t**. Crystallization from 5% methylene chloride/hexane at -5 °C afforded complexes **4p–t** as yellow to yellow-orange crystals.

$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(OCH_3)]W(CO)_5$ (4u). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at -78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After stirring at -78 °C for 30 min, a solution of **2a** (0.60 g, 1.3 mmol) in 50 mL of THF was introduced slowly through a cannula. The deep red color of **2a** was immediately discharged upon its addition to the solution of anion **1u**. The resulting mixture was stirred at -78 °C for 30 min and warmed to 25 °C, and the solvent was removed under high vacuum to give a yellow-brown residue. This residue was taken up in 30 mL of anhydrous THF and passed through a short column of silica gel with continued elution of the column with methylene chloride. All the yellow fractions were collected, and the solvent was removed under vacuum. The resulting residue was taken up in a minimum amount of methylene chloride and transferred to a column of silica gel. Eluting the column with 20% methylene chloride/hexane, collection of the first yellow-orange band, and removal of the solvent under vacuum afforded **4u** (0.58 g, 58%) as yellow crystals.

General Procedure for the Preparation of Complexes 4v,x,y. To a stirred THF (ca. 10 mL/mmol of 1) solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (1 equiv) at -78 °C was added 2.5 M *n*-BuLi/hexane (1.2 equiv). After stirring for 30 min at -78 °C, a solution of the appropriate complex **2** (Table I) (1 equiv) in THF (ca. 10 mL/mmol of **2**) was introduced slowly through a cannula. The deep red color of complex **2** was immediately discharged upon its addition to the solution of anion **1u**. The resulting mixture was then stirred at −78 °C for 30 min, the appropriate electrophilic quenching agent (E–X, Table I) (5 equiv, except for the preparation of **4y** which involved using 3 equiv of *trans*-cinnamyl bromide) added, and the mixture stirred at −78 °C for an additional 30 min. The solution was warmed to 25 °C, the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 20% methylene chloride/hexane, collection of all the yellow-orange fractions, and removal of the solvent under vacuum afforded complexes **4v,x,y** as yellow-orange substances.

$(CO)_5W[C(N(CH_3)_2)CH(Si(CH_3)_3)CH_2C(CH_3)(CH_2CH{=}CH_2)C(OCH_3)]W(CO)_5$ (4w). To a stirred solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After stirring for 30 min at −78 °C, chlorotrimethylsilane (0.20 mL, 1.6 mmol) was added with further stirring for 30 min. The resulting solution of $(CO)_5W[C(N(CH_3)_2)CH_2Si(CH_3)_3]$[12] (at −78 °C) was then treated with 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol) followed by slow addition (through a cannula) of a solution of **2b** (0.65 g, 1.6 mmol) in 50 mL of THF. The deep red color of **2b** was immediately discharged upon its addition to the solution of anion **1w**. The resulting solution was stirred at −78 °C for 30 min followed by the addition of allyl bromide (0.54 mL, 6.2 mmol) with continued stirring for an additional 30 min. The reaction mixture was then warmed to 25 °C, the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 20% methylene chloride/hexane, collection of all the yellow-orange fractions, and removal of the solvent under vacuum afforded **4w** (0.54 g, 47%).

$(CO)_5W[C(N(CH_3)_2)CH_2CH_2CH_2C(N(CH_3)_2)]W(CO)_5$ (4z). To a solution of $(CO)_5W[C(N(CH_3)_2)CH_3]$ (0.50 g, 1.3 mmol) in 50 mL of THF at −78 °C was added 2.5 M *n*-BuLi/hexane (0.61 mL, 1.6 mmol). After stirring for 30 min at −78 °C a solution of **2z** (0.51 g, 1.3 mmol) in 50 mL of THF was introduced slowly through a cannula. After the addition was complete, the mixture was stirred at −78 °C for 30 min followed by the addition of chlorotrimethylsilane (0.80 mL, 6.3 mmol). The resulting reaction mixture was stirred at −78 °C for 30 min, then warmed to 25 °C and the solvent removed under vacuum, and the resulting residue transferred, with a minimum amount of methylene chloride, to a column of silica gel. Eluting the column with 25% methylene chloride/hexane, collection of all the yellow fractions, and removal of the solvent under vacuum afforded **4z** (0.48 g, 46%) as yellow needles.

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Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, least-squares plane results, torsion angles, bond distances and angles, and final fractional coordinates (15 pages); listings of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

The Ge–H Bond Dissociation Energies of Organogermanes. A Laser-Induced Photoacoustic Study[1]

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The Ge–H bond dissociation energies (BDE's) of several alkyl- and aryl-substituted germanium hydrides have been measured in hydrocarbon solution at room temperature by a photoacoustic technique. The BDE's of these hydrides are unaffected by alkyl substitution when compared to those for GeH_4 and are in the range of 81.6–82.6 kcal/mol. Aryl substitution leads to a slightly weakened Ge–H bond (79.2–80.2 kcal/mol) in the cases of phenyl-, diphenyl-, and triphenylgermane. In an effort to further characterize the formation, spectral and decay properties of the germyl radicals some laser flash photolysis studies were carried out. The rate constants for hydrogen abstraction by *tert*-butoxy radicals were determined by nanosecond laser flash photolysis and fell in the range $(0.7–4.4) \times 10^8$ M^{-1} s^{-1}. The aryl-substituted germyl radicals add to the aromatic rings of the germane precursor. Diphenylgermyl radical adds to diphenylgermane with a rate constant of 2.9×10^5 M^{-1} s^{-1}, while phenylgermyl radical adds to phenylgermane with a rate constant of 1.2×10^6 M^{-1} s^{-1}.

Introduction

Determination of metal–hydrogen bond dissociation energies is an area of great interest for which we have found the technique of laser-induced photoacoustic calorimetry to be extraordinarily useful in determining the bond dissociation energies of organometallic compounds not conducive to classical methods of calorimetry. Homolytic bond dissociation energies (BDE's) of organometallic compounds, which are generally derived from the heats of formation of metal-centered radicals, are rather rare since these materials are unsuitable for conventional gas-phase techniques. For example, values of BDE's of organometallic compounds of group IVB are of considerable value in understanding the chemistry of these compounds.[2] Recent work from our laboratory, directed toward uncovering the bonding characteristics in a variety

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(2) Sakurai, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, Chapter 25.

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