Crystal and Molecular Structure of the Tungsten–Carbene Complex W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br₂ and of Its Gallium Tribromide Adduct. A Structural Approach to the Mechanism of Olefin Metathesis

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Abstract: The crystal structures of the tungsten carbene complex W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br₂ (**1**) and of its adduct W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br₂·GaBr₃ (**2**) are reported. Complex **1** crystallizes as red crystals in space group $P2_1/c$ with $a = 10.881$ (3) Å, $b = 18.738$ (5) Å, $c = 10.675$ (3) Å, $\beta = 112.39$ (2)°; and $Z = 2$. Least-squares refinement of 4333 reflections having $I > 3\sigma(I)$ gives a conventional R factor of 0.035. The structure contains discrete centrosymmetric dimers resulting from the association between two pentacoordinate monomeric units via two weak tungsten–bromine bridging interactions (W–Br = 3.052 Å). Each tungsten thus possesses a slightly distorted octahedral coordination geometry in which the two neopentoxo oxygens as well as the two bromo ligands are mutually trans and the carbene carbon occupies the position trans to the long W–Br bridge. Complex **2** crystallizes as orange crystals in space group $P2_1/n$ with $a = 17.453$ (5) Å, $b = 11.067$ (3) Å, $c = 13.669$ (4) Å, $\beta = 103.52$ (2)°, and $Z = 4$. Least-squares refinement of 2719 reflections having $I > 3\sigma(I)$ gives a conventional R factor of 0.029. The molecular structure of **2** is similar to that of **1**, one pentacoordinate monomeric unit of dimeric **1** being replaced in **2** by a tricoordinate GaBr₃ group. The Br → Ga coordination bond in **2** is however much stronger than the Br → W bridging interaction in **1** and enables **2** to be described alternatively as W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br·($\eta^2$-GaBr₄). The bond distances and angles of both compounds are discussed and compared in terms of π-donation effects between the ligands and the tungsten. Both **1** and **2** being active catalysts for the metathesis of olefins, the relations between the structural features found in the solid state and those in solution are discussed. For **1**, the dimer structure is not preserved in solution, and the pentacoordinate monomer produces the actual chain carrying species involved in catalysis. **2** appears to undergo dissociation into GaBr₄⁻ and the extremely active tetracoordinate cation W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br⁺ (**3**), and the X-ray diffraction data obtained for **1** and **2** have been extrapolated in an attempt to define more precisely the structural nature of this cation.
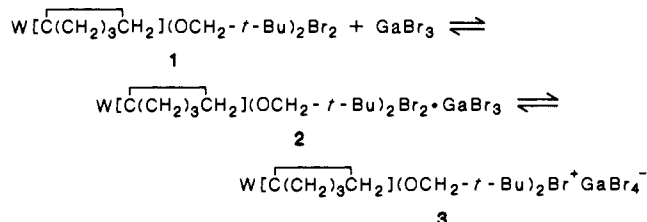
The determination of the detailed structure of intermediates in homogeneous catalytic processes is an essential task in the elucidation of the precise mechanism of these reactions, but the isolation of such reactive species in the solid state and their direct crystallographic characterization would seem to be a distant objective.

Two other closely related but more feasible approaches are more generally found in the literature where either a stabilized analogue or a direct precursor is subjected to a solid-state structural determination. In the former case, an analogue to a proposed intermediate, stabilized by steric or electronic means, is synthesized, and its analogue character is verified by comparison of its spectroscopic and reactivity properties (albeit diminished) with those observed or expected for the less stable intermediate. In the precursor case, the complex under investigation is able to give rise by a single fundamental (and preferably reversible) transformation (e.g., ligand dissociation) to a species directly lying on the catalytic cycle. These approaches can suffer from a further limitation, since the molecular structure in the solid state may differ from that of the species in solution. Extrapolation to solution species would however seem reasonable if solution structural information (e.g., NMR) is consistent with such X-ray diffraction data.

In this study we report the X-ray diffraction structure of two tungsten–carbene complexes behaving as both analogues *and* direct precursors of the metal–carbene intermediates likely to occur in olefin metathesis reactions,[1] W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br₂ (**1**) and W[$\overline{\text{C(CH}_2)_3\text{CH}_2}$](OCH₂-*t*-Bu)₂Br₂·GaBr₃ (**2**). When dissolved in chlorobenzene or dichloromethane, both compounds are effective catalysts for the metathesis of linear and cyclic olefins (like their analogues such as the neopentylidene complexes), but **2** is vastly more efficient than **1**.[2-4]

This large difference in activity appears to be related to the generally higher activity obtained with classical catalyst systems containing Lewis acid cocatalysts.[1] In earlier detailed studies,[5]

we suggested that the following equilibrium is set up in solution in the presence of GaBr₃ (Ga/W ≤ 1) and that the preeminent active species is the tetracoordinate cationic complex **3**, although

$$\text{W[}\overline{\text{C(CH}_2)_3\text{CH}_2}\text{](OCH}_2\text{-}t\text{-Bu)}_2\text{Br}_2 + \text{GaBr}_3 \rightleftharpoons$$
$$\textbf{1}$$

$$\text{W[}\overline{\text{C(CH}_2)_3\text{CH}_2}\text{](OCH}_2\text{-}t\text{-Bu)}_2\text{Br}_2\text{·GaBr}_3 \rightleftharpoons$$
$$\textbf{2}$$

$$\text{W[}\overline{\text{C(CH}_2)_3\text{CH}_2}\text{](OCH}_2\text{-}t\text{-Bu)}_2\text{Br}^+\text{GaBr}_4^-$$
$$\textbf{3}$$

this species is only present in low concentration. However, **2** may also have an intrinsic activity of its own similar to that of **1**, and the comparison of its molecular structure with that of **1** should help to define the role of Lewis acid cocatalysts not only in these catalysts but also in many classical catalyst systems.

A clear indication of the direct precursor nature of **1** and **2** has been also afforded by the observation in solution of the chain-carrying carbene complexes produced on addition of olefins.[2,4-6]

Preceding X-ray analyses on metal–carbene complexes which are active in metathesis are rare[8-10] and indeed involve complexes

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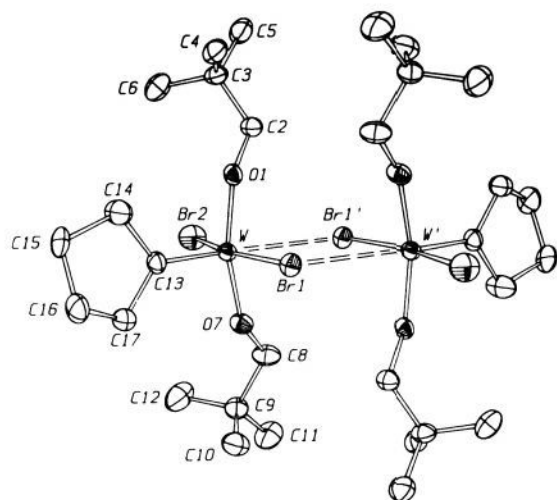
(6) We observe further that these complexes belong moreover to the first family of stable coordinatively unsaturated metal–carbene complexes possessing β-hydrogens on the carbene ligand.[3] **1** also shows Wittig type reactivity converting organic carbonyls to olefins.[7]

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$\overline{W[C(CH_2)_3CH_2]}(OCH_2\text{-}t\text{-}Bu)_2Br_2$

Table I. Positional Parameters and Their Estimated Standard Deviations for **1**[a]

atom	x	y	z	B(A2)
W	0.32962 (2)	0.48862 (1)	0.31067 (2)	1.667 (4)
Br1	0.56638 (6)	0.54107 (3)	0.38546 (5)	1.95 (1)
Br2	0.11237 (7)	0.42990 (4)	0.29335 (8)	3.16 (1)
O1	0.3916 (4)	0.3984 (2)	0.3129 (4)	1.83 (8)
C2	0.4024 (6)	0.3295 (3)	0.3705 (6)	2.0 (1)
C3	0.3952 (6)	0.2698 (3)	0.2759 (6)	2.2 (1)
C4	0.5102 (7)	0.2752 (4)	0.2293 (6)	2.9 (1)
C5	0.4053 (9)	0.1993 (4)	0.3512 (7)	3.4 (2)
C6	0.2640 (7)	0.2710 (4)	0.1546 (7)	3.1 (1)
O7	0.2697 (4)	0.5686 (3)	0.3676 (4)	2.15 (8)
C8	0.2176 (6)	0.5966 (3)	0.4603 (7)	2.8 (1)
C9	0.1241 (6)	0.6595 (4)	0.4005 (6)	2.5 (1)
C10	0.2005 (8)	0.7173 (4)	0.3615 (8)	3.4 (2)
C11	0.0815 (7)	0.6858 (5)	0.5143 (8)	3.8 (2)
C12	0.0028 (8)	0.6358 (5)	0.2758 (9)	4.6 (2)
C13	0.2888 (6)	0.5129 (3)	0.1274 (6)	2.0 (1)
C14	0.3180 (9)	0.4650 (5)	0.0223 (7)	3.6 (2)
C15	0.2634 (9)	0.5052 (4)	-0.1108 (7)	3.2 (2)
C16	0.2669 (8)	0.5833 (4)	-0.0717 (6)	3.3 (2)
C17	0.2314 (7)	0.5815 (4)	0.0556 (7)	2.8 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as the following: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table II. Positional Parameters and Their Estimated Standard Deviations for **2**[a]

atom	x	y	z	B(A2)
W	0.27257 (2)	0.06479 (3)	0.06021 (2)	1.490 (7)
Br1	0.35909 (5)	0.01231 (8)	-0.07729 (6)	2.21 (2)
Br2	0.19426 (5)	0.06137 (8)	0.18963 (6)	2.61 (2)
Br3	0.28144 (5)	-0.21397 (8)	0.06877 (6)	2.34 (2)
Ga	0.34901 (5)	-0.20367 (8)	-0.05895 (7)	2.26 (2)
Br4	0.22517 (6)	0.21500 (9)	-0.29503 (9)	3.90 (2)
Br5	0.52644 (5)	0.28039 (9)	0.01568 (8)	3.95 (2)
O1	0.1911 (3)	0.0328 (5)	-0.0447 (4)	2.0 (1)
C2	0.1568 (5)	-0.0268 (8)	-0.1382 (6)	2.2 (2)
C3	0.0671 (5)	-0.0329 (8)	-0.1569 (6)	2.3 (2)
C4	0.0389 (6)	-0.0937 (9)	-0.2592 (7)	3.7 (2)
C5	0.0478 (5)	-0.1081 (8)	-0.0740 (7)	3.1 (2)
C6	0.0310 (5)	0.0918 (8)	-0.1593 (7)	2.8 (2)
O7	0.3667 (3)	0.0476 (5)	0.1477 (4)	2.0 (1)
C8	0.4460 (4)	0.0114 (8)	0.1871 (6)	2.4 (2)
C9	0.4635 (4)	-0.0059 (8)	0.3010 (6)	2.3 (2)
C10	0.5513 (5)	-0.032 (1)	0.3339 (8)	4.1 (2)
C11	0.4186 (5)	-0.1125 (9)	0.3269 (6)	3.0 (2)
C12	0.4410 (7)	0.109 (1)	0.3503 (8)	5.0 (3)
C13	0.2765 (5)	0.2351 (8)	0.0476 (5)	2.1 (2)
C14	0.2180 (5)	0.3145 (8)	-0.0240 (6)	2.3 (2)
C15	0.2440 (6)	0.4459 (8)	0.0003 (9)	4.0 (2)
C16	0.3294 (6)	0.4369 (9)	0.0502 (8)	3.7 (2)
C17	0.3370 (5)	0.3200 (8)	0.1092 (6)	2.5 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as the following: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3.3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Figure 1. ORTEP view of complex **1** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity. Primed atoms refer to centrosymmetric equivalents.

of only very limited catalytic activity.[11,12]
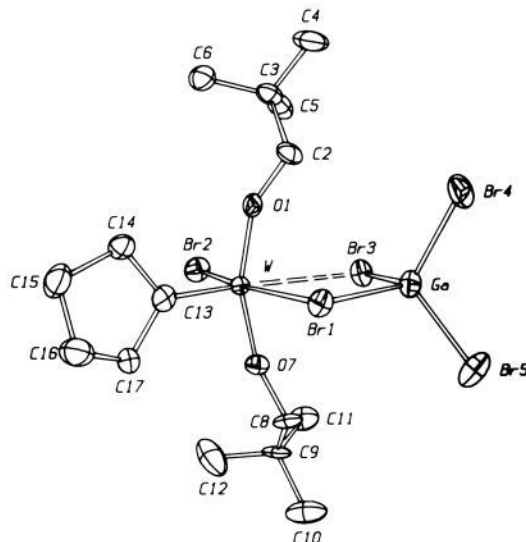
Results

Final atomic positional parameters for the non-hydrogen atoms of compounds **1** and **2** are given in Tables I and II, respectively, the ORTEP view of the corresponding molecular units are given in Figures 1 and 2 along with the atom labeling scheme, and the main bond distances and angles of both compounds are collected in Table III.

1. Crystal and Molecular Structure of $\overline{W[C(CH_2)_3CH_2]}$-(OCH₂-t-Bu)₂Br₂ (1). The molecular units consist of discrete dimers lying on an inversion center of the space group, the association between the two pentacoordinate monomeric units being

Figure 2. ORTEP view of complex **2** (50% probability thermal ellipsoids). Hydrogen atoms are omitted for clarity.

realized via two weak tungsten–bromine bridging interactions (W–Br(1') = W'·Br(1) = 3.0521 (5) Å). Each tungsten thus possesses a slightly distorted octahedral coordination geometry in which the two neopentoxo oxygens O(1) and O(7) as well as the two bromo ligands Br(1) and Br(2) are mutually trans, and the carbene carbon C(13) occupies the position trans to the long W–Br(1') bridge. The distortion is illustrated in particular by the deviations of the tungsten atom out of the least-squares planes defined by Br(1), Br(2), O(1), O(7) and O(1), O(7), C(13) (0.302 (0) and 0.053 (0) Å, respectively) and by the O(1)–W–O(7), Br(1)–W–Br(2), and C(13)–W–Br(1') angles less than 180° (159.37 (16), 167.05 (2), and 171.93 (18)°,respectively). The atoms Br(1), Br(1'), Br(2), W, and C(13) are however coplanar with deviations of less than 0.004 (2) Å from the corresponding least-squares plane.

The two tungsten–bromine bond lengths of each monomeric unit are much shorter than the W–Br(1') distance. However, W–Br(1) (2.5832 (6) Å) is slightly longer than W–Br(2) (2.5496

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Table III. Bond Lengths (Å) and Angles (deg) for 1 and 2

	1	2
W–O(1)	1.816 (4)	1.803 (6)
W–Br(2)	2.5496 (7)	2.4758 (9)
W–C(13)	1.890 (5)	1.896 (9)
W–O(7)	1.828 (4)	1.802 (6)
W–Br(1)	2.5832 (6)	2.7345 (8)
W–Br(1')	3.0521 (5)	
W–Br(3)		3.090 (1)
C(13)–C(14)	1.561 (8)	1.518 (12)
C(14)–C(15)	1.515 (9)	1.535 (13)
C(15)–C(16)	1.518 (10)	1.491 (15)
C(16)–C(17)	1.548 (9)	1.513 (13)
C(17)–C(13)	1.505 (8)	1.514 (12)
O(1)–C(2)	1.417 (6)	1.439 (10)
C(2)–C(3)	1.489 (7)	1.527 (12)
C(3)–C(4)	1.517 (8)	1.525 (13)
C(3)–C(5)	1.528 (8)	1.507 (13)
C(3)–C(6)	1.519 (9)	1.514 (12)
O(7)–C(8)	1.415 (7)	1.419 (10)
C(8)–C(9)	1.529 (8)	1.527 (12)
C(9)–C(10)	1.516 (9)	1.521 (13)
C(9)–C(11)	1.538 (9)	1.504 (12)
C(9)–C(12)	1.540 (9)	1.531 (14)
O(1)–W–O(7)	159.37 (16)	159.13 (24)
C(13)–W–Br(1')	171.93 (18)	
C(13)–W–Br(3)		173.62 (23)
Br(1)–W–Br(2)	167.05 (2)	166.83 (3)
Br(1)–W–Br(1')	79.55 (2)	
Br(1)–W–Br(3)		77.47 (2)
C(13)–W–Br(2)	100.56 (18)	96.76 (22)
Br(2)–W–Br(1')	87.51 (2)	
Br(2)–W–Br(3)		89.36 (3)
C(13)–W–Br(1)	92.39 (18)	96.39 (22)
O(1)–W–Br(1)	91.62 (12)	82.62 (16)
O(1)–W–Br(1')	80.27 (11)	
O(1)–W–Br(3)		81.78 (17)
O(1)–W–Br(2)	85.92 (12)	95.77 (16)
O(1)–W–C(13)	100.23 (21)	99.29 (32)
O(7)–W–Br(1)	91.48 (13)	82.49 (16)
O(7)–W–Br(1')	80.25 (12)	
O(7)–W–Br(3)		80.77 (18)
O(7)–W–Br(2)	86.52 (13)	95.41 (16)
O(7)–W–C(13)	100.02 (21)	96.83 (32)
W–O(1)–C(2)	145.41 (34)	152.07 (50)
O(1)–C(2)–C(3)	114.62 (44)	111.42 (64)
W–O(7)–C(8)	145.65 (38)	159.68 (53)
O(7)–C(8)–C(9)	111.99 (51)	111.55 (66)
W–Br(1)–W'	100.45 (2)	
W–Br(1)–Ga		94.22 (3)
W–Br(3)–Ga		87.27 (3)

Bond Distances (Å) and Angles (deg) for 2

Ga–Br(1)	2.414 (1)	Br(1)–Ga–Br(3)	100.86 (4)
Ga–Br(3)	2.327 (1)	Br(1)–Ga–Br(4)	109.77 (5)
Ga–Br(4)	2.294 (1)	Br(1)Ga–Br(5)	107.91 (5)
Ga–Br(5)	2.279 (1)	Br(3)–Ga–Br(4)	110.59 (5)
		Br(3)–Ga–Br(5)	114.02 (5)
		Br(4)–Ga–Br(5)	112.93 (5)

Other Distances (Å)

W–W' (1)	4.3414 (4)
W–Ga (2)	3.778 (1)

(7) Å) undoubtedly resulting from the existence of the weak Br(1)–W' interaction.

The W–C(13) bond length of 1.890 (5) Å is indicative of a double bond. It is close to that previously reported for the pentacoordinate complex WO(CH-*t*-Bu)(PEt₃)Cl₂,[9] but ca. 0.1 Å shorter than in the hexacoordinate WO(CH-*t*-Bu)(PEt₃)₂Cl₂.[10] The bond angles W–C(13)–C(14) and W–C(13)–C(17) are similar (125.00 (42) and 128.45 (42)°) and are in agreement with sp² hybridization expected at the carbene α carbon atom. The plane defined by C(13), C(14), C(17), and W is perpendicular to the W, C(13), Br(1), Br(2) plane, but the atoms C(14), C(13), C(17), W, O(1), and O(7) are not exactly coplanar, the 10.29 (15)° angle between the planes defined by O(1), W, O(7) and

C(14), C(13), C(17), W, indicating a slight rotation of the former toward the W–Br(1) bond. The C₅ cycle has a puckered geometry with C(15) and C(16) lying, respectively, 0.138 (9) and –0.435 (9) Å out of the C(14), C(13), C(17) plane.

The tungsten–oxygen bond lengths W–O(1) and W–O(7) are particularly short (1.816 (4) and 1.828 (4) Å), even shorter than those found for the Wᵛᴵ complex W(O-*t*-Bu)₄I₂ (1.840 (4) Å) which were previously among the shortest tungsten–alkoxo bonds yet reported.[13] Further, the W–O(1)–C(2) and W–O(7)–C(8) angles show large values of approximately 145.50 (36)°.

2. Crystal and Molecular Structure of W[C̅(CH₂)₃CH₂]-(OCH₂-*t*-Bu)₂Br₂·GaBr₃ (2). The molecular structure of compound 2 is analogous to that of 1, one pentacoordinate monomeric unit of dimeric 1 being replaced in 2 by a tricoordinate GaBr₃ group.

The geometry about the tungsten atom is only slightly modified, a significant difference consisting however of the rotation of the O(1), W, O(7) plane toward the W–Br(1) vector as shown by the increase of the angle between this plane and the plane defined by C(14), C(13), C(17), W from 10.29 (15) to 38.83 (18)°. This explains in particular the 9.00 (20)° lowering of the O(1)–W–Br(1) and O(7)–W–Br(1) angles and the almost equal increasing of the O(1)–W–Br(2) and O(7)–W–Br(2) angles without any significant change in O(1)–W–O(7). The W atom is moreover found 0.182 (0) Å out of the plane defined by O(1), O(7), C(13) instead of 0.053 (0) Å in 1. The angles Br(1)–W–Br(2) and C(13)–W–Br(3) remain practically unchanged, and the atoms Br(1), Br(3), Br(2), W, and C(13) remain coplanar.

The weak tungsten–bromine bridging interaction W–Br(3) is also similar to that observed in 1 (3.090 (1) Å instead of 3.0521 (5) Å), but the W–Br(1) bond length is considerably increased (up to 2.7345 (8) Å), whereas W–Br(2) is shortened from 2.5496 (7) Å in 1 to 2.4758 (9) Å in 2. The metal–carbene W–C(13) bond length is not modified with respect to 1, the C–C distances within the cyclopentylidene ligand varying however of about 0.04–0.01 Å. The tungsten–oxygen bond lengths W–O(1) and W–O(7) become even shorter (ca. 1.802 (6) Å) than in 1, and the angles W–O(1)–C(2) and W–O(7)–C(8) become particularly large (152.07 (50) and 159.68 (53)°, respectively).

The distance between Ga and Br(1) is short (2.414 (1) Å) and is only 0.120 (1) and 0.135 (1) Å superior to the length of the terminal Ga–Br(4) and Ga–Br(5) bonds, indicating the significant strength of the Ga–Br(1) coordination bond. The Ga–Br(3) bond length, on the other hand, is 0.033 (1) and 0.048 (1) Å superior to Ga–Br(4) and Ga–Br(5) owing to the weak W–Br(3) interaction. The four bromine atoms Br(1), Br(3), Br(4), and Br(5) thus form an only slightly distorted tetrahedral geometry about the gallium, allowing to describe alternatively compound 2 as

W[C̅(CH₂)₃CH₂](OCH₂-*t*-Bu)₂Br(η²-GaBr₄).

Discussion

Molecular Structure of 1 and 2. The most striking initial observation concerning the structures of 1 and 2 is their great similarity. In both compounds tungsten atoms are formally hexacoordinate, but given the extremely long W–Br bridging interaction, the complexes may be regarded as pentacoordinate structures slightly perturbed by a weak sixth interaction.

Also in both 1 and 2 the very short W–O bond length and the large W–O–C bond angles clearly indicate significant pπ–dπ oxygen–tungsten overlap and rehybridization at oxygen (more s character in the σ bonds). The alkoxo ligands are thereby serving to stabilize through π-donation the electron deficient tungsten center. This is probably also responsible for the particular orientation of the carbene ligand found in both complexes, in which competition between the p electrons of the carbene α carbon and those of the neopentoxo oxygens for a same vacant d orbital of W is thus avoided, and the pπ–dπ interactions are maximized. The same preference was found in solution for analogous com-

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plexes for which the barrier to rotation about the metal–carbene double bond was investigated by NMR and measured as superior to 23 kcal·mol^{-1}.[14]

We note, however, some significant differences between the two structures. Apart from the 28.54 (23)° rotation of the O(1), W, O(7) plane already mentioned above, the main modifications in the pentacoordinate tungsten unit on replacement of one W-[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2 unit of 1 by GaBr_3 concern metal–ligand bond lengths and W–O–C bond angles. These modifications are in good agreement with the occurrence of a Br(1)–Ga interaction in 2 which is much stronger than the corresponding Br(1)–W' interaction in 1. The electron-withdrawing effect exerted by the strong Lewis acid thus weakens the W–Br(1) bond (+0.1513 (10) Å) but causes further strengthening of the W–Br(2), W–O(1), and W–O(7) bonds, as the π-donation from the ligands to the metal increases to compensate for the electron deficiency at tungsten.

The stronger effect observed on W–Br(2) (–0.0738 (11) Å) compared to W–O(1) (–0.013 (7) Å) and W–O(7) (–0.026 (7) Å) is probably related to the trans position of the Br(2) ligand with respect to Br(1), whereas O(1) and O(7) are both cis to W–Br(1). This cis location does not impede further opening up of the W–O(1)–C(2) and W–O(7)–C(8) angles (+6.66 (60)° and +14.03 (65)°, respectively). The fact that the metal–carbon double bond distance W–C(13) is identical in 1 and 2 might also be a consequence of the cis position of the carbene ligand with respect to Br(1).

The ability of the ligands to vary their donor power might be envisaged to serve during catalysis and help to stabilize the various tungsten intermediates. Such a ligand effect would of course be similar to that proposed for the oxo group, i.e., the "spectator" effect,[15] although this role appears to a more important and active one than that implied by the rather passive "spectator" terminology.

Implications for Olefin Metathesis. (a) Catalyst 1. The tungsten–carbene complex 1 would at first seem to be a good analogue of the intermediates propagating olefin metathesis reactions and even one of the true chain-carrying species in the metathesis of methylenecyclopentane into ethylene and cyclopentylenecyclopentane. However, spectroscopic results show that the dimeric structure established for the solid state is apparently not maintained in solution. The ^{1}H NMR spectrum (CD$_2$Cl$_2$) thus does not show either the AB splitting expected for the two diastereotopic methylene protons of the neopentoxo ligands, even at low temperature, or a similar splitting expected for the two multiplets assigned to the CH$_2$ groups of the cyclopentylidene ring. This indicates that either 1 is totally dissociated in solution (through cleavage of the weak W–Br(1') and W'–Br(1) bridges) or rapid dynamic exchange of dimers occurs via a pentacoordinate intermediate. The fact that the IR spectrum of 1 in cyclohexane solution does show notable differences with that carried out on the crystals of 1 is in favor of the first suggestion.

This, of course, could seemingly be easily checked by means of molecular weight measurements in solution. However, owing to the extreme sensitivity of these complexes to molecular oxygen and water, such measurements carried out under the most careful conditions yielded variable results. Comparison with analogous alkylidene complexes indeed affords further arguments in favor of the dissociation of 1 in solution. Some of these compounds such as W(CH-n-Bu)(OCH_2-t-Bu)_2Br_2 and W(CH-sec-Bu)(OCH_2-t-Bu)_2Br_2[14] are thus crystalline and moderately soluble in organic solvents, like 1, whereas others such as W(CH-t-Bu)(OCH_2-t-Bu)_2Br_2 are fully miscible liquids at 25 °C. Such differences in the physical properties may suggest that the latter complexes are monomeric when isolated and the former dimeric like 1. The crystalline compounds moreover show IR spectra similar to that of 1 in the solid state, whereas the oily highly soluble compounds reveal spectra similar to that shown by 1 in solution (vide infra). In summation we believe that complexes of this type can exist in

the pure state at room temperature either as solids in the form of weakly associated dimers or as oils which are monomeric but that dissociation of the dimers into pentacoordinate monomers readily occurs in solution.

The molecular structure of 1 in solution may thus be close to the idealized trigonal bipyramid suggested earlier from spectroscopic results for such pentacoordinate monomeric entities[2,3] (A). The present X-ray structure indicates the availability of a vacant site in (A) located between the two neopentoxo ligands and that

(A)

(B)   (C)

(D)
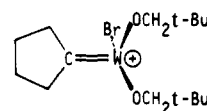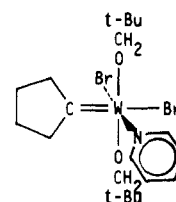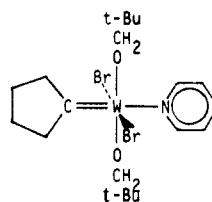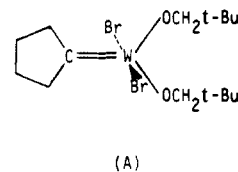
the formation of the Br → W bridges leading to the dimer in the solid state is seemingly accompanied by opening up of the O–W–O angle. The observation of two IR active W–O stretching frequencies for dissolved 1 and liquid W(CH-t-Bu)(OCH_2-t-Bu)_2Br_2 (at 700 and 665 cm^{-1}) instead of one for crystalline 1, W(CH-n-Bu)(OCH_2-t-Bu)_2Br_2, and W(CH-sec-Bu)(OCH_2-t-Bu)_2Br_2 (at 700 cm^{-1}) is in agreement with such a change in geometry.

The Lewis acid character of the tungsten center has been confirmed by the obtaining of various adducts with Lewis bases. Addition to 1 of 1 equiv of pyridine thus leads to the 1:1 adduct W[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2·Py (4). According to the ^{1}H NMR spectra in C$_6$D$_6$, initial coordination of pyridine also occurs trans to the cyclopentylidene ligand to give (B). However, a slow isomerization process is observed in CD$_2$Cl$_2$ consisting of ca. 30% conversion of (B) into a second isomer of probable structure (C), which shows AB type spectra for both OCH$_2$-t-Bu and cyclopentylidene protons and in which pyridine has moved cis to the carbene moiety.

These data allow us to advance a further possible explanation for the limited catalytic efficiency of 1 and analogous complexes for the metathesis of olefins. We have already suggested[4] that this might arise from several factors such as the high coordination number,[4,5,16] the apparently rather high electron density on the carbene ligand,[4,7] or the high barrier-to-carbene rotation.[14] We can see that the position of the vacant site in monomeric 1 also seems unsuitable for efficient metathesis. Olefins do weakly interact with 1,[4] but metallacyclobutane formation, the key step of the catalytic reaction, clearly cannot occur directly if the olefin approaches trans to the carbene ligand. A trans → cis isomerization process similar to that observed for the pyridine adduct 4 might thus be necessary, and the corresponding activation energy required may also be at the origin of the modest activity of 1 in metathesis.

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(14) Kress, J.; Osborn, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 3953.
(15) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 448.

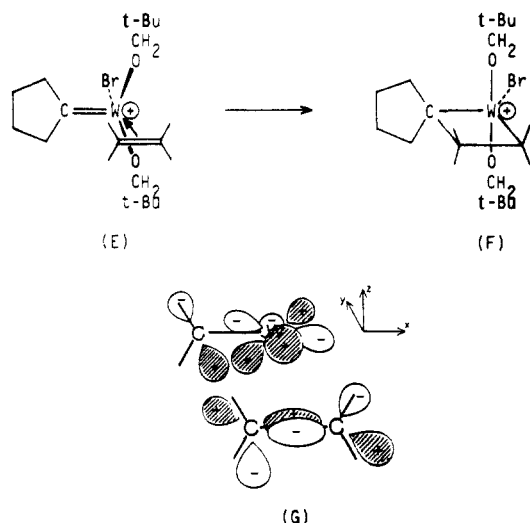(16) Very active tetracoordinate carbene complexes have recently been reported.[17]

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(b) Catalyst 2. The ^{1}H NMR spectrum of **2** in CD_2Cl_2 is similar to that of **1** and only differs by the chemical shift variations of the four resonances. Not only the weak W–Br(3) bridge appears thus to be cleaved as for **1** but also rapid dynamic exchange of $GaBr_3$ from Br(1) to Br(2) is shown to occur in solution, probably through an intermolecular dissociative mechanism.

As mentioned in the introduction, we concluded from earlier studies that complexes such as **2** are moreover weakly dissociated into $GaBr_4^-$ and a catalytically extremely active ionic species such as $W[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br^+$ (**3**)[4,5] in rapid equilibrium. The X-ray structure of **2** reinforces the conclusions of these solution studies, confirming that $GaBr_3$ is effectively interacting in **2** with one of the bromo ligands of **1** and to an extent that, by the continued lengthening of the W–Br(1) bond, would lead in a relatively polar solvent (C_6H_5Cl or CH_2Cl_2) to separation of the cationic species and the $GaBr_4^-$ anion. The nearly tetrahedral arrangement of the four bromine atoms Br(1), Br(3), Br(4), and Br(5) about the gallium in **2** would appear to prepare for such a dissociation. However, we do not know yet whether such ions form a tight ion pair or are well separated in solution.

The X-ray structure of **2** also allows us, by extrapolating the changes found on passing from **1** to **2**, to try to anticipate the molecular structure of the tetracoordinate true catalytic intermediate **3**.[18] A geometry between a pseudotetrahedron and a trigonal pyramid can thus be proposed for this cation (D), in which the carbene plane will remain perpendicular to the symmetry plane of the molecule. The O–W–O angle will probably be close to 159° found in both **1** and **2**, whereas the C(13)–W–Br(2) angle might be expected to be close to 90°.

The tungsten–carbon bond length should also not be very different from that observed in **1** and **2** and keep its double bond character, but the W–Br and W–O bond lengths would need to become extremely short (in any case inferior to 2.45 and 1.80 Å, respectively) owing to the drastic electron demanding character of the 10e tungsten center and the very strong π-donation thus necessary to stabilize this species. For the same reason, extreme values are also expected for the W–O–C angles which might be only slightly inferior to 180°.

Such a geometry with such large O–W–O and W–O–C angles clearly leaves a sterically very unhindered vacant site available in the trans position to Br, between the two neopentoxo ligands, in which an olefin can be seen (E) to enter in position cis to the carbene ligand. In this site and with the particular orientation shown in (E), the appropriate orbital interactions can take place which enable formation of the metallacyclobutane intermediate involved in the olefin metathesis reaction (F).

(E)   (F)

(G)

For the formation of this metallacyclic intermediate, the filled π orbital of the olefin will donate into a vacant acceptor orbital on tungsten (cf. H) (probably 6s, 6p, and/or $5d_{x^2-y^2}$), which will eventually lead to a tungsten–carbon σ-bond. Concomitantly, the filled $d_{xy}(W)-p_y(C(13))$ π bond will overlap with the empty π^* orbital of the olefin and give rise to the carbon–carbon bond of the developing metallacycle. It is important to note that if tungsten were to be in a lower oxidation state, for example, with an additional two electrons in the d_{yz} orbital (d^4), the olefin would then orient perpendicular to the metal–carbene bond and *not* align with it in order to maximize the backbonding interaction with the metal and avoid competition with the carbene moiety for the filled d_{xy} orbital.[19] Hence in this d^4 case, metallacycle formation would require prior rotation about the metal–olefin bond, no doubt creating a barrier to metathesis. It is thus not surprising that for unstrained olefins the active catalysts are in the d^2 configuration (i.e., W(IV), Mo(IV), and probably Re(V)), supposing the carbene ligand to be considered as a neutral π-acceptor ligand.

For the metallacyclobutane so formed to be the transition state for a catalytic olefin metathesis reaction, microscopic reversibility would further necessitate a symmetric arrangement of the ligands in this transition state. A structure which satisfies this condition is shown in (F). The formation of this entity would only require a slight bending of the stabilizing ligands of **3**, the O–W–O angle having to open up by ca. 20° to form a linear arrangement, whereas the bromide ligand would have to move by ca. 30° to be aligned with the C(β)–W axis. Recently, cationic pentacoordinate metallacyclobutane species consistent with such a structure have been identified at low temperature as intermediates in the metathesis polymerization of norbornene derivatives catalyzed by **2**.[20,21]

Experimental Section

Preparation of Compounds. $W[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2$ (**1**). Exomethylenecyclopentane (3.42 mmol, 0.36 mL) was added to an orange solution of 127 mg of $W(CH-t-Bu)(OCH_2-t-Bu)_2Br_2^2$ (0.215 mmol) in dichloromethane (10 mL). After 4 h, the volatiles of the red reaction mixture were removed in vacuo, and the orange residue was washed twice with pentane to give 110 mg (87%) of product as an orange powder;[22a] ^{1}H NMR (CD_2Cl_2) δ (ppm) 5.78 (m, 4 H, W=CCH_2), 4.22 (s, 4 H, OCH_2), 1.59 (m, 4 H, =CCH_2CH_2–), 0.98 (s, 18 H, OCH_2-t-Bu); ^{13}C NMR (CD_2Cl_2, gated decoupled) δ (ppm) 90.2 (t, $^1J_{CH}$ = 149 Hz, OCH_2), 47.1 (t, $^1J_{CH}$ = 134 Hz, W=CCH_2), 34.1 (s, OCH_2CMe_3), 28.2 (t, $^1J_{CH}$ = 131 Hz, =CCH_2CH_2), 26.4 (q, $^1J_{CH}$ = 127 Hz, OCH_2CMe_3). The W=C signal could surprisingly not be observed. IR (Nujol mull) ν_{W-O} = 700 cm^{-1} (strong), ν_{W-Br} (>200 cm^{-1}) = 205 cm^{-1} (medium); in cyclohexane ν_{W-O} = 700 cm^{-1} (strong) and 665 cm^{-1} (medium).

$W[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2\cdot GaBr_3$ (**2**). To 78 mg of **1** (0.133 mmol) in 5 mL of dichloromethane was added 41 mg of $GaBr_3$ in dichloromethane (0.132 mmol). The solvent was evaporated from the reaction mixture, and the residue was washed with small quantities of pentane and dried in vacuo, yielding the crude product as a dark yellow powder. This is recrystallized as yellow crystals from hexane or pentane (83 mg, 70%). Notable physical differences between **1** and its adduct **2** are the higher solubility in hydrocarbons and the extreme sensitivity to air observed for the latter: ^{1}H NMR (CD_2Cl_2) δ (ppm) 5.94 (m, 4 H, W=CCH_2), 4.45 (s, 4 H, OCH_2), 1.62 (m, 4 H, =CCH_2CH_2), 1.03 (s, 18 H, OCH_2-t-Bu); ^{13}C NMR (CD_2Cl_2, gated decoupled, 220 K) δ (ppm) 335.7 (s, W=C), 90.0 (t, $^1J_{CH}$ = 150 Hz, OCH_2), 48.8 (t, $^1J_{CH}$ = 133 Hz, W=CCH_2), 34.2 (s, OCH_2CMe_3), 27.7 (t, $^1J_{CH}$ = 132 Hz, =CCH_2CH_2-), 25.8 (q, $^1J_{CH}$ = 125 Hz, OCH_2CMe_3); IR (Nujol mull) ν_{W-O} = 695 cm^{-1} (strong), ν_{Ga-Br} = 305 (medium), 285 (strong) cm^{-1}.

$W[C(CH_2)_3CH_2](OCH_2-t-Bu)_2Br_2\cdot C_5H_5N$ (**4**). Pyridine (0.068

(17) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771.

(18) We recognize that such an extrapolation is speculative, but, given the reactivity of this intermediate, it would appear to be at present the only means to cast some light on fine structural details of this important species.

(19) Volatron, F.; Eisenstein, O. *J. Am. Chem. Soc.* **1986**, *108*, 2173.

(20) Kress, J.; Osborn, J. A.; Greene, R.; Ivin, K. J.; Rooney, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 899.

(21) Kress, J.; Osborn, J. A.; Ivin, K. J.; Rooney, J. J. *Advances on Mechanistic Aspects and Synthetic Aspects in Polymerization*; Reidel Publishing Company, in press.

(22) Other methods of synthesis of complexes of this type have recently been described: (a) Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 1937. (b) Quignard, F.; Leconte, M.; Basset, J. M. *J. Chem. Soc., Chem. Commun.* **1985**, 1816.

Table IV. Crystal Data, Intensity Collections, and Structure Refinement Parameters for 1 and 2

	1	2
formula	$C_{30}H_{60}O_4Br_4W_2$	$C_{15}H_{30}O_2Br_5GaW$
mol weight	1172.14	895.52
cryst syst	monoclinic	monoclinic
a, Å	10.881 (3)	17.453 (5)
b, Å	18.738 (5)	11.067 (3)
c, Å	10.675 (3)	13.669 (4)
β, deg	112.39 (2)	103.52 (2)
V, Å^3	2012.4	2567.0
Z	2	4
d calcd, g·cm^{-3}	1.934	2.317
$F(000)$	1120	1664
abs coeff, μ, cm^{-1}	9.8	13.3
space group	$P2_1/c$	$P2_1/n$
cryst dim, mm	0.35 × 0.27 × 0.20	0.40 × 0.38 × 0.25
scan mode	$\theta/2\theta$ flying step-scan	$\theta/2\theta$ flying step-scan
scan speed, deg·s^{-1}	0.024	0.024
scan width, deg	1.0 + 0.34 tan θ	0.9 + 0.34 tan θ
2θ range, deg	6–60	5–45
octants	$+h,+k,\pm l$	$+h,+k,\pm l$
unique total data	6196	3702
unique obsd data	4333	2719
criterion for observ.	$I > 3\sigma(I)$	$I > 3\sigma(I)$
$n°$ of variables	181	217
transmiss factors (max/min)	1.30/0.93	1.50/0.68
$R_F/R_{\omega F}$, %	3.5/6.2	2.9/4.7
GOF	1.36	1.03

mmol, 5.5 μL) was added to 40 mg (0.068 mmol) of 1 in dichloromethane. Rapid removal of the solvent in vacuo yielded 45 mg (99%) of product as an orange powder. When its ^{1}H NMR spectrum was run just after dissolution in CD_2Cl_2, it showed this product to be the trans isomer (B).[22] After a few minutes at room temperature, this spectrum began to decrease in intensity, and a new set of signals assigned to the cis isomer (C) developed. A 30% conversion of (B) into (C) was reached after 2 h. The formation of the cis isomer (C) was not observed in C_6D_6, even after obtaining a mixture of (B) and (C) in CD_2Cl_2, evaporation to dryness, and further dissolution of the residue in this solvent: ^{1}H NMR (CD_2Cl_2) trans isomer δ (ppm) 8.96 (s, br, 2 H, o-Py), 7.83 (t of t, 1 H, p-Py), 7.43 (t of t, 2 H, m-Py), 6.28 (m, 4 H, W=CCH_2), 3.74 (s, 4 H, OCH_2), 1.56 (m, 4 H, =CCH$_2$CH_2-), 0.79 (s, 18 H, OCH$_2$-t-Bu); cis isomer δ (ppm) 9.02 (d of d, 2 H, o-Py), 8.05 (t of t, 1 H, p-Py), 7.61 (t of t, 2 H, m-Py), 6.55 (d, br, 2 H, $^2J_{H_AH_B}$ = 20 Hz, W=CCH_AH$_B$), 6.02 (d, br, 2 H, $^2J_{H_AH_B}$ = 20 Hz, W=CCH$_A$$H_B$), 4.46 (d, 2 H, $^2J_{H_AH_B}$ = 12 Hz, OCH_AH$_B$), 4.22 (d, 2 H, $^2J_{H_AH_B}$ = 12 Hz, OCH$_A$$H_B$), 1.27 (m, 4 H, =CCH$_2CH_2$), 0.94 (s, 18 H, OC$H_2$-$t$-$Bu$).

X-ray Experimental Section. Suitable red crystals of 1 were obtained by slow cooling to room temperature of a warm saturated solution in

hexane. Orange crystals of 2 were grown by slow evaporation of a pentane solution at room temperature; the sample selected for study was cleaved from a very large crystal. In both cases, standard inert atmosphere techniques were used, and the crystals were transferred above a liquid nitrogen bath to a goniostat where they were cooled to -100 °C. All the data were collected on a Philips PW 1100/16 diffractometer at -100 °C equipped with a low-temperature self-built device with use of graphite monochromatized Mo K$\bar{\alpha}$ radiation (λ = 0.71073 Å). The crystal data and data collection parameters are summarized in Table IV. No significant intensity changes were observed upon monitoring three standard reflections every hour during the entire data collection period. For all computations, the Enraf-Nonius SDP package was used[23] on a PDP 11/60 computer with the exception of local data reduction programs. The raw step-scan data were converted to intensities by using the Lehmann–Larson method[24] and then corrected for Lorentz, polarization, and absorption factors, with the latter being computed by the empirical method of Walker and Stuart.[25]

Both structures were solved by using the heavy atom method. After refinement of the heavy atoms, a difference Fourier map revealed maxima of residual electron density close to the positions expected for hydrogen atoms; they were introduced in structure factor calculations by their computed coordinates (C–H = 0.95 Å) and isotropic temperature factors such as B(H) = 1 + B eqv(C) Å^2 but not refined. Full least-squares refinements minimizing $\Sigma\omega(|F_o| - |F_c|)^2$ results are summarized in Table IV. Final difference Fourier series showed no significant maximum. Scattering factors and anomalous dispersion coefficients were taken from ref 26 (a and b).

Supplementary Material Available: Tables V and VI, anisotropic temperature factors for 1 and 2, and Tables VII and VIII, hydrogen atom coordinates for 1 and 2 (6 pages); Tables IX and X, observed and calculated structure factors amplitudes (×10) for all observed reflections for 1 and 2 (31 pages). Ordering information is given on any current masthead page.

(23) Frenz, B. A. "*The Enraf-Nonius CAD4-SDP*, In *Computing in Crystallography*; Schenk, H., Olthof-Hazekamp, R., von Koningsveld, H., Bassi, G. C., Eds.; Delft University: Delft, 1978; pp 64–71.

(24) Lehmann, M. S.; Larson, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580–584.

(25) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A398*, 158–166.

(26) (a) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2b. (b) Cromer, D. T., *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.