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Synthesis, Structure, and Unusual Reactivity of the First Norbornene Carbonyl Complexes of Tungsten

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Two new norbornene complexes of tungsten(0), $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (**1**) and *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ (**2**), have been obtained and characterized by IR and NMR spectroscopy, and initial studies of their reactivity are reported here. The molecular structure of compound **1**, relatively unstable in solution, was established by single-crystal X-ray diffraction studies. Complex **1** can, depending on reaction conditions, give rise to different types of reactions: in a pure polychloromethane solution, it transforms to a species initiating the ring-opening metathesis polymerization of norbornene (ROMP), whereas in the presence of alcohol (ca. 1%), it leads to catalytic C−C bond formation with selective addition of polychloromethane to the olefinic bond of norbornene. The two-electron chemical oxidation of stable *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ (**2**) by $SnCl_4$ gives a very labile norbornene complex of tungsten(II) (**3**). The latter compound decomposes in $CDCl_3$ solution to give chloronorbornane, whereas in benzene-d_6 or toluene-d_8 solution the products of the hydroarylation of norbornene are formed. The identities of the organometallic and organic products were established by IR, NMR, ESI-MS, and GC-MS studies.

Introduction

Due to their intermediacy in homogeneous catalysis, carbonyl−olefin complexes are some of the most important kinds of transition-metal compounds and have been the subject of considerable interest.[1,2] Some η^2-olefin complexes were detected in most homogeneous catalytic reactions of olefins, including hydrogenation, isomerization, hydrosilylation, oligomerization, polymerization, and metathesis.[1] In recent years many tungsten−olefin complexes have been prepared, and considerable insights have been gained into the metal−olefin geometry from X-ray structure analysis, spectral investigations, and theoretical studies.[2] However, some aspects of the reactivity of η^2-olefin complexes have not been completely elucidated yet. There have been no systematic studies of the influence of metal electronic configuration on the stability and reactivity of η^2-olefin ligands of tungsten carbonyl complexes. The oxidation state of the transition metal seems very important in the catalytic process.[2k,m,3]

For the past few years we have been particularly intrigued by reactions of certain tungsten carbonyls with cyclic olefins and the opportunity to initiate the ring-opening metathesis polymerization (ROMP) of cyclic olefins.[4] Concentrating our efforts on the study of tungsten(II) carbonyl complexes that contain cyclic diene ligands, we have found that the coordination of cyclic olefin to the tungsten atom is a very important step in the ROMP reaction. An η^4-diene ligand such as bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) can rearrange to give a species initiating the catalytic reaction. Tungsten(II) complexes have also been found as initiators for ROMP of bicyclo[2.2.1]hept-2-ene (norbornene, NBE).[4b] How this cyclic olefin is activated by tungsten carbonyls is an intriguing question for us.

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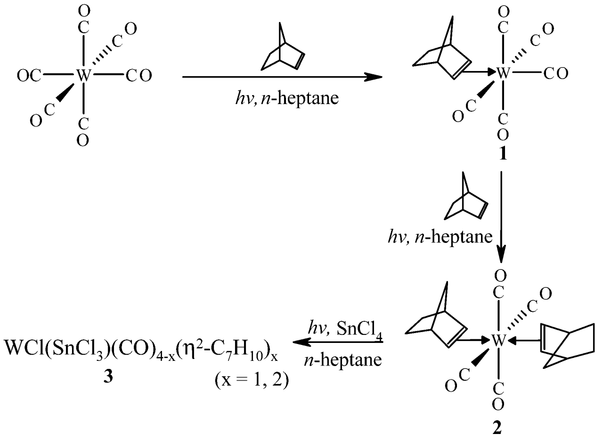
Scheme 1. Photochemical Synthesis of Norbornene Complexes of Tungsten



Here, we describe the photochemical synthesis of two novel norbornene complexes of tungsten(0), $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (**1**) and *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ (**2**), and their subsequent thermal reactions with an excess of olefins in different solvents. It has been shown that, depending upon the solvent applied, the unstable pentacarbonylnorbornene complex of tungsten(0) initiates different catalytic reactions of olefins. In a dry and pure chloroform solution, the $W(CO)_5(\eta^2\text{-}C_7H_{10})$ compound decomposes to give quantitatively the ROMP polymer, i.e., poly(1,3-cyclopentylenevinylene), and initiates the catalytic ROMP process, whereas in polychloromethane solution containing 1% of ethanol, the same compound catalyzes the selective addition of $CHCl_3$, $CDCl_3$ or CCl_4 to NBE.

Two-electron chemical oxidation of stable *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ leads to the formation of a very unstable NBE complex of tungsten(II) that in an aromatic hydrocarbon solution initiates the addition of NBE to the aromatic ring of arene with the formation of a C−C bond.

In this paper we have tried to explain how the catalytically active species can be formed from the NBE complex of tungsten.

Results and Discussion

Synthesis and Spectroscopic Properties of Norbornene Complexes of Tungsten(0). It has been known since 1963 that UV photolysis of tungsten hexacarbonyl in the presence of an olefin gives a CO-substituted product of the type $W(CO)_{6-n}(\eta^2\text{-olefin})_n$ (n = 1, 2).[5] Most of the known cyclic and acyclic olefin complexes of tungsten have been synthesized in such a photochemical reaction.[1a−h,2a−g,5,6]

As expected, the photolysis of an alkane solution of $W(CO)_6$ and NBE leads to the formation of stable *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ (**2**) via the less stable $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (**1**) (Scheme 1). Even prolonged irradiation of $W(CO)_6$ in the presence of NBE gives a mixture of compounds **1** and **2**. Separation of these two compounds can be easily achieved, due to their different stabilities. In a slowly evaporated alkane solution, compound **1** decomposes, leaving **2** in the form of air-stable, colorless needles. Regrettably, no crystals of **2** suitable for a single-crystal X-ray diffraction study were isolated. All crystals examined by X-ray crystallography appeared twinned, and consequently their detailed structure remains unknown. Separation of **1** from **2** was achieved by slow sublimation of **1** under vacuum at 40 °C. During the latter process light yellow crystals of **1** suitable for X-ray analysis were grown.

It is interesting to compare the NMR data of **1** and **2**, i.e., the coordination shifts $\Delta\delta$, of olefinic protons and carbons. In chloroform-*d* solution $\Delta\delta_H = 1.16$ and 2.70 ppm for **1** and **2**, respectively. Similarly, the $\Delta\delta_C$ value of olefinic carbon is much lower for **1** than for **2** (47.2 and 74.3 ppm, respectively). These data prove the very loose coordination of NBE to tungsten in **1** and much stronger coordination in **2**. This results from competition between the vacant π orbitals of the CO group and those of the alkene ligand for the same d−π orbitals of the tungsten atom. Another characteristic feature of NMR data for **1** is a very high value of $^1J_{WC}$: 155 Hz for a carbonyl ligand trans to an olefin ligand, while for the mutually trans carbonyl groups in **1** $^1J_{WC} = 126$ Hz, as for $W(CO)_6$. The higher value of $^1J_{WC}$ proves the stronger interaction with the tungsten atom of the CO ligand in the position trans to the olefin ligand.

Periodic monitoring of the photochemical reaction of $W(CO)_6$ in the presence of NBE by IR spectroscopy at room temperature did not indicate the formation of *cis*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$, although such an isomer was observed by IR spectroscopy, due to the characteristic four ν_{CO} bands, in several previously investigated reactions of $W(CO)_6$ and olefins.[2d−g] When the effects of photolysis of $W(CO)_6$ were followed by ^1H NMR spectroscopy at ca. 7 °C in cyclohexane-d_{12} solution containing NBE, only signals of compounds **1** and **2** were detected. As was shown by ^1H NMR, photolysis of **2** in methylcyclohexane-d_{14} solution at −50 °C leads to the formation of free NBE and compound **1**. However, photolysis of **2** at −50 °C in toluene-d_8 solution results in new proton signals characteristic for the η^2-NBE ligand appearing at δ 2.96, 2.47, 1.24, 1.16, 0.54, and ca. 0.3. The latter signals are shifted to lower field at higher temperatures and disappear above −10 °C. The changes of the chemical shift with temperature for the olefin proton signal ($\Delta\delta_H = 0.08$ at $\Delta T = 30$) are rather similar to those observed for **2** and other *trans*-$W(CO)_4(\eta^2\text{-alkene})_2$ complexes.[2f,g] Those signals could be assigned to the norbornene ligand in the $W(CO)_4(\eta^2\text{-}C_7H_{10})$(s) complex formed as a result of photochemical substitution of one olefin ligand by a molecule of the solvent (s), viz. toluene-d_8. This experiment proved that compound **2**, like other *trans*-bis(alkene) complexes losing an alkene ligand, gives very unstable coordinatively unsaturated species which can undergo trans−cis isomerization and then rearrange to the more stable compound **1**.[2d−g] Thus, if *cis*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ is formed, it must be more labile than complexes of this type involving other olefins and could not be observed even by ^1H NMR at low temperature.

Effect of Temperature on the NMR Spectra. With toluene-d_8 as solvent, the chemical shifts of most proton signals due to the norbornene ligands move to lower

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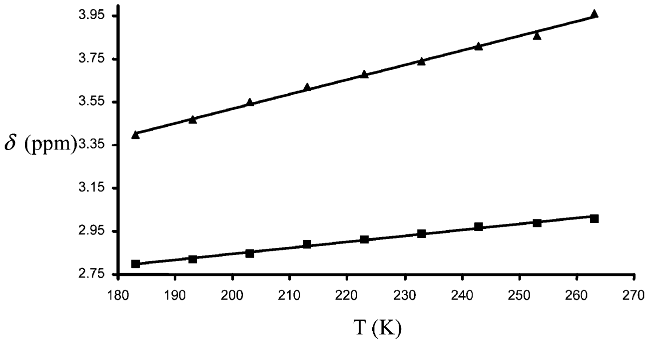

Figure 1. Plot of chemical shifts in toluene-d_8 of the olefin proton signals vs temperature in ^{1}H NMR spectra of compounds **1** (▲) and **2** (■). For **1** (▲), $y = 0.0068x + 2.1714$ and $R^2 = 0.997$, and for **2** (■), $y = 0.0027x + 2.2994$ and $R^2 = 0.994$.

field as the temperature increases in the range from −90 to +25 °C (Figure 1). However, the olefin proton signal changes are greater than for other proton signals. Most conspicuous are the shifts displayed by the protons of compound **1**. With chloroform-*d* as solvent, the proton signals vary little with temperature. However, in this solvent, chemical shifts displayed by the protons of all norbornene compounds investigated here are at lower field compared with their positions in toluene-d_8.

As previously reported,[2a,c,f,6] complexes of the *trans*-W(CO)$_4$(η^2-alkene)$_2$ type show dynamic behavior due to the possible rotation of olefin ligands around the W−(η^2-olefin) bond, and usually their NMR spectra are temperature dependent. The ^{1}H NMR spectra of complex **2** show sharp signals for all protons, suggesting relatively fast rotation around the W−(η^2-olefin) bond at room temperature (Figure 2a). Lowering the temperature to −90 °C in methylcyclohexane-d_{14} or toluene-d_8 makes it possible to observe the coalescence temperature of olefin proton signals ($T_c = -82$ °C) (Figure 2b), from which the free energy barrier to olefin rotation, $\Delta G^\ddagger = 9.3$ kcal mol^{-1}, was calculated by means of the approximate relationship.[7] This value is the lowest of those reported for *trans*-W(CO)$_4$(η^2-alkene)$_2$ complexes.[2a,c,f,6]

Single-Crystal X-ray Diffraction Studies. The molecular structure of **1** is illustrated in Figure 3. Details of the X-ray crystal structure analyses are provided in Table 1, and selected bond distances and angles are listed in Table 2. The crystal structure of complex **1** appears to be the first example of a norbornene tungsten(0) compound, although the crystal structure of several mono and bis(alkene) analogues are known.[2a,b,e,g,3b,6] The structure of complex **1** represents a distorted-octahedral arrangement of the ligands around the tungsten atom. The C−W−C angles in the *trans*-W(CO)$_2$ units are 178.3(7) and 173.4(6)°. The W−CO bond length falls in the range 1.98(1)−2.08(2) Å. The shortest W−CO bond distance is observed for CO in the trans position to the η^2-norbornene ligand. Both the C=C and W−C bond lengths are in the normal range noted for related tungsten(0) complexes containing the η^2-alkene ligand.[2a,b,e,g,3b,6] However, it is interesting that the W−C bond lengths (2.497(16) and 2.510(15) Å) are the longest of this type reported to date. Measuring 1.37(3) Å, the η^2-(C=C) bond length is practically the same as in the analogous compounds of tungsten(0), e.g. 1.38(2) Å in W(CO)$_5$(η^2-*cis*-cyclooctene)[2b] and 1.384(6) Å in W(CO)$_5$(η^2-*trans*-cyclooctene).[2e] These data are in good agreement with NMR results, indicating the very loose coordination of the alkene ligand in **1**. As was shown in Figure 4 and proved by the calculation of the four C(11)−C(12)−W−C(equatorial carbonyl) torsion angles, 42.29(7), −47.60(3), −136.24(5), and, 131.47(7)°, the C=C bond of the norbornene ligand is staggered with the respective CO−W−CO axes of an almost square planar W(CO)$_4$ moiety. A similar staggered orientation of an alkene ligand was observed for W(CO)$_5$(η^2-*cis*-cyclooctene),[2b] while an eclipsed structure was previously found for W(CO)$_5$(η^2-*trans*-cyclooctene)[2e] and theoretically predicted for W(CO)$_5$(η^2-ethene).[2k,m]

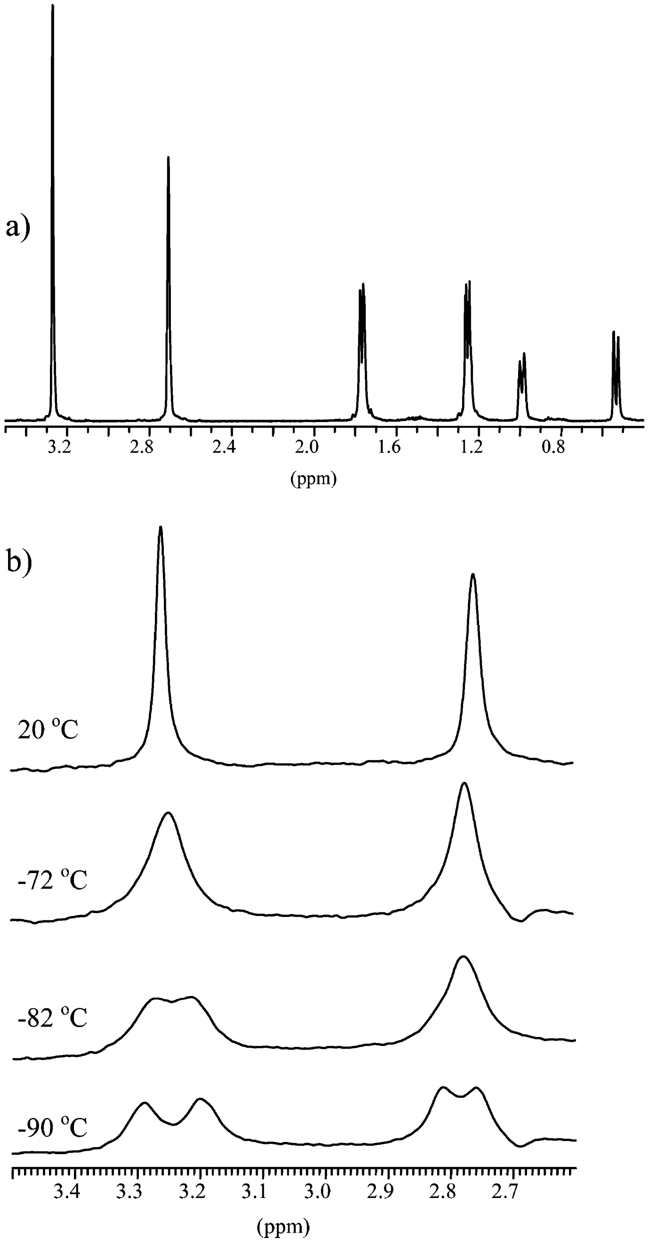

Figure 2. (a) ^{1}H NMR spectrum of **2** in CDCl$_3$ at 25 °C. (b) Part of the spectra showing changes of olefin and methine proton signals in the ^{1}H NMR spectra of **2** (500 MHz, methylcyclohexane-d_{14}) with temperature.

There is a distinctive difference between norbornene coordination to tungsten(0) in **1** and to tungsten(IV) in

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[7] Günter, H. *NMR Spectroscopy*; Georg Thieme: Stuttgart, Germany, 1973.

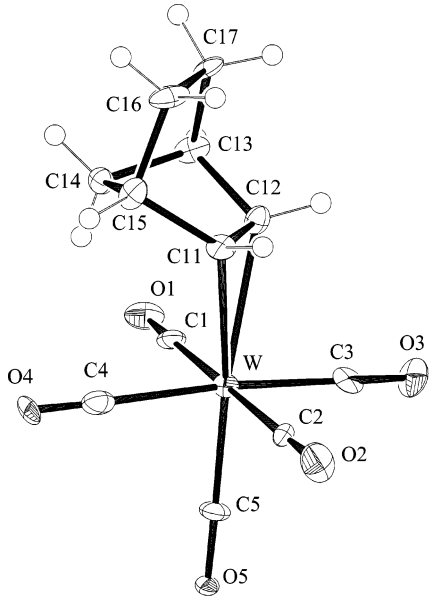

Figure 3. Molecular structure of $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (**1**).

Table 1. Crystal Data and Structure Refinement Parameters for 1

empirical formula	$C_{12}H_{10}O_5W$
fw	418.04
cryst size (mm)	0.07 × 0.03 × 0.03
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	7.162(1)
b (Å)	9.362(5)
c (Å)	10.414(2)
α (deg)	69.27(3)
β (deg)	89.51(3)
γ (deg)	72.10(3)
V (Å^3)	617.5(2)
Z	2
D_{calcd} (g/cm^3)	2.259
diffractometer	Kuma KM4CCD
radiation	Mo Kα (λ = 0.710 73 Å), graphite monochromated
temp (K)	100
μ, mm^{-1}	9.363
F(000)	396
data collected, θ(min/max) (deg)	3.01/27.00
index ranges	$-9 \le h \le 9$, $-11 \le k \le 11$, $-13 \le l \le 13$
no. of rflns collected	5491
R_{int}	0.0594
abs coeff, min/max	0.412/0.803
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	2666/0/164
final residuals: R1, wR2 ($I > 2\sigma(I)$)	0.0766, 0.1826
R1, wR2 (all data)	0.0831, 0.1853
GOF	1.160

the complex W{p-Bu^t-calix[4]-(O)$_4$}(η^2-C_7H_{10}).[2h] In the latter compound considerably shorter W–C bond lengths (2.120 and 2.139 Å) and longer C═C bond length (1.471 Å) were detected.

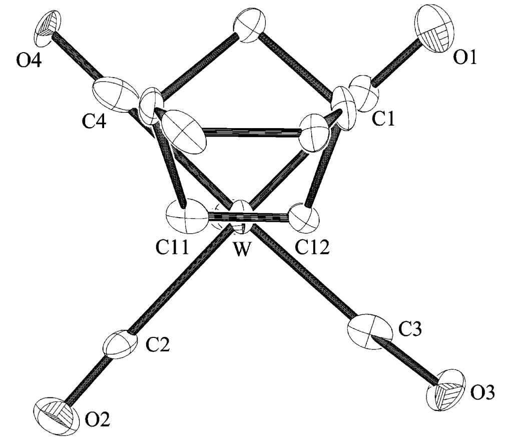

Figure 4. Projection of the norbornene ligand in **1** on a square-planar W(CO)$_4$ moiety, illustrating the staggered position of the C═C bond with the respective CO–W–CO axes. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 1

W–C(1)	2.049(16)	W–C(12)	2.510(15)
W–C(2)	2.077(19)	C(11)–C(12)	1.37(3)
W–C(3)	2.042(19)	C(11)–C(15)	1.54(2)
W–C(4)	2.071(19)	C(12)–C(13)	1.54(3)
W–C(5)	1.983(14)	C(15)–C(16)	1.56(3)
W–C(11)	2.497(16)	C(16)–C(17)	1.53(3)
C(1)–W–C(3)	87.0(7)	C(1)–W–C(4)	90.3(6)
C(1)–W–C(2)	178.3(7)	C(5)–W–C(4)	86.3(6)
C(3)–W–C(2)	91.8(7)	C(4)–W–C(2)	90.8(6)
C(1)–W–C(5)	89.8(6)	C(5)–W–C(11)	163.6(6)
C(3)–W–C(5)	87.6(7)	C(5)–W–C(12)	164.6(6)
C(2)–W–C(5)	88.9(7)	C(11)–W–C(12)	31.8(6)
C(3)–W–C(4)	173.4(6)		

Norbornene Complex of Tungsten(II). The treatment of an n-heptane solution of complex **2** with $SnCl_4$ resulted in the oxidative addition of the tin–chlorine bond to the tungsten(0) center to yield a novel, very labile norbornene complex of tungsten(II) (**3**) (Scheme 1). Characterization of complex **3** was possible only by NMR studies at low temperature. The chemical shifts of olefin proton and carbon signals of the η^2-NBE ligand at δ_H 5.05 and δ_C 89.68 in NMR spectra of **3** are very close to those observed for **1** and other tungsten compounds, in which the η^2-olefin bond is in the position trans to the CO ligand,[2a,b,e–g,6,8] e.g. δ_H 5.04 and δ_C 81.81 for one of the olefin bonds in WCl(SnCl$_3$)(CO)$_3$(η^4-C_7H_8).[8] However, the distinctive feature of the ^{1}H NMR spectrum of **3** is an unprecedented high-field position of one proton signal (δ_H −0.72 and −1.70 in chloroform-d and toluene-d_8, respectively). As was shown by two-dimensional ^{1}H–^{1}H and ^{1}H–^{13}C NMR spectra, the latter signal is due to the syn proton of the C^{7}H$_2$ bridges. The unusual upfield chemical shift of this proton signal can result from a three-center C–H···W agostic interaction involving an sp^3 C–H bond. Such interactions occur frequently in electronically unsaturated organometallic compounds.[9]

The above data suggest that the oxidative addition of tin tetrachloride to the stable *trans*-bis(norbornene) complex **2** leads to trans–cis isomerization and the formation of a complex in which alkene ligands are no longer mutually trans but, rather, trans to the CO ligand. Trans–cis isomerization of metal carbonyls

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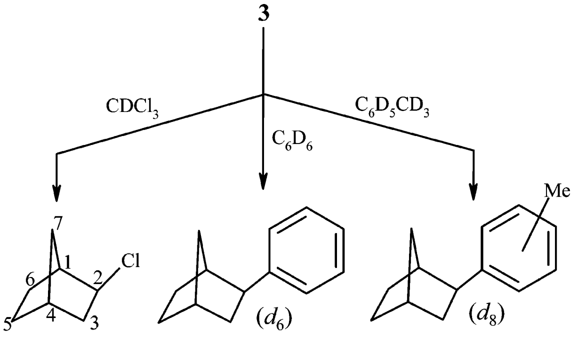
Scheme 2. Products of Decomposition of Compound 3 in Different Solvents



4a, 4b **5a** **5c**

induced by electrochemical oxidation is a very well-known process.[2m,10] In the photochemical oxidation addition reaction of tin tetrachloride to complex **2**, the latter process can be accompanied by CO and/or alkene ligand dissociation and the formation of a 16-electron complex stabilized by a three-center C−H···W agostic interaction.[9] Due to its instability, repeated attempts to isolate **3** for complete characterization were unsuccessful. As was shown by IR spectra (ν_{CO} 2100 (m), 2020 (vs), 1990 (s), and 1942 (s) cm^{-1} in the KBr pellet), during the isolation process compound **3** decomposes, losing the norbornene ligand, and (μ-Cl)$_3$W$_2$(SnCl$_3$)(CO)$_7$ is formed.[11] ^{13}C NMR spectra in chloroform-*d* solution also indicate the appearance of the latter tungsten(II) compound due to a signal at δ_{CO} 204.04 ($^1J_{WC}$ = 104 Hz), characteristic for carbonyl groups.[11] Although the unstable compound **3** decomposes to several uncharacterized products (by NMR spectroscopy), in chloroform-*d* solution it gives almost exclusively *exo*- and *endo*-2-chloronorbornane (**4a**,**b**) (Scheme 2). These derivatives were detected by ^{1}H NMR, due to the characteristic proton resonances in the region 4.30−3.80 ppm.[12] *exo*-2-Chloronorbornane (**4a**), characterized by a proton signal at δ 3.87 (doublets of doublets, J_{HH} = 7, 2, 2 Hz), is formed in 84% yield. *endo*-2-Chloronorbornane (**4b**; 16% yield by ^{1}H NMR) was observed due to a signal at δ_H 4.21 (doublets of doublets, J_{HH} = 10.6, 4.2, 4.2, 2 Hz). Compound **4a** was identified by NMR spectroscopy (^{1}H, ^{1}H−^{1}H COSY, and ^{13}C NMR) and by comparing the results with those for an authentic sample.[12e]

The most probable way in which **4** is formed is the insertion of an η^2-NBE ligand into the W−Cl bond of compound **3** followed by reductive elimination with the solvent as H or D atom donor.

However, compound **3**, when dissolved in the aromatic hydrocarbon solvent, decomposes with the formation of a C−C bond to give the products of a hydroarylation reaction of the C═C double bond of norbornene (Scheme 2). In benzene-d_6 solution *exo*-2-(phenyl-d_5)-3-*d*-norbornane (**5a**) is formed. Compound **5a** was detected by ^{1}H and ^{1}H−^{1}H COSY NMR spectroscopy and GC-MS analysis and by comparing the results with those for *exo*-2-phenylnonorbornane (**5b**) synthesized according to a previously described procedure.[13] C−C bond formation similar to that in benzene-d_6 solution was observed in toluene-d_8. *exo*-2-(Methylphenyl-d_7)-3-d_1-norbornane (**5c**) formed in the reaction of **3** in toluene-d_8 was identified by GC-MS analysis as three positional isomers, appearing with the retention time increasing in the order *meta*, *para*, *ortho*, and formed in the ratio 1:5:3, respectively. Arylnorbornane derivatives were easily detected by ^{1}H NMR spectroscopy due to the resonances of the proton at carbon C^{2}H: viz., a doublet of doublets (J_{HH} = 8.6, 5.7 Hz) at δ_H 2.65 and a triplet (J_{HH} = 7.2 Hz) at δ_H 2.60 in toluene-d_8 but after vacuum transfer and dissolution in CDCl$_3$ at δ_H 2.78 and 2.68, respectively. The intensity ratio of the latter signals (ca. 1:2) indicates an overlapping of signals due to the para and meta derivatives. The resonance of the neighboring proton in the C^{3}HD group was observed as a doublet (J_{HH} = 7.2 Hz) at δ_H 1.63 and 1.70 in toluene-d_8 and CDCl$_3$, respectively.

It is very probable that the C−C-bond-forming reaction occurs through a chloronorbornyl intermediate, which forms as the product of the insertion of an η^2-NBE ligand into the W−Cl bond, thus opening the coordination sphere of tungsten for an incoming arene ligand. The formation of C−C and C−D bonds, followed by the elimination of **5c**, regenerates the W−Cl bond of the starting tungsten(II) compound (**3**). It must be noted that the hydroarylation reaction of the C═C double bond has been observed in reactions catalyzed mainly by ruthenium, rhodium, iridium, and palladium compounds.[14]

Reactivity of 1 toward Olefins. Initiation of ROMP. Although the chemistry of olefin complexes formed during the photolysis of W(CO)$_6$ in the presence of olefin has been rather extensively explored,[1,2] there was no example of the use of this type of compound as a precatalyst in the ROMP reaction of cyclic olefins. ^{1}H NMR monitoring of **1** and **2** (6:1 ratio by NMR) in chloroform-*d* solution showed the complete disappearance of **1** over a period of 24 h and the formation of poly(1,3-cyclopentylenevinylene) (**6**) with a yield of ca. 100% by NMR (Scheme 3). Thus, in CDCl$_3$ solution compound **1** yields an organic product derived from the original η^2-olefin ligand. Compound **6** was identified due to the characteristic proton signals (Figure 5a).[4] A comparison of the integrals of the signals at 5.33 and 5.19 ppm leads

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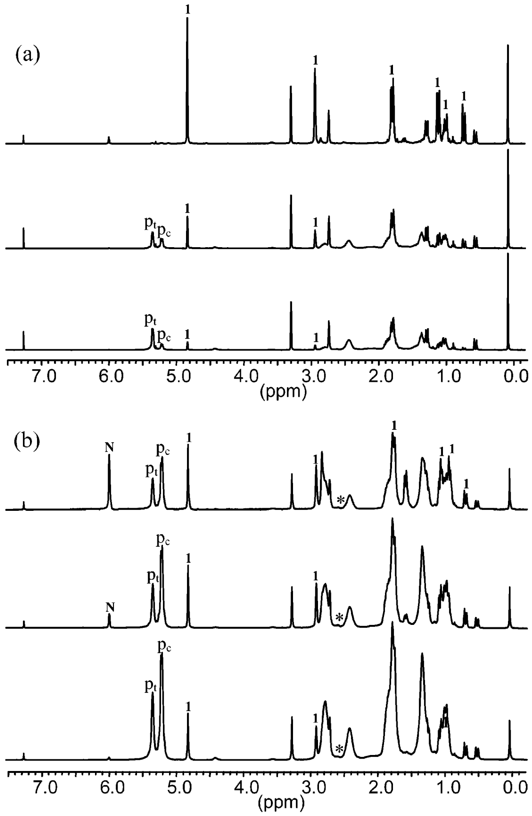
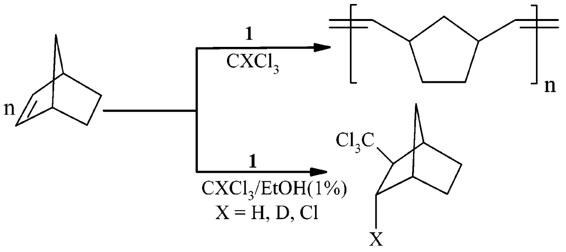


Figure 5. (a) ^1H NMR spectra (300 MHz, 25 °C, $CDCl_3$) showing the decay of **1** and the formation of a ROMP polymer containing trans (p_t) and cis (p_c) olefin units. (b) Formation of a ROMP polymer initiated by **1** in the presence of an excess of NBE (N). Unchanged peaks are due to compound **2**. The signal denoted by an asterisk is due to the proton (C^2H) of the NBE−$CDCl_3$ adduct.

Scheme 3. Reactivity of Compound 1



to the determination of the content of trans olefin units in the polymer at ca. 77%. However, in the presence of an excess of NBE, the disappearance of **1** is much slower and 70% of the polymer formed has the cis configuration. A similar high content of cis units in polynorbornene (65−86%) was observed earlier in a reaction initiated in $CDCl_3$ solution by a pentacarbonyl carbene complex of tungsten(0), $(CO)_5W{=}C(OMe)Ph$.[15] After the additional amounts of norbornene were completely consumed and transformed quantitatively to the ROMP polymer, the decomposition of **1** continued (Figure 5b). Different geometric configurations of the polymer formed suggest variant structures of propagation metallacarbene species in ROMP reactions presented in Figure 5.[4] During the ROMP process complex **2** remained unchanged (Figures 5 and 6). Thus, it is clear that only **1** transforms to the species initiating ROMP. In this conversion the solvent plays a very important part. What is an interesting feature of this reaction is the formation of $CHCl_3$ in the reaction carried out in $CDCl_3$ or CCl_4 solution, as indicated by the increase in the intensity of the signal at δ_H 7.24 in Figures 5 and 6 and in the additional experiments with the external standard D_2O. This result suggests that, due to the electron transfer from the tungsten(0) center to a polychloromethane molecule, the $^{\bullet}CCl_3$ radical must be formed, which is capable of abstracting a hydrogen atom from the η^2-NBE ligand in **1** to give $CHCl_3$. Thus, the carbene species can be generated by a mechanism involving an initial charge-transfer interaction between the metal complex and polychloromethane, followed by an electron transfer and the formation of the cationic complex $\mathbf{1}^+$. There is a considerable amount of evidence for such interactions between organometallic compounds as electron donors and polyhaloalkanes as electron acceptors.[16]

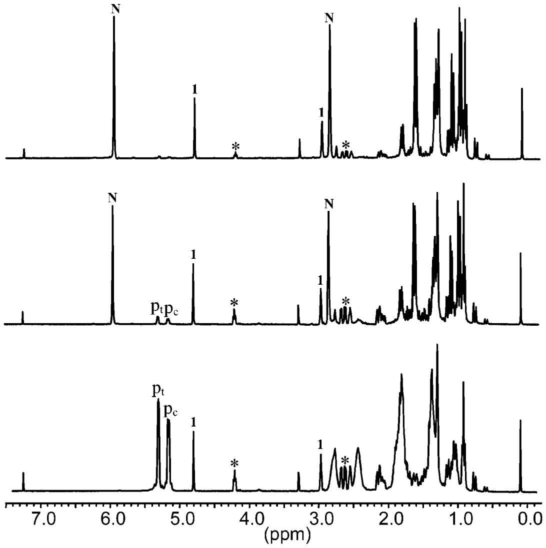


Figure 6. ^1H NMR spectra (300 MHz, 25 °C, CCl_4/$CDCl_3$ (10%) showing the decay of NBE (signals denoted by N) and the formation of ROMP polymer (p_t and p_c) and the NBE−CCl_4 adduct (signals denoted by an asterisk) in reactions initiated by **1**.

A possible mechanism for the formation of carbene species initiating the ROMP reaction is shown in Scheme 4: (i) electron transfer from **1** to the polychloromethane molecule $CXCl_3$ (X = D, H, Cl) to give the organometallic radical cation $\mathbf{1}^{\bullet+}$ and the radical anion $CXCl_3^{\bullet-}$; (ii) polarization of the C=C double bond of the η^2-NBE ligand in the organometallic radical cation $\mathbf{1}^{\bullet+}$ and simultaneous appearance of the $^{\bullet}CCl_3$ radical and the X^- anion as a consequence of C−X bond splitting in the radical anion $CXCl_3^{\bullet-}$; (iii) addition of the X^- anion to a positively charged carbon atom (C_β) in $\mathbf{1}^{\bullet+}$ to give an η^1-norbornyl ligand; (iv) rearrangement of the η^1-norbornyl ligand to a carbene species as a result of hydrogen atom abstraction from α-carbon by the $^{\bullet}CCl_3$ radical and the formation of a $CHCl_3$ molecule.

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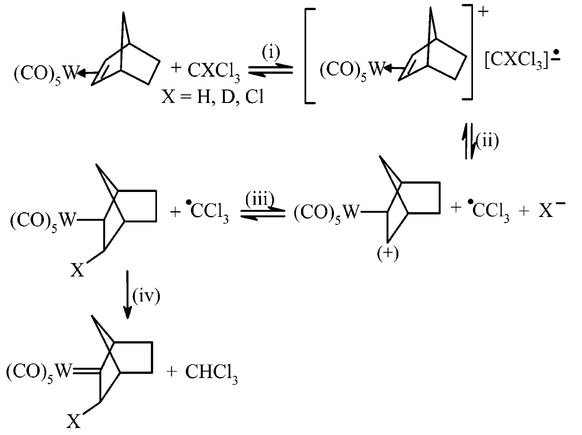
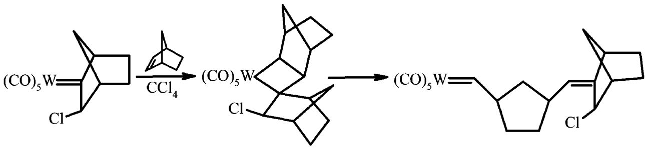
Scheme 4. Proposed Mechanism for the Formation of the Carbene Ligand from the η^2-Olefin Ligand of 1 in Polychloromethane Solution



A key role in the formation of carbene species from **1** is played by one-electron oxidation of **1** and the appearance of the $^{\bullet}CCl_3$ radical. The formation of the trichloromethyl radical was observed earlier by the EPR method in photochemical reactions of $M(CO)_6$ (M = W, Mo, Cr) and CCl_4.[17] Simultaneously generated organometallic radicals, 17-electron complexes of the type $M(CO)_5Cl$, were also detected.[17] However, to our knowledge nobody has observed stable bonding of the $^{\bullet}CCl_3$ radical to the tungsten atom, although such metal−carbon bond formation has been detected with iron, osmium, or cobalt[18] and has been considered in the carbene-species-initiated metathesis of olefins.[1e,19] For comparison, during the reaction of $W(\eta^5\text{-}C_5H_5)_2(CO)$ with CCl_4 carried out in the dark, the addition of the $^{\bullet}CCl_3$ radical to the η^5-cyclopentadiene ligand and the chloride anion to the tungsten atom was observed.[20] It seems very probable that the reactivity of the one-electron-oxidized species $\mathbf{1}^{\bullet+}$ is centered at the ligand, similarly as in previously observed reactions of organometallic compounds with polyhaloalkanes.[16d,e,20]

Although there is no proof that the carbene species formed from **1** would still contain the same number or arrangement of carbonyl groups, we can suppose that the formation of tungstacarbene and tungstacyclobutane (Schemes 4 and 5) is accompanied by a change in the formal oxidation state of tungsten from 0 to II and the increase of the coordination number from 6 to 7. Seven-coordinate tungsten(II) carbonyl complexes are well-known precatalysts for ROMP of cyclic olefins.[4,21]

Scheme 5. Formation of ROMP Polymer in the Reaction Initiated by 1 in CCl_4 Solution



It must be noted that the activation of the C−Cl bond and the formation of a $^{\bullet}CHCl_2$ or $^{\bullet}CH_2Cl$ radical have always been observed in the course of photoassisted oxidative addition reactions of chloroform or dichloromethane to a transition-metal complex.[17a,b,18a,c,19e] However, in the dark reaction of **1** with chloroform investigated here, the activation of the C−D or C−H bond is predominant. This fact is proved by the selective formation of *exo*-2-trichloromethylnorbornane (**7a**) when the formation of the carbene species and ROMP reaction were stopped by the addition of small amounts of alcohol (1%) to the $CHCl_3$ solution of **1**.

Careful examination of ^1H NMR spectra measured during the ROMP reaction in CCl_4 solution revealed the presence of a CHCl unit indicated by a low-intensity signal at δ ca. 3.8 (Figure 6). The latter signal is also observed in ^1H NMR spectra of the polymer separated from the reaction mixture by precipitation with methanol. The presence of chlorine atoms in that polymer was also proved by elemental analysis (Cl:C = 1:17.3) and by ESI-MS analysis. The ESI technique enabled us to detect fragments containing from two to five molecules of NBE and one or two chlorine atoms.

The addition of polychloromethane to the olefin bond of NBE and the formation of the NBE−$CHCl_3$ or NBE−CCl_4 adduct is a competitive reaction to ROMP initiated by **1**. The appearance of small amounts of this type of adduct was observed by ^1H NMR during the reaction of NBE initiated by **1** in $CDCl_3$ or CCl_4 solution (Figures 5 and 6).

Addition of Halomethanes to Olefin Catalyzed by 1. During the investigation of ROMP reaction initiation by **1**, a significant solvent effect, which changed the course of the reaction, was observed. In dry chloroform solution containing ca. 1% of alcohol (MeOH, EtOH, or *i*-PrOH), compound **1** selectively transformed NBE to *exo*-2-trichloromethylnorbornane (**7a**)[12b] (Scheme 3). Using this very labile norbornene complex of tungsten(0) as the initiator, compound **7a** was synthesized at room temperature with high yield (87%) and 100% selectivity, as was shown by NMR spectroscopy and GC-MS analysis. Under similar conditions, but in CCl_4/EtOH (1%) solution, compound **1** selectively converts NBE to the NBE−CCl_4 adduct (**7c**)[12a,b,d] in 4 h. In the reaction carried out in $CDCl_3$/EtOH (1%) the formation of *exo*-2-trichloromethyl-3-*d*-norbornane (**7b**) was observed by ^1H NMR spectroscopy.

Upon prolonged heating (ca.. 100 °C) compound **7a** eliminates hydrogen chloride to give $C_7H_{10}(=CCl_2)$,[12b] but in moist air the trichloromethyl group of compound **7a** undergoes hydrolysis to give the carboxy unit of *exo*-

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2-carboxynorbornane.[12e] The latter products were identified by NMR spectroscopy.

The presented catalytic activity of tungsten carbonyl complex **1** in the reaction known as Kharasch addition[22] is comparable with catalytic activity observed recently in reactions catalyzed by Ru, Rh, Ni, Pd, and Mo complexes.[23] However, the main advantages of our catalytic system are the high selectivity and the extremely mild conditions of the C−C bond-forming reaction.

Studies on the application of compound **1** as the catalyst in the addition reaction of NBE and other cyclic and acyclic olefins to different polyhalomethanes are in progress.

Conclusions

Photochemical substitution of CO by norbornene in $W(CO)_6$ was used in the synthesis of new norbornene carbonyl complexes of tungsten(0). The structure of those compounds was characterized by IR and NMR spectroscopy. The molecular structure of compound **1**, relatively unstable in solution, was established by single-crystal X-ray diffraction studies.

In this paper we present evidence that the described norbornene complexes of tungsten are long-lived precatalytic intermediates in the transformation of olefins proceeding under extremely mild conditions. They participate in a sequence of carbon−carbon bond-forming reactions such as hydroarylation, ring opening metathesis polymerization, and addition of polyhalomethanes to the olefin bond of norbornene.

The compound $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (**1**) in pure and dry chloroform or carbon tetrachloride solution transforms in the dark to a species initiating the catalytic ring opening metathesis polymerization of norbornene, but in the presence of 1% of alcohol this reaction initiates the addition of polychloromethanes to the olefin bond. This is the first effective W-based catalyst playing the role of a hydrogen atom transfer agent in chloroform addition to a cyclic olefin.

Also, it is worth pointing out that the oxidative addition of $SnCl_4$ to a very stable norbornene complex of tungsten(0) leads to the formation of a labile norbornene compound of tungsten(II), which in aromatic hydrocarbon solution initiates C−C bond formation and the addition of norbornene to the aromatic ring of arene, thus activating the arene C−H bond.

Experimental Section

General Procedures. The synthesis and manipulation of all chemicals were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Solvents and liquid reagents were predried with CaH_2 (hydrocarbons) or P_2O_5 (chloromethanes) and vacuum-transferred into small storage flasks prior to use. Bicyclo[2.2.1]hept-2-ene (norbornene, NBE) was used as supplied (Aldrich, 99% grade). IR spectra were measured with a Nicolet-400 FT-IR instrument. ^1H and ^{13}C NMR (proton coupled and decoupled) and two-dimensional $^1H-^1H$ COSY and $^1H-^{13}C$ HMQC NMR spectra were recorded with a Bruker AMX 300 or 500 MHz instrument. All chemical shifts are referenced to residual solvent protons for ^1H NMR (δ 7.24, $CDCl_3$; δ 2.10, toluene-d_8; δ 7.20, benzene-d_6; δ 1.38 cyclohexane-d_{12}; δ 1.21, methylcyclohexane-d_{14}) and to the chemical shift of the solvent for ^{13}C NMR (δ 77.00, $CDCl_3$; δ 20.4, toluene-d_8; δ 27.8, cyclohexane-d_{12}). The photolysis source was an HBO 200 W high-pressure Hg lamp. Elemental analyses were performed by the Analytical Laboratory of the Faculty of Chemistry at the University of Wrocław with a Perkin-Elmer 2400 CHN instrument. Analyses of organic reaction products were performed on a Hewlett-Packard GC-MS system as well as on a Finnigan MAT TSQ 700 triple-stage quadrupole mass spectrometer equipped with an electrospray ionization (ESI) source.

Photochemical Reactions. Photochemical reactions involving $W(CO)_6$ and NBE carried out in alkane solution at room temperature were investigated by following the IR spectra. The products of these reactions in toluene-d_8 or $CDCl_3$ solution were tracked by ^1H and ^{13}C NMR measurements at temperatures in the range from −90 to +25 °C. In a typical experiment, a solution of $W(CO)_6$ (0.1 g, 0.28 mmol) and NBE (0.1 g, 1.1 mmol) in freshly distilled heptane (30 mL) was irradiated through quartz at room temperature. After different times of photolysis (0.5−4.5 h) the solvent was removed under vacuum at room temperature, the residual solid dissolved in toluene-d_8 or $CDCl_3$ (0.7 mL), and the resulting solution transferred to the NMR tube.

NMR Tube Reactions. The photochemical reactions were also followed directly by ^1H NMR measurements at low temperature. In a typical experiment, a solution of a carbonyl complex of tungsten (ca. 0.01 g) in toluene-d_8, methylcyclohexane-d_{14}, or cyclohexane-d_{12} (0.7 mL) was cooled to an appropriate temperature and the NMR tube was subjected to broad-band UV−visible irradiation. The tube was transferred to a precooled sample holder of the NMR spectrometer and the ^1H NMR spectrum of the solution recorded.

Synthesis of $W(CO)_5(\eta^2\text{-}C_7H_{10})$ (1) and *trans*-$W(CO)_4(\eta^2\text{-}C_7H_{10})_2$ (2). A solution of $W(CO)_6$ (0.1 g, 0.28 mmol) and NBE (0.1 g, 1.1 mmol) in *n*-heptane (30 mL) was irradiated through quartz at room temperature. The course of the reaction was monitored by IR measurements, and photolysis was stopped when the IR band of **1** at 2078 cm^{-1} reached its maximum intensity (after about 1.5 h). The volatile materials were then stripped off the reaction mixture at room temperature. The residue was analyzed immediately by ^1H NMR in $CDCl_3$ or toluene-d_8 solution, which showed that the ratio of compounds **1** and **2** was about 6:1. In $CDCl_3$ solution compound **1** decays within 24 h, but in the solid state it is stable for weeks. To obtain pure compound **2**, the above reaction mixture was left in the open air to allow compound **1** to decompose and the solvent to evaporate. During this process compound **2** crystallized as colorless needles on the reactor walls. Repeated crystallization from *n*-heptane made it possible to obtain analytically pure crystals of **2** (15 mg, 11% yield). Separation of **1** and **2** and preparation of **1** in a pure crystal form was possible by slow sublimation under vacuum at 40 °C.

Data for **1** are as follows. IR (ν_{CO}, cm^{-1}; *n*-heptane): 2078 (w), 1951 (vs). IR (ν_{CO}, cm^{-1}; KBr pellet): 2077 (m), 1998 (m), 1923 (vs). ^1H NMR (δ, $CDCl_3$, 300 MHz, 25 °C): 4.81 (s, 2H, $^1J_{CH} = 170$ Hz, $^2J_{CH} = 38$, $^3J_{HH} = 4.7$ Hz; $C^{2,3}H$), 2.91 (s, 2H, $^1J_{CH} = 149$ Hz; $C^{1,4}H$), 1.77 (d, $J_{HH} = 8.2$ Hz, 2H; *exo*-$C^{5,6}H_2$), 1.09 (dd, $J_{HH} = 8.2$, 2.4 Hz, 2H; *endo*-$C^{5,6}H_2$), 0.98 (d, $J_{HH} =$

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10.4 Hz; 1H, *syn*-C^7H_2), 0.71 (d, J_{HH} = 10.4 Hz, 1H; *anti*-C^7H_2). ^{1}H NMR (*δ*, toluene-d_8, 300 MHz, 25 °C): 4.13 (2H; $C^{2,3}H$), 2.37 (2H; $C^{1,4}H$), 1.27 (2H; *exo*-$C^{5,6}H_2$), 0.75 (1H; *syn*-C^7H_2), 0.56 (2H; *endo*-$C^{5,6}H_2$), 0.21 (1H; *anti*-C^7H_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$, 125 MHz, 25 °C): 200.60 (1 CO, $^1J_{WC}$ = 155 Hz), 197.48 (4 CO, $^1J_{WC}$ = 126 Hz), 88.55 (2C; $C^{2,3}H$), 42.55 (2C; $C^{1,4}H$), 37.58 (1C; C^7H_2), 26.47 (2C; $C^{5,6}H_2$). $^{13}C\{^1H\}$ NMR (*δ*, toluene-d_8, 125 MHz, −10 °C): 199.99 (1 CO), 196.88 (4 CO), 87.95 (2C; $C^{2,3}H$), 41.95 (2C; $C^{1,4}H$), 36.98 (1C; C^7H_2), 25.87 (2C; $C^{5,6}H_2$). UV−vis (λ_{max}, nm (*ε*, L mol^{-1} cm^{-1}), *n*-heptane): 252 (6.0×10^4), 270 (1.4×10^4), 312 (7.2×10^3), 352 (2.1×10^3).

Data for **2** are as follows. IR (ν_{CO}, cm^{-1}, *n*-heptane): 1940 (vs). IR (ν_{CO}, cm^{-1}, KBr pellet): 1948 (s), 1926 (vs), 1909 (vs). ^{1}H NMR (*δ*, $CDCl_3$, 300 MHz, 25 °C): 3.27 (s, 2H, $^1J_{CH}$ = 166 Hz, $^2J_{CH}$ = 40, $^3J_{HH}$ = 5.3 Hz; $C^{2,3}H$), 2.71 (s, $^1J_{CH}$ = 148 Hz, 2H; $C^{1,4}H$), 1.77 (d, J_{HH} = 7.6 Hz, 2H; *exo*-$C^{5,6}H_2$), 1.26 (dd, J_{HH} = 7.6, 2.2 Hz, 2H; *endo*-$C^{5,6}H_2$), 0.99 (d, J_{HH} = 10.5 Hz, 1H; *syn*-C^7H_2), 0.54 (d, J_{HH} = 10.5 Hz, 1H; *anti*-C^7H_2). ^{1}H NMR (*δ*, toluene-d_8, 300 MHz, 25 °C): 3.07 (2H; $C^{2,3}H$), 2.57 (2H; $C^{1,4}H$), 1.54 (2H; *exo*-$C^{5,6}H_2$), 1.03 (1H; *syn*-C^7H_2), 1.00 (2H; *endo*-$C^{5,6}H_2$, 0.33 (1H; *anti*-C^7H_2). ^{13}C NMR (*δ*, $CDCl_3$, 125 MHz, 25 °C): 201.00 (4 CO, $^1J_{WC}$ = 124 Hz), 60.94 (d, 2C, $^1J_{CH}$ = 168 Hz; $C^{2,3}H$), 41.34 (d, 2C, $^1J_{CH}$ = 144 Hz; $C^{1,4}H$), 34.28 (t, 1C, $^1J_{CH}$ = 133 Hz; C^7H_2), 28.88 (t, 2C, $^1J_{CH}$ = 135 Hz; $C^{5,6}H_2$). $^{13}C\{^1H\}$ NMR (*δ*, toluene-d_8, 125 MHz, −10 °C): 201.50 (4 CO), 60.40 ($C^{2,3}H$), 41.65 ($C^{1,4}H$), 34.62 (C^7H_2), 28.93 ($C^{5,6}H_2$); UV−vis (λ_{max}, nm (*ε*, L mol^{-1} cm^{-1}), *n*-heptane): 242 (3.3×10^4), 308 (3.8×10^3). Anal. Calcd for $C_{18}H_{20}O_4W$ (M_r = 484.19): C, 44.65; H, 4.16. Found: C, 44.32, H; 4.22.

X-ray Diffraction Studies. Crystal data for **1** were collected at 100 K on a KM4 Kodak CCD chip diffractometer with graphite-monochromated Mo Kα radiation, generated from a Glass Diffraction X-ray tube operated at 50 kV and 35 mA. The images were indexed, integrated, and scaled using the KUMA data reduction package.[24] A light yellow crystal with approximate dimensions of 0.07 × 0.05 × 0.03 mm was cut from a larger one and used for data collection. The experimental details together with crystal data are given in Table 1. The structure was solved by the heavy-atom method using SHELXS97[25] and refined by the full-matrix least-squares method on all F^2 data.[26] The non-H atoms were included in the refinement, with anisotropic displacement parameters, and the H atoms were included from the geometry of the molecules and were not refined. The data were corrected for absorption,[24] with minimum/maximum absorption coefficients of 0.412/0.803. Crystallographic data for compound **1** have been deposited at the Cambridge Crystallographic Data Centre (No. CCDC-227647). More comprehensive crystallographic data are available as Supporting Information.

Photolysis of 2 Followed by ^{1}H NMR. A solution of **2** (0.01 g, 0.02 mmol) in toluene-d_8 (0.7 mL) was cooled in the NMR tube to −60 °C and subjected to broad-band UV−visible irradiation. The tube was transferred to the precooled sample holder of the NMR spectrometer and the ^{1}H NMR spectrum of the solution recorded in the range from −60 to +25 °C. As a result of irradiation new proton signals appeared which can be assigned to free NBE (*δ* 5.96 s, 2H, $C^{2,3}H$; *δ* 2.76 s, 2H, $C^{1,4}H$; *δ* 1.53 d, 2H, *exo*-$C^{5,6}H_2$; *δ* 1.41, d, *syn*-C^7H_2; *δ* 0.99 d, 2H, *endo*-$C^{5,6}H_2$; *δ* 0.97, d, 1H, *anti*-C^7H_2), compound **1**, and the new norbornene complex of tungsten. The chemical shifts of proton signals of the new norbornene ligand were observed at −50 °C at *δ* 2.96 (s, 2H; $C^{2,3}H$), 2.47 (s, 2H; $C^{1,4}H$), 1.24 (d, J_{HH} = 8.3 Hz, 2H; $C^{5,6}H_2$), 1.16 (d, J_{HH} = 10.1 Hz, 1H; *syn*-C^7H_2), 0.54 (d, J_{HH} = 8.3 Hz, 2H; $C^{5,6}H_2$). The signal due to the anti proton at the C^7H_2 group is about 0.3 ppm but is obscured by signals due to **1** and **2**. At higher temperature (−20 °C) the first two signals were shifted to lower field, *δ* 3.04 and 2.49, respectively, and all signals disappeared at temperatures above −10 °C. Irradiation of **2** in methylcyclohexane-d_{14} at −50 °C leads to the formation of free NBE and compound **1**.

Oxidation of 2 by $SnCl_4$: Formation of 3. A solution of **2** (0.1 g, 0.23 mmol) and $SnCl_4$ (0.03 cm^3, 0.23 mmol) in *n*-heptane (25 mL) was irradiated at 0 °C. The course of the reaction was monitored by IR measurements, and photolysis was stopped when the IR band of **2** at 1940 cm^{-1} decayed (about 10 min). During this time the solution became yellow and a yellow precipitate formed. The volatile materials were then evaporated under vacuum at 0 °C. The residue was analyzed immediately by ^{1}H NMR in $CDCl_3$ solution at −15 °C and showed the formation of the new norbornene complex **3**. ^{1}H NMR (*δ*, $CDCl_3$, 300 MHz, −15 °C): 5.04 (s, 2H; $C^{2,3}H$), 3.11 (s, 2H; $C^{1,4}H$), 2.10 (d, J_{HH} = 9.5 Hz, 2H; *exo*-$C^{5,6}H_2$), 1.46 (d, J_{HH} = 8.6 Hz, 2H; *endo*-$C^{5,6}H_2$), 0.88 (d, J_{HH} = 11 Hz, 1H; *anti*-C^7H_2), −0.72 (d, J_{HH} = 11 Hz, 1H; *syn*-C^7H_2). ^{1}H NMR (*δ*, toluene-d_8, 500 MHz, −10 °C): 4.05 (2H; $C^{2,3}H$), 1.94 (2H; $C^{1,4}H$), 1.04 (2H; *exo*-$C^{5,6}H_2$), 0.34 (2H; *endo*-$C^{5,6}H_2$), −0.28 (1H; *anti*-C^7H_2), −1.70 (1H; *syn*-C^7H_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$, 125 MHz, −15 °C): 212.74 ($^1J_{WC}$ = 128 Hz, CO), 205.26 ($^1J_{WC}$ = 110 Hz, CO), 89.68 ($C^{2,3}H$), 42.76 ($C^{1,4}H$), 38.12 (C^7H_2), 25.24 ($C^{5,6}H_2$).

Decomposition of 3 in $CDCl_3$: Formation of *exo*-2-Chloronorbornane (4a) and *endo*-2-Chloronorbornane (4b). Periodic monitoring of compound **3** by ^{1}H NMR in chloroform-*d* solution showed the decay of signals due to the norbornene ligand in **3** and the appearance of signals which as a result of ^{1}H, ^{1}H−^{1}H COSY, and $^{13}C\{^1H\}$ NMR studies were assigned to compounds **4a** and **4b** formed in the ratio 5.1:1. **4a**: ^{1}H NMR (*δ*, $CDCl_3$, 500 MHz, 25 °C) 3.87 (ddd, J_{HH} = 7, 2, 2 Hz, 1H; C^2HCl), 2.38 (d, J_{HH} = 4.7 Hz, 1H; C^1H), 2.30 (t, J_{HH} = 4.4 Hz, 1H; C^4H), 1.90−1.80 (m, 2H; C^3H_2), 1.75 (dd, J_{HH} = 10, 2.0 Hz, 1H; C^7H_2), 1.70−1.00 (m, 5H, $C^{5,6,7}H_2$); $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$, 125 MHz, 25 °C) 62.55 (1C; C^2HCl), 46.00 (1C; C^1H), 43.57 (1C; C^3H_2), 36.50 (1C; C^4H_2), 35.05 (1C; C^7H_2), 28.08 (1C; C^5H_2), 26.70 (1C; C^6H_2); **4b**: ^{1}H NMR (*δ*, $CDCl_3$, 500 MHz, 25 °C) 4.20 (dddd, J_{HH} = 10.6, 4.2, 4.2, 2 Hz, 1H; C^2HCl); $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$, 125 MHz, 25 °C) 61.34 (1C; C^2HCl), 43.60 (1C; C^1H), 40.89 (1C; C^3H_2), 38.04 (1C; C^4H_2), 37.07 (1C; C^7H_2), 29.43 (1C; C^5H_2), 22.23 (1C; C^6H_2).

Decomposition of 3 in C_6D_6: Formation of *exo*-2-Phenyl-d_5-3-*d*-norbornane (5a). Periodic monitoring of compound **3** by ^{1}H NMR in benzene-d_6 solution showed the decay of signals due to the norbornene ligand in **3** and the appearance of signals which as a result of ^{1}H and ^{1}H−^{1}H COSY NMR studies were assigned to compound **5a** ($C_{13}H_{10}D_6$, M_r = 178.30). GC-MS (*m*/*z* (relative intensity)): 175 (35), 160 (1), 147 (10) 132 (18), 118 (17), 107 (100), 94 (71), 81 (58), 67 (41), 53 (8), 41 (12). ^{1}H NMR (*δ*, benzene-d_6, 500 MHz, 25 °C): 2.64 (t, J_{HH} = 7.2 Hz, 1H; C^2H), 2.31 (s, 1H; C^1H), 2.23 (s, 1H; C^4H), 1.64 (d, J_{HH} = 7.2, 1H; C^3HD), 1.49 (m, 3H; $C^{6,5,7}H_2$), 1.23 (m, 1H; C^6H_2), 1.18 (m, 1H, C^5H_2), 1.08 (d, J_{HH} = 9.6, 1H; C^7H_2).

Characteristics of *exo*-2-Phenylnorbornane (5b). Compound **5b** was prepared by the reaction of benzene with norbornene in concentrated sulfuric acid, according to a previously described procedure,[13a] and characterized by GC-MS analysis and ^{1}H, ^{1}H−^{1}H COSY, ^{1}H−^{13}C HMQC, and $^{13}C\{^1H\}$ NMR studies.[13b,c] **5b** ($C_{13}H_{16}$): M_r = 172.27. GC-MS (*m*/*z* (relative intensity)): 172 (40), 157 (1), 144 (10), 129 (15), 115 (17), 104 (100), 92 (44), 81 (33), 67 (20), 51 (5), 39 (7). ^{1}H NMR (*δ*, $CDCl_3$, 300 MHz, 25 °C): 7.3−7.1 (m, 5H; Ph), 2.73 (dd, J_{HH} = 8.6 and 6 Hz, 1H; C^2H), 2.36 (d, J_{HH} = 3.4 Hz, 1H; C^1H), 2.34 (s, 1H; C^4H), 1.76 (m, 1H; C^3H_2), 1.66 (m, 1H, C^3H_2), 1.58 (m, 2H; $C^{5,6}H_2$), 1.54 (d, J_{HH} = 9.6, 1H; C^7H_2), 1.35 (m, 1H; C^6H_2), 1.26 (m, 1H, C^5H_2), 1.17 (d, J_{HH} = 9.6, 1H; C^7H_2). $^{13}C\{^1H\}$ NMR (*δ*, $CDCl_3$, 75 MHz, 25 °C): 147.55 (1C; ipso Ph), 128.16 (2C; meta Ph), 127.02 (2C, ortho Ph), 125.32 (1C, para

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(24) Oxford Diffraction Poland Sp., CCD data collection and reduction GUI, Version 1.173.13 beta (release 14.11.2003), 1995−2003.

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Ph), 47.30 (1C; C^2H), 42.87 (1C; C^1H), 39.10 (1C; C^3H_2), 36.81 (1C; C^4H_2), 36.05 (1C; C^7H_2), 30.58 (1C; C^6H_2), 28.90 (1C; C^5H_2).[13b]

Decomposition of 3 in Toluene-d_8: Formation of *exo*-2-(Methylphenyl-d_7)-3-*d*-norbornane (5c). Periodic monitoring of compound **3** by ^1H NMR in toluene-d_8 solution showed the decay of signals due to the norbornene ligand in **3** and the appearance of signals which, as a result of ^1H and $^1H-^1H$ COSY NMR and GC-MS studies, were assigned to compound **5c** ($C_{14}H_{10}D_8$, $M_r = 194.34$). The latter compound is formed as three positional isomers with meta (**5c-m**), ortho (**5c-o**), and para (**5c-p**) methyl substituents at the arene ring. The isomer distributions were determined by GC-MS analyses as 1:3:5, respectively. **5c-m**: GC-MS (*m/z* (relative intensity)) 194 (11), 175 (2), 164 (2), 147 (3) 133 (9), 125 (45), 112 (100), 95 (21), 82 (34), 67 (30), 53 (12), 41 (23). **5c-o**: GC-MS (*m/z* (relative intensity)) 194 (18), 176 (2), 165 (3), 148 (3) 133 (10), 125 (54), 113 (100), 95 (68), 82 (30), 67 (34), 54 (10), 41 (20). **5c-p**: GC-MS (*m/z* (relative intensity)) 194 (19), 176 (3), 165 (3), 147 (4) 133 (11), 125 (68), 113 (100), 95 (48), 82 (33), 67 (35), 54 (10), 41 (20). ^1H NMR (δ, toluene-d_8, 500 MHz, 25 °C): 2.66 (dd, $J_{HH} = 8.6$ and 5.7 Hz, 1H; C^2H, **5c-o**), 2.60 (t, $J_{HH} = 7.2$ Hz, 1H; C^2H, **5c-(m+p)**), 2.27 (1H; C^1H), 2.23 (s, 1H; C^4H), 1.63 (d, $J_{HH} = 7.2$, 1H; C^3HD), 1.50 (m, 3H; $C^{5,6,7}H_2$), 1.24 (m, 1H; C^6H_2), 1.19 (m, 1H, C^5H_2), 1.07 (d, $J_{HH} = 9.6$, 1H; C^7H_2). ^{13}C-$\{^1H\}$ NMR (δ, $CDCl_3$, 125 MHz, 25 °C): **5c-o**, 44.21 (1C; C^2H), 41.80 (1C; C^1H), 38.97 (1C; C^3H_2), 37.33 (1C; C^4H_2), 36.57 (1C; C^7H_2), 30.75 (1C; C^6H_2), 29.49 (1C; C^5H_2); **5c-m**, 47.57 (1C; C^2H), 43.31 (1C; C^1H), 39.41 (1C; C^3H_2), 37.15 (1C; C^4H_2), 36.36 (1C; C^7H_2), 29.28 (1C; C^5H_2), 30.92 (1C; C^6H_2); **5c-p**, 47.26 (1C; C^2H), 43.43 (1C; C^1H), 39.39 (1C; C^3H_2), 37.24 (1C; C^4H_2), 36.26 (1C; C^7H_2), 30.86 (1C; C^6H_2), 29.30 (1C; C^5H_2).

Initiation of ROMP by 1: Formation of Poly(1,3-cyclopentylenevinylene) (6). In a typical experiment, 20 mg of a mixture of **1** and **2** (6:1 molar ratio by ^1H NMR) and NBE in $CDCl_3$, CCl_4, or $CDCl_3/CCl_4$ (1:10) solution was monitored by ^1H NMR at room temperature. The conversion of NBE was confirmed by the decay of signals due to protons of NBE and the appearance of signals of **6** at δ_H 5.33 (*trans*-$HC^2{=}C^3H$), 5.19 (*cis*-$HC^2{=}C^3H$), 2.77 ($C^{1,4}H$ in *cis*-polymer), 2.41 ($C^{1,4}H$ in *trans*-polymer), 1.79 (C^7H_2 and $C^{5,6}H_2$), 1.33 ($C^{5,6}H_2$), 1.01 (C^7H_2).[4] The simultaneous formation in $CDCl_3$ solution of *exo*-2-(trichloromethyl)-3-*d*-norbornane is indicated by a signal at δ_H 2.6 (ca. 1% yield). In carbon tetrachloride solution *exo*-2-(trichloromethyl)-*endo*-3-chloronorbornane is detected due to a proton signal at δ_H 4.19 in ca. 8% yield.[12d] Elemental analysis of low-molecular-weight polymer separated from the carbon tetrachloride solution by precipitation with methanol at an early stage of the reaction shows a Cl:C atom ratio of ca. 1:17.3. ESI-MS (*m/z):* calcd for $C_{14}H_{20}Cl$ (M^+), 223.8, found 223.3; calcd for $C_{21}H_{32}Cl_2$ 355.4, found 355.5; calcd for $C_{27}H_{34}Cl_2$ 429.5, found 429.6; calcd for $C_{28}H_{36}Cl_2$ 445.5, found 445.1; calcd for $C_{35}H_{47}Cl$ 503.2, found 503.3.

Addition of Polyhaloalkanes to Olefins Initiated by 1. Formation of *exo*-2-(Trichloromethyl)norbornane (7a). In a typical experiment, compound **1** (ca. 0.1 g, prepared as in the procedure described above) was dissolved in the reaction mixture composed of $CHCl_3$/EtOH (1%; 6 mL), *n*-heptane as the internal chromatographic standard (0.3 mL), and NBE (0.5 g, 0.84 mol L^{-1}) and stirred at room temperature under nitrogen in a 50 mL glass reactor provided with a septum through which liquid reactants were introduced and removed by means of a syringe. The conversion of NBE was confirmed by the GC method. After completion of the reaction (100% conversion after ca. 100 h) chloroform was removed under reduced pressure at room temperature and an oily residue was vacuum-transferred at ca. 60 °C to give ca. 0.6 g of a colorless oily product (reaction yield ca. 87%). GC-MS analysis showed that the product was the compound $C_8H_{11}Cl_3$,[12b] $M_r = 213.53$. GC-MS (*m/z* (relative intensity)): 214 (0.03), 177 (2) 141 (5), 109 (5), 95 (100), 67 (40). ^1H NMR (δ, $CDCl_3$, 500 MHz, 25 °C): 2.61 (dd, $J_{HH} = 7.9$, 7.9 Hz, 1H; C^2H), 2.59 (s, 1H; C^1H), 2.34 (s, 1H; C^4H), 1.90 (d, $J_{HH} = 10.2$ Hz, 1H; *syn*-C^7H_2), 1.67−1.17 (m, 6H; $C^{3,5,6}H_2$), 1.13 (d, $J_{HH} = 10.2$ Hz, 1H; *anti*-C^7H_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 125 MHz, 25 °C): 104.09 (1C; C^8Cl_3), 64.16 (1C; C^2H), 41.13 (1C; C^1H), 37.23 (1C; C^3H_2), 36.56 (1C; C^4H_2), 36.20 (1C; C^7H_2), 31.08 (1C; C^5H_2), 27.67 (1C; C^6H_2).

After prolonged heating (ca.. 100 °C) compound **7a** eliminates hydrogen chloride to give 2-(dichloromethylene)norbornane, $C_8H_{10}Cl_2$;[12b] $M_r = 177.07$. GC-MS (*m/z* (relative intensity)): 176 (36), 147 (74), 113 (62), 105 (53), 80 (100), 77 (90), 67 (49), 51 (46), 39 (61).^1H NMR (δ, $CDCl_3$, 300 MHz, 25 °C): 3.06 (s, 1H; C^1H), 2.44 (s, 1H; C^4H), 2.21 (d, $J_{HH} = 16.5$ Hz, 1H; *syn*-C^7H), 1.92 (d, $J_{HH} = 16.5$ Hz, 1H; *anti*-C^7H), 1.48−1.30 (m, 6H; C^3H_2, C^5H_2, C^6H_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 75 MHz, 25 °C): 145.03 (1C; C^2), 108.03 (1C; C^8Cl_2), 44.41 (1C; C^1H), 39.92 (1C; C^7H_2), 39.73 (1C; C^3H_2), 37.03 (1C; C^4H), 27.73 (1C; C^5H_2), 27.51 (1C; C^6H_2).

In moist air the trichloromethyl group of compound **7a** is hydrolyzed to give the carboxy unit of *exo*-2-carboxynorbornane.[12d] ^1H NMR (δ, $CDCl_3$, 300 MHz, 25 °C): 2.53 (s, 1H; C^1H), 2.34 (d, $J_{HH} = 9.2$ Hz, 1H; C^2H), 2.28 (s, 1H; C^4H), 1.84−1.17 (m, 6H; C^7H_2, C^5H_2, C^6H_2), 1.45 (d, $J_{HH} = 9.2$ Hz, 2H; C^3H_2). $^{13}C\{^1H\}$ NMR (δ, $CDCl_3$, 75 MHz, 25 °C): 181.64 (1C; C^8O_2H), 46.21 (1C; C^2H), 40.92 (1C; C^1H), 36.51 (1C; C^7H_2), 36.00 (1C; C^4H), 34.04 (1C; C^3H_2), 29.43 (1C; C^5H_2), 28.56 (1C; C^6H_2)

Formation of *exo*-2-(Trichloromethyl)-3-*d*-norbornane (7b). The addition reaction of chloroform to NBE was also followed directly by ^1H NMR measurements. In a typical experiment, compound **1** (ca. 5 mg prepared as in the procedure described above), EtOH (15 mg, 0.34 mmol), and $CDCl_3$ (0.5 cm^3) were introduced to an NMR tube containing NBE (0.022 g, 0.23 mmol). The tube was closed and the ^1H NMR spectrum of the solution recorded. The formation of **7b** was indicated by a proton signal at δ_H 2.60 (d, $J = 7.1$ Hz, C^2H) and the mass spectrum for the $C_7H_{10}D$ ion at *m/z* 96; $C_8H_{10}DCl_3$, $M_r = 214.54$. GC-MS (*m/z* (relative intensity)): 142 (3), 110(3), 96 (100), 68 (33).

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Supporting Information Available: Tables of crystal data and structure refinement parameters, atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and all bond lengths and angles and a figure showing the crystal packing; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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