Intramolecular Stabilization of Carbene Complexes $(CO)_4W{=}C(NRR')Si(aryl)_2X$ ($X = H, CMe{=}CHMe, NEt_2$) by Interaction of the Metal Center with the Silicon Substituent X

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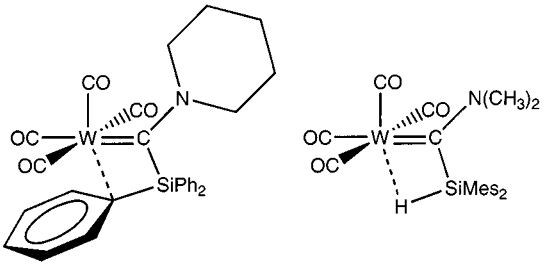
The degree of intramolecular stabilization by the substituent X in the carbene complexes $(CO)_4W{=}C(NRR')Si(aryl)_2X$ was investigated by density functional calculations and reactivity studies. Calculations carried out for $(CO)_4W{=}C(NH_2)SiH_2X$ ($X = H, Ph, Me, CMe{=}CHMe$) or $(CO)_4W{=}C(NH_2)OMe$ show that the agostic Si–H interaction in $(CO)_4W{=}C(NH_2)SiH_3$ transfers as much electron density to the metal as the π–interaction of the olefinic group in $(CO)_4W{=}C(NH_2)SiH_2CMe{=}CHMe$. An agostic interaction is not observed if the silicon atom is replaced by a carbon atom. Interaction of the phenyl group in $(CO)_4W{=}C(NH_2)SiH_2Ph$ is much weaker and can be described as a weak π–interaction. Owing to the agostic Si–H interaction, $(CO)_5W{=}C(NHR)SiHMes_2$ (R = Me, Et) does not eliminate $HSiR'_3$ upon thermolysis, as observed in the corresponding complexes $(CO)_5W{=}C(NHR)SiR'_3$, but instead gives the 16-electron complex $(CO)_4W{=}C(NHR)SiHMes_2$. When the complexes $(CO)_5W{=}C(NMe_2)SiPh_2CMe{=}CHMe$ or $(CO)_5W{=}C(NHMe)SiPh_2NEt_2$ are thermolyzed or photolyzed, CO is eliminated and either the olefinic or amino group coordinates intramolecularly to the empty coordination site. The corresponding reaction was not observed when the stable 16-electron complexes $(CO)_4W{=}C(NR_2)SiPh_3$ were allowed to react with olefins or tertiary amines respectively. The X-ray structure analysis of $(CO)_4W{=}C(NMe_2)SiPh_2CMe{=}CHMe$ is reported.

Introduction

Stable 16-electron carbene complexes $(CO)_4M{=}C(NR_2)SiR'_3$ (M = Cr, Mo, W) were previously obtained by thermal or photochemical CO cleavage from the corresponding 18-electron complexes $(CO)_5MC(NR_2)SiR'_3$.[1] These complexes are stabilized by intramolecular interaction of one of the silicon substituents with the metal center. In $(CO)_4W{=}C(NMe_2)SiHMes_2$ (Mes = 2,4,6-$C_6H_2Me_3$), the Si−H group interacts with the tungsten atom,[1c] and with one of the phenyl groups in $(CO)_4W{=}C(NC_5H_{10})SiPh_3$ (Scheme 1).[1a] In the $SiPh_3$ derivative, the $W{-}C_{phenyl}$ distances indicate that the *ipso* carbon atom is mainly involved in the interaction with the metal atom. The intramolecular interactions result in severe distortions of the bond angles at the carbene carbon atom (W−C−Si bond angle of 87.8(6)° in $(CO)_4W{=}C(NMe_2)SiHMes_2$ and of 101.2(4)° in $(CO)_4W{=}C(NC_5H_{10})SiPh_3$).



Scheme 1

Despite the agostic interactions in the silylcarbene complexes, the coordination site is still accessible. Reaction of $(CO)_4W{=}C(NMe_2)SiR_3$ ($SiR_3 = SiPh_3, SiPh_2Me$) with CO, phosphanes, phosphites or isonitriles quantitatively yielded the 18-electron carbene complexes *cis*-$(CO)_4LW{=}C(NMe_2)SiR_3$ (L= CO, RNC, PR_3, $P(OR)_3$).[1b][1d] The latter complexes showed no tendency towards eliminating a ligand. However, addition of acetonitrile or pyridine to $(CO)_4W{=}C(NMe_2)SiPh_2Me$ was reversible, i.e. the complexes *cis*-$(CO)_4LW{=}C(NMe_2)SiPh_2Me$ (L = MeCN, C_5H_5N) eliminated L on evaporation of the reaction solutions, and the 16-electron complexes were re-formed. No adduct formation was observed when triethylamine, olefins or acetylenes were added to solutions of the 16-electron complex $(CO)_4W{=}C(NMe_2)SiPh_2Me$.[1d]

16-Electron carbene complexes are postulated as key intermediates in many reactions of Fischer-type carbene complexes. The stable analogues allow us to study how intramolecular interactions influence the stability and hence the reactivity of electron-deficient carbene complexes and how such interactions are controlled by electronic and steric effects. If these are properly tuned, a coordination site at the metal could be reversibly opened and protected during the reaction. In this paper, we report theoretical and experimental results of intramolecular interactions in silyl-substituted 16-electron carbene complexes.

Results and Discussion

Theoretical Calculations

To examine the nature of the intramolecular interaction and the role of steric and electronic factors in the silyl-sub-

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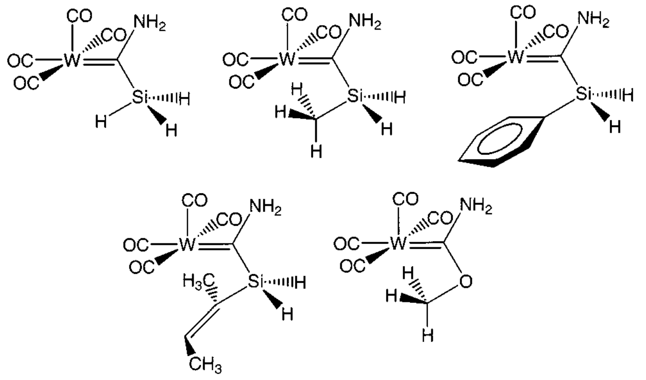
stituted 16-electron carbene complexes $(CO)_4W=C(NC_5H_{10})SiPh_3$ [1a] and $(CO)_4W=C(NMe_2)SiMes_2H$,[1c] we carried out density functional calculations on these and related compounds, with the NR_2 replaced by NH_2 and the SiR_3 groups replaced by SiH_2R (R = H, Ph, Me, CMe=CHMe) or OMe (Scheme 2).



Scheme 2

The first question was whether steric crowding at the carbene carbon atom or the electronic interaction between the tungsten center and the substituents on silicon cause the small W−C−Si angles observed in the structurally investigated complexes. Therefore, the bulky substituents at the nitrogen and silicon atoms were substituted by hydrogen atoms. Geometrical optimization of the model structures were carried out from two starting points, the crystallographically determined structures (if known) on the one hand, and artificial structures with the bond angles around the carbene carbon atom set at 120°, on the other. In both cases, the optimizations gave very similar minimum structures, which should therefore correspond to the global minimum. This was also indicated by a frequency analysis, where no imaginary frequencies were observed. Structural parameters of the optimized structures are given in Table 1. The obtained bond lengths and angles are in good agreement with the experimental values from X-ray structure analyses. The fact that the geometry optimizations without the bulky ligands achieved the geometries of the real complexes allows us to conclude that steric reasons for the distorted arrangement around C(carbene) can be excluded. Instead, electronic reasons should be the driving force for the agostic interactions and associated structural phenomena.

The orbital responsible for the intramolecular interaction between the 16-electron tungsten carbene fragment and a donating group is the empty metal d_z^2-orbital. Stabilization of the empty coordination site can be achieved by either an agostic interaction with a suitable σ-bond or by interaction with π-orbitals of an organic substituent such as a phenyl or olefinic group.

Geometry optimization of $(CO)_4W=C(NH_2)SiH_3$ showed that one Si−H bond is preferentially located in the W−C−Si plane, as is observed in the solid-state structure of $(CO)_4W=C(NMe_2)SiMes_2H$. This conformation gives the best interaction of the Si−H bond with the empty d_z^2-orbital at the tungsten atom as shown in the electron density plot (Figure 1). The plot shows that both the H and the Si atom participate in a delocalized occupied orbital. Thus, the Si−H bond acts as an intramolecular electron donor which results in charge transfer from Si−H to the metal,

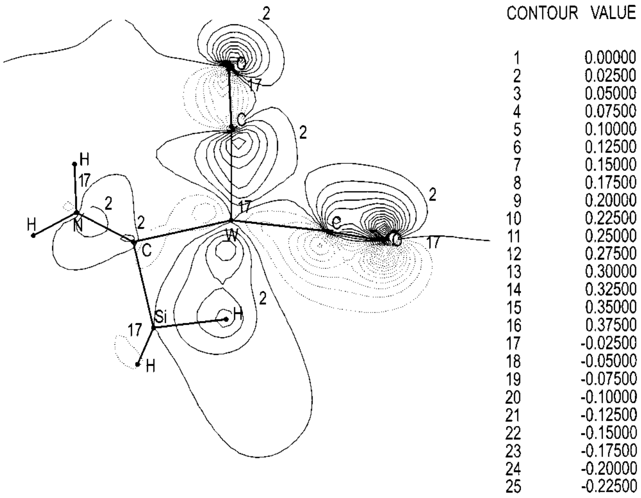


Figure 1. Contour plot of the calculated electron density for the molecular orbital participating to the greatest extent in the agostic interaction in the W=C−Si−H plane of $(CO)_4W=C(NH_2)SiH_3$.

Table 1. Selected parameters of the optimized structures of $(CO)_4W=C(NH_2)X$ (distances in pm and angles in deg; C_c = carbene carbon atom). In the $SiMeH_2$ and OMe derivative, the orientation of the methyl group was fixed (see Text)

	X = SiH_3	$SiMeH_2$	OMe	$SiPhH_2$	$Si(CMe=CHMe)H_2$
$W-C_c$	209.9	212.1	218.9	212.2	214.4
C_c-Si	185.3	189.6	C_c-O: 137.8	187.9	191.0
C_c-N	134.0	134.5	134.5	134.4	134.1
Si−C	−	187.4	O−C: 146.9	187.1	190.3
Si−H	153.3, 146.9, 146.9	147.4, 147.6	−	147.5, 147.5	148.5, 149.4
$W-C_c-Si$	89.2	110.0	$W-C_c-O$: 122.33	105.3	103.3
$W-C_c-N$	140.2	130.6	128.3	131.6	132.3
C_c-Si-H	96.5, 116.9, 116.9	107.9, 111.1	−	110.9, 111.0	110.5, 115.2
C_c-Si-C	−	106.6	115.7	104.3	95.5
$W-C_c-Si-H$	0.0	−	−	−	−
$W-C_c-Si-C$	−	−14.4	$W-C_c-O-C$: 3.1	0.4	−12.9
$C_{CO}-W-C_c-N$	0.0	4.0	0.8	−0.3	20.7
W···H	207.7	−	−	−	−
W···C	W···Si: 277.0	319.9	322.9	290.9	263.3, 270.8
Natural charge on W	−0.54	−0.33	−0.33	−0.37	−0.46

i.e. an increase in the natural charge on the metal center (−0.54) compared to systems where no such interaction is present (Table 1).

The agostic interaction has interesting structural consequences, such as an increase in the bond length of the agostic Si−H bond (153.3 pm) as compared to the other two Si−H bonds (146.9 pm). The bending of the agostic Si−H bond ($C_{carbene}$−Si−H 96.5°, compared to 116.9° of the other two hydrogen atoms) also reflects the extraordinary bonding situation in the W−C−Si−H moiety. Furthermore, the W−$C_{carbene}$−Si angle is very small (89.2°) and the W−H distance rather short (207.7 pm). The calculated structural parameters correspond very well with the corresponding values observed in the solid-state structure of $(CO)_4W{=}C(NMe_2)SiMes_2H$ [W−$C_{carbene}$−Si 87.8(6)°, W−H 210(10) pm, Si−H 150(10) pm].[1c]

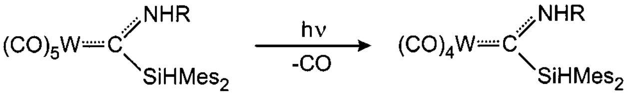
The WH interaction is restricted to the cases where the hydrogen atom is bound to silicon. This was confirmed by density functional calculations on $(CO)_4W{=}C(NH_2)SiMeH_2$ and $(CO)_4W{=}C(NH_2)OMe$ in which only the conformers with the methyl group pointing into the empty coordination site of the tungsten atom were considered (Scheme 2). In both compounds, the carbon-bonded hydrogen atoms could approach the W center with much less geometric distortion around $C_{carbene}$ than in $(CO)_4W{=}C(NH_2)SiH_3$. Nevertheless, an agostic interaction was not observed due to the fact that in the optimized structures (in which rotation of the CH_3 group was allowed) the CH_3 group was oriented in such a way that the C−H bond located in the W=C−Si plane was pointing away from the W atom.

Another possible means of stabilizing the 16-electron fragment are intramolecular π-interactions. In the investigated complexes, this was achieved either by an interaction of the *ipso* C atom of a phenyl substituent at silicon or by the coordination of the double bond of a butenyl substituent. The calculations revealed that the interaction of the SiPh substituent with the tungsten atom does not lead to a large transfer of electron density to the metal center and thus is a rather weak interaction. Interaction with the butenyl substituent is much stronger, as expected. This is also reflected in the relatively long W−C_{ipso} distance of 290.0 pm in $(CO)_4W{=}C(NH_2)SiPhH_2$ compared to the W−C_{olefin} distances of 263.3 pm and 270.8 pm in $(CO)_4W{=}C(NH_2)Si(CMe{=}CHMe)H_2$ (see also the X-ray structure analysis of **7** described below). The calculated W−C distances between the metal and the olefin in $(CO)_4W{=}C(NH_2)Si(CMe{=}CHMe)H_2$ differ by approximately 20 pm from the values in the X-ray structural analysis (W−C(81) 246.9(7) pm, W−C(82) 252.3 pm). One reason for these observations is that substitution of the bulky phenyl groups at silicon by H atoms in the calculation has a more significant effect, due to the bulkiness of the butenyl group, than in other substitution patterns. The charge on the tungsten atom in the butenyl derivative (−0.46) is close to that of the SiH_3 substituted compound with an efficient agostic interaction. The butenyl derivative corresponds to the many known alkenyl-substituted carbene complexes in which the olefinic group is connected to the carbene carbon by carbon and/or nitrogen atoms (see below).

Thermal Decomposition of $(CO)_5W{=}C(NHR)SiHMes_2$

We wanted to test whether the agostic Si−H interaction affects reactions of silyl carbene complexes in which the silyl group is involved. Contrary to the corresponding NHR-substituted alkyl or arylcarbene complexes, the silylcarbene complexes $(CO)_5W{=}C(NHR)SiR_3$ (SiR_3 = $Si(aryl)_3$, $SiPh_2Me$) undergo a thermally[2] or photochemically[3] induced fragmentation reaction that quantitatively yields $HSiR_3$ and the isonitrile complexes $(CO)_5WCNR$.

When solutions of the SiR_2H-substituted complexes $(CO)_5W{=}C(NHR)SiHMes_2$ (R = Me, Et) (**1a,b**)[4] were photolyzed, this fragmentation was not observed. The spectroscopic data clearly showed that the 16-electron complexes $(CO)_4W{=}C(NHR)SiHMes_2$ (**2a,b**) were formed instead (Equation 1). The complexes **2a,b** are relatively stable. On heating, they gave **1a,b** and $W(CO)_6$, but no isonitrile complex.



1a,b **2a,b**

The complexes **2a,b** showed the same spectroscopic features as previously observed for NR_2-substituted 16-electron carbene complexes. The ν(CO) bands in the IR spectra were shifted to lower wavenumbers relative to **1a,b**, the ν(SiH) band was no longer observed, and the SiH signal in the ^1H NMR spectrum was shifted to higher field. The SiH coupling constants (**2a**: 104 Hz, **2b**: 105 Hz) were the same as previously observed in $(CO)_4W{=}C(NMe_2)SiHMes_2$ (106 Hz) as a result of a strong agostic W···H···Si interaction (see above). The configuration of the amino group was assigned (only the *Z* isomer is formed) on the basis of the chemical shifts of the alkyl substituents.[5]

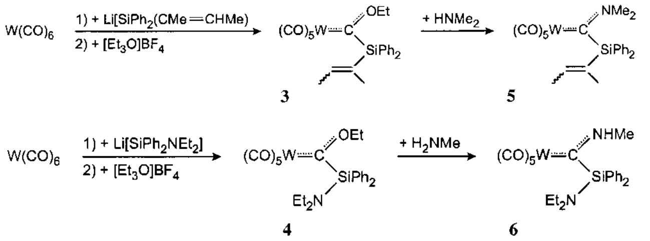
These results show that the agostic interaction of the Si−H group with the metal center blocks the fragmentation reaction of the silylcarbene ligand (i.e. the cleavage of $HSiR_3$) that is observed in the absence of this interaction.

Intramolecular Stabilization of Silyl Carbene Complexes by Stronger Interactions

Although we did not observe the addition of amines or olefins to the empty coordination site of the stable 16-electron complexes $(CO)_4M{=}C(NR_2)SiR_3$,[1d] we anticipated that such groups could interact with the metal center when they were part of the silyl substituent.

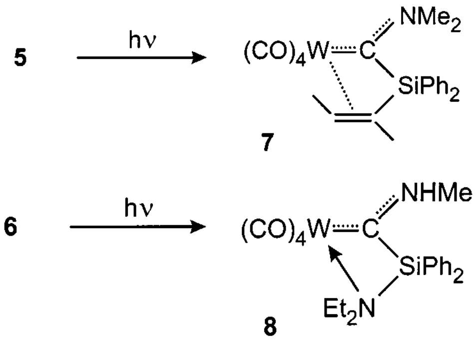
The ethoxy(silyl)carbene complexes $(CO)_5W{=}C(OEt)SiPh_2X$ (**3**: X = CMe=CHMe; **4**: X = NEt_2) were prepared by the Fischer route starting from $W(CO)_6$ and $LiSiPh_2X$, followed by alkylation of the formed anionic acyl complex with $[Et_3O]BF_4$ (Equation 2 and 3). The 2-butenyl-substituted complex **3** was obtained with the (*Z*)- and (*E*)-butenyl groups in a 3:1 ratio. For the synthesis of **4**, an excess of

$[Et_3O]BF_4$ has to be avoided, because otherwise the amino group is cleaved.



Reaction of **3** with Me_2NH and of **4** with $MeNH_2$ resulted in the formation of the corresponding amino(silyl)carbene complexes **5** and **6** in high yields (Equation 2 and 3). Surprisingly, the ratio of the (*Z*/*E*) isomers of **5** (different configuration of the butenyl group) changed from 3:1 in the ethoxy-substituted complex **3** to 10:1 in the amino-substituted complex **5**. The (*E*/*Z*) isomers of **6** (relative to the C(carbene)−N bond) were formed in equal portions, according to the NMR spectroscopic data.

When ether solutions of **5** or **6** were irradiated with UV light, CO was evolved, and the thermally stable tetracarbonyl complexes **7** and **8** were obtained in high yields (Equation 4 and 5). The spectroscopic data clearly showed that the olefinic group in **7** and the amino group in **8** are coordinated to the metal center.



Comparison of the NMR chemical shifts and the coupling constants of the butenyl group in **5** and **7** showed clear differences caused by π-coordination in **7**. The =CH signal in **7** is shifted to higher field by 1.2 ppm, while the signals of the CH_3 groups are shifted to lower field. Due to the weakening of the C=C bond by π-coordination, the ^4J(HCCCH) and ^5J(HCCCCH) couplings were only observed in **5**, but not in **7**. In the ^{13}C NMR spectrum of **7**, the carbon atoms of the C=C bond were strongly shifted to higher field relative to **5**, as expected. In the (aminosilyl)carbene complex **8**, the $N-CH_2$ protons became diastereotopic upon coordination to the metal. The quadruplet observed in the ^1H NMR spectrum of the pentacarbonyl complex **6** was therefore split to a multiplet in **8**.

Only one isomer was observed for both **7** and **8**. Only the isomer with the *Z* configuration of the butenyl group was formed for **7**. The *E* isomer either gives no stable complex or is isomerized during irradiation. Comparison of the chemical shift of the NMe group and the ^3J(HNCH) coupling constant with complexes of known configuration did not allow an unequivocal determination of the geometry along the C(carbene)−N bond in **8**. Since the (*E*/*Z*) ratio in the pentacarbonyl complex was 1, and the yield of **8** was larger than 50%, isomerization must have occurred during irradiation. Photochemical isomerization of the amino group in aminocarbene complexes was previously observed for $(CO)_4W=C(NHCH_2CH=CH_2)Tol$[6] and theoretically explained for $(CO)_5Cr=C(NMe_2)Ph$.[7] The same photochemical process was found to be responsible for the isomerization of the ethoxy group in $(CO)_5W=C(OEt)SiPh_3$ and the CO elimination in $(CO)_5W=C(NC_4H_8)SiPh_3$.[8]

The ν(CO) bands in the IR spectra of **7** and **8** had the typical pattern of *cis*-$(CO)_4WLL'$ complexes with local C_{2v} symmetry. The spectra clearly showed that the electron density at the metal increases in the order **2a** < **7** < **8** (Table 2). However, the similarity of the IR spectra of **2a** and **7** indicates that intramolecular interaction of the η^2-coordinated SiH group and the π-alkenyl substituent with the tungsten atoms are electronically comparable. This is in agreement with the density functional calculations discussed above. Similar results were previously found in competition experiments between $HSiR_3$ and olefins for coordination to unsaturated metal centers.[9]

Table 2. Comparison of the ν(CO) bands of the complexes **2a**, **7** and **8** (petroleum ether or pentane solutions)

2a	2027(m)	1947(s)	1937 (vs)	1895(s)
7	2024(s)	1938(sh,s)	1928(vs)	1894(s)
8	1995(m)	1940(vs)	1915(vs)	1845(m)

The molecular structure of **7** was determined by an X-ray structure analysis (Figure 2, Table 3). The alkenyl group coordinates in a π fashion despite the relatively short spacer (C(5), Si) tethering it to the metal. In other structurally characterized alkenyl-substituted tungsten carbene complexes, such as $(CO)_4W=C(NHCH_2CH=CH_2)Tol$,[6] $(CO)_4W=C(OEt)(CH_2)_nCH=CHR$ (n = 2, 3)[10] or related cyclopentenyl derivatives,[11] the linkage between the olefinic group and the metal atom is longer, and therefore the bonding situation is less strained. That coordination of the C=C bond occurs at all is probably due to the strong distortion of the W−C(carbene)−Si (98.0(3)°) and the C(carbene)−Si−C(81) angle (93.1(3)°). Similarly large distortions have been observed in the structurally characterized 16-electron silylcarbene complexes;[1a,1c] they would hardly be possible in silicon-free systems.

Although the W−CO and W−C(carbene) bond lengths and angles around the tungsten atom in **7** are very similar to $(CO)_4W=C(NHCH_2CH=CH_2)Tol$,[6] the W−C(olefin) interaction in **7** is less optimal. The observed W−C(81)/C(82) distances [246.9(7) and 252.3(8) pm] are significantly longer and less symmetric than the corresponding distances in the known alkenyl-substituted complexes mentioned above (238−251 pm).

The geometry of *cis*-olefin carbene complexes can be characterized by the torsional angles α and β (Scheme 3). The angle α represents the dihedral angle between the car-

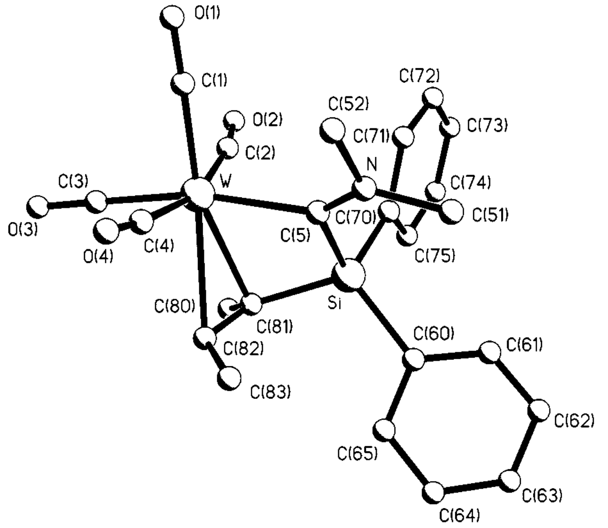
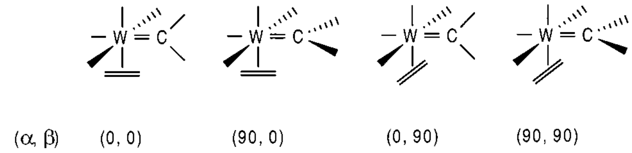


Figure 2. Molecular structure of **7**. Important distances (in pm) and angles (in deg): W−C(1) 198(1), W−C(2) 204(1), W−C(3) 199(1), W−C(4) 203(1), W−C(5) 220.4(8), W−C(81) 246.9(7), W−C(82) 252.3(8), C(5)−N 131.1(9), C(5)−Si 190.7(7), Si−C(81) 187.7(8). C(1)−W−C(5) 98.1(3), C(2)−W−C(5) 96.84, C(3)−W−C(5) 167.5(3), C(4)−W−C(5) 94.4(3), C(2)−W−C(4) 164.5(4), W−C(5)−N 136.4(6), W−C(5)−Si 98.0(3), C(5)−Si−C(81) 93.1(3), Si−C(81)−C(82) 121.6(6).

Table 3. Summary of crystal data, data collection and structure analysis of **7**

Chemical formula	$C_{23}H_{23}NO_4SiW{\cdot}1.5C_6H_6$
Formula weight	706.53
Crystal size [mm]	0.27 × 0.22 × 0.17
T [K]	293
Crystal system	monoclinic
Space group	$P2_1/c$
a [pm]	1199.96(2)
b [pm]	1040.48(2)
c [pm]	2566.30(2)
β [°]	91.824(1)
Volume × 10^6 [pm^3], Z	3202 pm^3, 4
D_c [g cm^{-3}]	1.465
μ (Mo-K_α) [mm^{-1}]	3.678
θ range [°]	1.59−24.99
Reflections collected	17950
R_{int}	0.1537
No. independent reflections	5643
Final R [$I > 2\sigma(I)$]	$R_1 = 0.054$, $wR_2 = 0.097$
Maximum difference Fourier peaks e/Å^{-3}	1.28
Weighting Scheme	$w=1/[\sigma^2(F_o^2) + 0.36P]$ with $P = (F_o^2 + 2F_c^2)/3$

bene plane (plane of the carbene carbon atom and the atoms directly bonded to it) and the plane $C_{carbene}$,W,C=$C_{centroid}$, and β the dihedral angle between the olefin plane (W,C(81),C(82)) and the plane $C_{carbene}$,W,C=$C_{centroid}$.



Scheme 3

According to Extended-Hückel calculations,[12] the (90,0) conformation is the most favorable, and the (0,0) conformation the least favorable. The calculated energy difference between both conformations is 16.2 kcal/mol for $(CO)_4(C_2H_4)W{=}CH_2$. The conformation of **7** (34.4, 73.8) is clearly between the two extremes, but close to that of $(CO)_4W{=}C(NHCH_2CH{=}CH_2)Tol$ (25.7, 77.0). Thus, a similar mutual orientation of the carbene and olefin planes is reached owing to the strong angular distortions within the carbene ligand of **7**. This geometry is obviously maintained in solution. While only three signals are observed for the carbonyl ligands in the ^{13}C NMR spectra of **2** and **8**, the chemical inequivalence of all CO ligands in **7** is a consequence of the observed geometry. Contrary to the alkenyl substituent in **7**, the amino substituent in **8** has no preferred orientation in its interaction with the metal, and therefore the complex appears to be more fluxional.

Conclusions

The 16-electron carbene complexes $(CO)_4M{=}C(NR_2)SiR'_2H$ are stabilized by a strong agostic interaction of the Si−H group with the metal center. In contrast, the stabilization of $(CO)_4M{=}C(NR_2)SiPh_3$ can be traced back to a weak η^1-coordination of the phenyl group by π-interaction. Theoretical calculations indicate that electron transfer to the metal by the agostic Si−H interaction is of a similar magnitude to the π-coordination of an olefinic ligand. The agostic Si−H interaction is strong enough to inhibit the previously observed thermal elimination of $HSiR'_3$ from $(CO)_5M{=}C(NHR)SiR'_3$. Heating the complexes $(CO)_5W{=}C(NHR)SiR'_2H$ results in CO cleavage instead; the resulting 16-electron complexes $(CO)_4W{=}C(NHR)SiR'_2H$ are stabilized by the W···H···Si interaction.

When the group X in $(CO)_5W{=}C(NR_2)SiR'_2X$ is an olefinic or amino substituent, it is coordinated to the metal center once a CO ligand is eliminated. While external olefins or tertiary amines did not coordinate to the vacant coordination site of the 16-electron complexes $(CO)_4W{=}C(NR_2)SiR'_3$, *intra*molecular coordination of the same groups results in stable complexes. The interaction of the substituent X in $(CO)_4W{=}C(NR_2)SiR'_2X$ with the metal center can thus be tuned from a very weak π-type bonding for X = Ph to a rather strong agostic bond for X = H, a classic π-bond for X = $CR{=}CR_2$, or a Lewis acid/base interaction for X = NR_2.

Experimental Section

All operations were performed in an atmosphere of dry and oxygen-free N_2, using dried and nitrogen-saturated solvents. A high pressure Hg lamp (Heraeus TQ 150) was used for the photochemical reactions. − Column chromatography was performed with silica (Woelm, 0.063−0.200 mm mesh) as the stationary phase, from which oxygen was removed by heating in vacuo and storage under N_2. − IR spectra: Perkin−Elmer 283, CaF_2-cuvettes. − ^1H NMR and ^{13}C NMR spectra: Bruker AC 250.

Computational Methods: Calculations were carried out at the gradient corrected density functional level by using the local spin density approximation,[13] combined with Becke's gradient correction[14] and Lee, Yang and Parr's correlation functional (B3LYP),[15] implemented in the GAUSSIAN94[16] package. The effective core potential of Hay and Wadt[17] implemented in the GAUSSIAN94 package (LANL2DZ) was used for the tungsten atom. Silicon atoms were described by the same potential with additional polarization functions (α(Si) = 0.45). Carbon, nitrogen and oxygen atoms were described with the [6/1/1/1/4/1] basis set of Dunning.[18] The natural bond orbital formalism [19] was applied for the population analysis. The contour plots were prepared with the program MOLDEN.[20]

$(CO)_4W{=}C(NHR)SiHMes_2$ (2a,b): A solution of **1a** (330 mg) or **1b** (340 mg, 0.55 mmol)[4] in diethyl ether (120 mL) was irradiated at −20 °C with UV light. A slight stream of argon was passed through the solution to expel CO and thus to prevent the back reaction. The volume of the solution was kept at 120 mL by occasionally adding ether. The reaction was monitored by IR spectroscopy. Irradiation was stopped and the solvent removed in vacuo when the CO bands of **2** no longer increased in intensity. The oily residue was dissolved in a minimum amount of petroleum ether/ether (2:1) and chromatographed on silica at −20 °C with the same solvent mixture. Unreacted **1** was eluted first, followed by an orange red zone of **2**. After elution, the solvent was removed and the orange red product powder washed with small amounts of pentane at 0 °C.

2a: Yield 241 mg (73%). − IR (pentane): ν_{NH} = 3234(w), ν_{CO} = 2027 (m), 1947 (s), 1937 (vs), 1895 (s) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = −2.61 [s, *J(Si*H) = 104 Hz, ^1J(WH) = 35 Hz, 1 H, W···H···Si], 2.01 (s, 6 H, *p*-CH$_3$), 2.26 (s, 12 H, *o*-CH$_3$), 2.64 [d, ^3J(HNCH) = 4.5 Hz, 3 H, *Z*-NCH$_3$], 6.58 (s, 4 H, C$_6$H$_2$), 8.37 (br s, 1 H, NH). − ^{13}C NMR (C_6D_6): δ = 20.9 (*p*-CH$_3$), 23.5 (*o*-CH$_3$), 44.6 (*Z*-NCH$_3$), 203.7 [^1J(WC) = 128 Hz, *eq*/*cis*-CO], 214.8, 218.4 (*eq*/*trans*- + ax/*cis*-CO), 288.7 (C_{Carben}).

2b: Yield 235 mg (69%). − IR (diethyl ether): ν_{CO} = 2020 (m), 1925 (vs, br), 1890 (s) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = −2.54 [s, *J*(*Si*H) = 105, ^1J(WH) = 35 Hz, 1 H, W···H···Si], 0.84 [t, ^3J(HCCH) = 7.5 Hz, 3 H, CH$_2$−C*H*$_3$], 2.02 (s, 6 H, *p*-CH$_3$), 2.32 (s, 12 H, *o*-CH$_3$), 3.23 (m, 2 H, Z/N−CH$_2$), 6.58 (s, 4 H, C$_6$H$_2$), 8.76 (br s, 1 H, NH). − ^{13}C NMR (C_6D_6): δ = 12.7 (CH$_2$−*C*H$_3$), 21.0 (*p*-CH$_3$), 23.6 (*o*-CH$_3$), 52.9 (*Z*-NCH$_2$), 203.8 (eq/*cis*-CO), 214.8, 218.4 (eq/trans- + ax/*cis*-CO), 286.3 ($C_{Carbene}$).

$(CO)_5W{=}C(OEt)SiPh_2CMe{=}CHMe$ (3): To a solution of *E*/*Z*-Ph$_2$ClSi−CMe=CHMe (1.97 g, 7.22 mmol) in THF (30 mL), Li (250 mg, 36.0 mmol) was added in small pieces. The solution turned dark red after 10 min and was stirred for additional 4 h at room temperature. The solution was then filtered into a dropping funnel and added dropwise over 1.5 h to a suspension of W(CO)$_6$ (2.11 g, 6.0 mmol) in diethyl ether (200 mL) at −78 °C. The solution was allowed to warm to 0 °C and stirred at this temperature for 2 h. After cooling to −50 °C, [Et$_3$O]BF$_4$ (5 g) was added, and the mixture was stirred at 0 °C for 1 h. All steps of the reaction were monitored by IR spectroscopy. The solution was then filtered and the solvent removed in vacuo. The product complex was extracted from the residue with several 20 mL portions of petroleum ether (until the added solvent remained colorless). The combined solutions were concentrated to 15 mL and chromatographed on silica at −15 °C with a petroleum ether/ether (50:1) mixture). Elution of the red zone and removal of the solvent resulted in a red oil. Yield 2.64 g (59%). − IR (petroleum ether): ν_{CO} 2070 (s), 1960 (sh, vs), 1950 (vs, br) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.10 [t, ^3J(HCCH) = 7.1 Hz, 3 H, *trans*-OCH$_2$C*H*$_3$], 1.13 [t, ^3J(HCCH) = 7.1 Hz, 3 H, *cis*-OCH$_2$C*H*$_3$], 1.41 [d, ^3J(HCCH) = 7.1 Hz, 3 H, *trans*-CHC*H*$_3$], 1.42 [d, ^{3}J(HCCH) = 7.1 Hz, 3 H, *cis*-CHC*H*$_3$], 1.78 [d, ^4J(HCCCH) = 11.4 Hz, 3 H, *trans*-SiCC*H*$_3$], 1.79 [d, ^4J(HCCCH) = 1.4 Hz, 3 H, *cis*-SiCC*H*$_3$], 4.74 [q, ^3J(HCCH) = 7.1 Hz, 2 H, *trans*-OCH$_2$], 4.77 [q, ^3J(HCCH) = 7.1 Hz, 2 H, *cis*-OCH$_2$], 6.23 (m, *cis*/*trans*-CH, 1 H), 7.00−7.80 (m, 10 H, Ph). − ^{13}C NMR (C_6D_6): δ = 14.3 (*cis*-OCH$_2$*C*H$_3$), 14.4 (*trans*-OCH$_2$*C*H$_3$), 14.8 (*trans*-CH*C*H$_3$), 20.4 (*cis*-CH*C*H$_3$), 25.6 (*cis*-SiC*C*H$_3$), 27.2 (*trans*-SiC*C*H$_3$), 85.0 (*cis*-OCH$_2$), 85.1 (*trans*-OCH$_2$), 127−145 (Ph and C=C), 197.7 [^1J(WC) = 127 Hz, *cis*/*cis*-CO], 197.8 (*trans*/*cis*-CO), 206.1 (*cis*/*trans*-CO), 206.2 (trans/trans-CO), 400.3 (*cis*-$C_{Carbene}$), 402.3 (*trans*-$C_{Carbene}$). − ^{29}Si NMR (C_6D_6): δ = −18.0 [^2J(WC*Si*) = 12.9 Hz].

$(CO)_5W{=}C(OEt)SiPh_2NEt_2$ (4): To a solution of Ph$_2$ClSiNEt$_2$[21] (1.80 g, 6.2 mmol) in THF (30 mL), Li (180 mg, 25.9 mmol) was added in small pieces at 0 °C. The solution was stirred for 4 h at 0 °C, filtered into a dropping funnel cooled to 0 °C and then added dropwise within 1 h to a suspension of W(CO)$_6$ (1.62 g, 4.6 mmol) in diethyl ether (200 mL) at −78 °C. The solution was allowed to warm to 0 °C and stirred at this temperature for 2 h. After cooling to −50 °C, [Et$_3$O]BF$_4$ (437 mg, 2.3 mmol) was added, and the mixture was stirred at 0 °C for 1 h. Then more [Et$_3$O]BF$_4$ (two portions of 50 mg, together 0.52 mmol) were added. All steps of the reaction were monitored by IR spectroscopy. The solution was then filtered and the solvent removed in vacuo. The residue was extracted with benzene (30 mL), filtered and dried in vacuo. Dark red oil; yield 1.74 g (60%). − IR (diethyl ether): ν_{CO} 2065 (s), 1970 (s), 1955 (vs), 1935 (vs, br) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 0.90 [t, ^3J(HCCH) = 7.1 Hz, 6 H, NCH$_2$C*H*$_3$], 1.14 [t, ^3J(HCCH) = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$], 2.90 [q, ^3J(HCCH) = 7.1 Hz, 4 H, NCH$_2$), 4.77 [q, ^3J(HCCH) = 7.1 Hz, 2 H, OCH$_2$], 7.10−7.80 (m, 10 H, Ph). − ^{13}C NMR (C_6D_6): δ = 14.5 (OCH$_2$*C*H$_3$), 14.9 (NCH$_2$*C*H$_3$), 41.0 (NCH$_2$), 85.1 (OCH$_2$), 128.2, 130.2, 134.3, 136.7 (Ph), 198.0 [^1J(WC) = 128 Hz, *cis*-CO], 206.5 (*trans*-CO), 404.5 ($C_{Carbene}$). − ^{29}Si NMR (C_6D_6) δ = −22.0.

$(CO)_5W{=}C(NMe_2)SiPh_2CMe{=}CHMe$ (5): A stream of dry diethylamine was passed through a solution of **3** (1.86 g, 3.01 mmol) in diethyl ether (150 mL). Over 1 h, the dark red solution turned yellow. The progress of the reaction was monitored by IR spectroscopy. The solution was concentrated in vacuo, re-dissolved in petroleum ether/ether mixture (10 mL, 10:1) and chromatographed on silica at −15 °C. First, a small red zone containing **3** was eluted with petroleum ether, and then a yellow zone containing the product with petroleum ether/ether (20:1). A yellow solid was obtained after removal of the solvent. Yield 1.32 g (71%). M.p. 109 °C. − IR (petroleum ether): ν_{CO} 2060 (m), 1972 (w), 1933 (vs, br), 1925 (sh, vs) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 1.57 [dq, ^3J(HCCH) = 7.1, ^5J(HCCCH) = 1.4 Hz, 3 H, *cis*-CHC*H*$_3$], 1.64 [dq, ^4J(HCCCH) = 1.5, ^5J(HCCCH) = 1.4 Hz, 3 H, *cis*-SiCC*H*$_3$], 2.57 (s, 3 H, *trans*-*E*-NCH$_3$), 2.68 (s, 3 H, *cis*-*E*-NCH$_3$), 3.35 (s, 3 H, *trans*-*Z*-NCH$_3$), 3.41 (s, 3 H, *cis*-*Z*-NCH$_3$), 5.95 [qq, ^3J(HCCH) = 7.1 Hz, ^4J(HCCCH) = 1.5 Hz, 1 H, *cis*-CH), 7.10−7.60 (m, 10 H, Ph). − ^{13}C NMR (C_6D_6): δ = 20.7 (CH*C*H$_3$), 24.4 (SiC*C*H$_3$), 54.0 (*E*-NCH$_3$), 58.6 (*Z*-NCH$_3$), 127−145 (Ph, C=C), 199.1 [^1J(WC) = 127 Hz, *cis*-CO], 203.7 (*trans*-CO), 291.3 [^1J(WC) = 86 Hz, $C_{Carbene}$]. − ^{29}Si NMR (C_6D_6): δ = −19.6. − $C_{24}H_{23}NO_5SiW$ (617.39): calcd. C 46.69, H 3.75, N 2.27; found C 46.74, H 3.69, N 2.28.

$(CO)_5W{=}C(NHMe)SiPh_2NEt_2$ (6): A stream of dry methylamine was passed through a solution of **4** (1.50 g, 2.52 mmol) in diethyl ether (150 mL). Over 15 min, the dark red solution turned yellow.

The progress of the reaction was monitored by IR spectroscopy. The solution was concentrated in vacuo and re-dissolved in a petroleum ether/ether mixture (20 mL, 10:1). On cooling to −30 °C, a yellow precipitate was obtained which was separated and dried in vacuo. Yield 1.48 g (95%). − IR (diethyl ether): ν_{CO} 2070 (s), 1975 (s), 1935 (vs), 1925 (vs, sh) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 0.68 [t, ^{3}J(HCCH) = 7.1 Hz, 6 H, *E*-NCH_2CH_3], 0.81 (t, ^{3}J(HCCH) = 7.1 Hz, 6 H, *Z*-NCH_2CH_3], 2.01 [d, ^{3}J(HNCH) = 5.0 Hz, 3 H, *E*-NCH_3], 2.59 [q, ^{3}J(HCCH) = 7.1 Hz, 4 H, *E*-NCH_2], 2.82 [q, ^{3}J(HCCH) = 7.1 Hz, 4 H, *Z*-NCH_2], 3.03 [d, ^{3}J(HNCH) = 4.3 Hz, 3 H, *Z*-NCH_3], 7.10−7.80 (m, 10 H, Ph), 9.35 (br s, 1 H, *Z*-NH), 9.63 (br s, 1 H, *E*-NH). − ^{13}C NMR (C_6D_6): δ = 14.7 (NCH_2CH_3), 40.6 (NCH_2), 42.1 (*E*-NCH_3), 45.2 (*Z*-NCH_3), 200.0 (*cis*-CO), 204.0 (*trans*-CO), 287.3 ($C_{Carbene}$). − ^{29}Si NMR (C_6D_6): δ = −13.1.

$(CO)_4W{=}C(NMe_2)SiPh_2CMe{=}CHMe$ (7): A solution of **5** (0.72 g, 1.22 mmol) in diethyl ether (150 mL) was irradiated with UV light at −20 °C. A light stream of argon was passed through the reaction solution to expel liberated CO. The reaction was monitored by IR spectroscopy and stopped when all bands of **5** had disappeared (about 2 h). The solution was concentrated in vacuo, and the residue washed with petroleum ether at −20 °C. Orange red crystals were obtained after drying in vacuo. Yield 0.67 g (93%). − IR (petroleum ether): ν_{CO} 2024 (s), 1938 (sh, s), 1928 (vs), 1894 (s) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 2.11 [d, ^{3}J(HCCH) = 6.4 Hz, 3 H, $CHCH_3$], 2.32 (s, 3 H, $SiCCH_3$), 2.68 (s, 3 H, *E*-NCH_3), 3.08 (s, 3 H, *Z*-NCH_3), 4.75 [q, ^{3}J(HCCH) = 6.4 Hz, 1 H, CH], 7.00−7.50 (m, 10 H, Ph). − ^{13}C NMR (C_6D_6): δ = 27.8 ($SiCCH_3$), 28.4 ($CHCH_3$), 54.1 (*E*-NCH_3), 54.9 (*Z*-NCH_3), 84.4 (CH), 98.3 ($SiCCH_3$), 207.1, 209.7 [^{1}J(WC) = 125 Hz, *eq*/*cis*-CO], 214.2 [^{1}J(WC) = 130 Hz, *eq*/*trans*-CO], 216.5 [^{1}J(WC) = 155 Hz, *ax*/*cis*-CO], 291.4 [^{1}J(WC) = 82 Hz, $C_{Carbene}$]. − ^{29}Si NMR (C_6D_6): δ = −35.8. − $C_{23}H_{23}NO_4SiW$ (589.38): calcd. C 46.87, H, 3.93, N 2.38; found C 47.04, H 4.25, N 2.29.

$(CO)_4W{=}C(NHMe)SiPh_2NEt_2$ (8): A solution of **6** (1.40 g, 2.26 mmol) in diethyl ether (150 mL) was irradiated with UV light at −20 °C. A light stream of argon was passed through the reaction solution to expel liberated CO. The reaction was monitored by IR spectroscopy and stopped when all bands of **6** had disappeared (about 3 h). The solution was concentrated in vacuo, re-dissolved in a petroleum ether/ether mixture (10 mL, 20:1) and chromatographed on silica at −15 °C with the same solvent mixture. First, a yellow zone of **6** (re-formed by decomposition of **8**) was eluted, and then, with a 2:1 mixture of petroleum ether and ether mixture, an orange red zone containing the product. An orange red oil was obtained after removal of the solvent. Yield 0.83 g (62%). − IR (petroleum ether): ν_{CO} 1995 (m), 1940 (vs), 1915 (vs), 1845 (m) cm^{-1}. − ^{1}H NMR (C_6D_6): δ = 0.65 [t, ^{3}J(HCCH) = 7.1 Hz, 6 H, NCH_2CH_3], 1.71 [d, ^{3}J(HNCH) = 4.3 Hz, 3 H, NCH_3], 2.86, 3.06 (m, 4 H, NCH_2), 7.20−7.80 (m, 10 H, Ph), 8.58 (br s, 1 H, NH). − ^{13}C NMR (C_6D_6): δ = 13.8 (NCH_2CH_3), 51.4 (NCH_2), 52.3 (NCH_3), 209.9 [^{1}J(WC) = 130 Hz, *eq*/*cis*-CO], 217.3 [^{1}J(WC) = 165 Hz, *ax*/*cis*-CO], 224.1 [^{1}J(WC) = 128 Hz, *eq*/*trans*-CO], 302.3 (C_{Carben}). − ^{29}Si NMR (C_6D_6): δ = −6.0.

X-ray Structure Analysis of 7: (see also Table 3) Selected crystals were sealed in a glass capillary and mounted on a Siemens SMART diffractometer with a CCD area detector. Graphite-monochromated Mo-K_{α} radiation (71.073 pm) was used for all measurements. The crystal-to-detector distance was 5.85 cm. A hemisphere of data was collected by a combination of three sets of exposures at 293 K. Each set had a different φ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was applied. The cell dimensions were refined with all unique reflections. The structure was solved by direct methods (SHELXS86). Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL93) with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 140737. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk).

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