ORGANOMETALLICS

# A novel dinuclear tetrahydride bridged ruthenium complex, (.eta.5-C5Me5)Ru(.mu.-H)4Ru(.eta.5-C5Me5)

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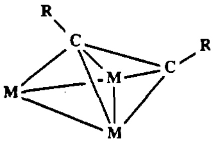
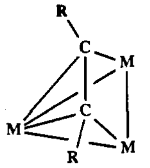
ordination mode. There are two bridging hydride ligands as shown in Figure 1.

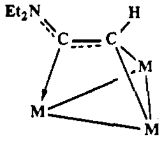
An ORTEP diagram of 3 is shown in Figure 2.[9] Compound 3 consists of a triangular triosmium cluster with a triply bridging $HC_2NEt_2$ ligand.[10,11] Although this ligand could be described formally as an "ynamine", for the reasons listed below, we feel that it is more appropriately described as a (dimetalliomethyl)(diethylamino) carbene ligand. The $HC_2NEt_2$ ligand in 3 differs from all other 48-electron trimetallic alkyne cluster complexes in that it possesses the $\mu_3$-$\perp$ coordination mode A.[12] All the others possess the $\mu_3$-$\|$ mode B. The latter is observed in the very similar complex $Ru_3(CO_9(\mu_3\text{-}MeC_2OMe)(\mu\text{-}H)$ that was prepared by Keister.[11] The only examples of trimetallic clusters possessing the $\mu_3$-$\perp$ mode are the 46-electron clusters $M_3(CO)_9(\mu_3\text{-}C_2Ph_2)$ ($M_3$ = $Fe_3$[14a] or $Fe_2Ru$[14b]), $W_2Fe(CO)_6Cp_2[\mu_3\text{-}C_2(p\text{-tolyl})_2]$,[13] and $W_2Fe(CO)_5Cp_2(O)[\mu_3\text{-}C_2(p\text{-tolyl})_2]$.[15] However, the coordination of the $HC_2NEt_2$ ligand 3 differs significantly from the 46-electron clusters with the $\mu_3$-$\perp$ alkyne mode. In the latter examples, both alkyne carbon atoms are bonded to the $\perp$ edge of the cluster. In 3, the ligand is shifted away from the $\perp$ edge toward the structure C. This is shown by the very long distances to C(2), Os(1)–C(2) = 2.91 (2) Å and Os(2)–C(2) = 2.80 (2) Å. We feel that the ligand in C can be described alternatively as a (dimetalliomethyl)(diethylamino)carbene. This formulation is also supported by the observation of the short C(2)–N distance of 1.33 (2) Å that is characteristic of aminocarbene ligands.[1] In addition, the nitrogen atom is planar and the ethyl groups are inequivalent (by $^1H$ NMR spectroscopy) due to the hindered rotation about the C(2)–N bond.[6] The two inequivalent hydride ligands (not observed crystallographically) are believed to bridge the Os(1)–Os(2) and Os(1)–Os(3) metal–metal bonds. Finally, it was found that the amino group in the $HC_2NEt_2$ ligand in 3 is readily exchanged by reaction with secondary amines as is also characteristic of carbene ligands.[1] The reaction of 3 with $NHPr^n_2$ at 97 °C gave the derivative $Os_3(CO)_9(\mu_3\text{-}HC_2NPr^n_2)(\mu\text{-}H)_2$ (4) in 74% yield.[16]



A



B



C

The transformation of 1 to 2 occurs presumably by a photoinduced decarbonylation at the $Os(CO)_4$ group and is followed by a C–H activation at the bridging carbon atom of the C(H)C(H)$NEt_2$ group; see Scheme I. This is probably similar to the transformation of $Os_3(CO)_{10}(\mu\text{-}CH_2)(\mu\text{-}H)_2$ to $Os_3(CO)_9(\mu_3\text{-}CH)(\mu\text{-}H)_3$.[17] Overall, the transformation of 2 to 3 involves a 1,2 shift of the hydrogen atom from C(2) to C(1). Mechanistically, this may involve a metal-promoted C–H activation with formation of an acetylide trihydride cluster intermediate that subsequently shifts a hydride ligand to the acetylide carbon to yield 3. The reverse of this transformation (i.e. $\mu_3$-alkyne to $\mu_3$-alkenylidene) has been observed in other metal cluster complexes.[18]

The novel mode of coordination exhibited by the $HC_2NEt_2$ ligand in 3 can be attributed in part to the formation of C–N multiple bonding caused by donation from the lone pair of electrons on the nitrogen atom. This is more important than metal–carbon bonding, and the coordination mode C thus becomes more important than A. However, the novel reactivity of 3 is also directly dependent on the unique triply bridging coordination of the $HC_2NEt_2$ ligand. This example thus provides a further confirmation of the general principle that multicenter coordination can promote novel ligand reactivity.[19]

**Acknowledgment.** These studies were supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. NMR measurements were made on a Brüker AM-300 spectrometer purchased with funds from the National Science Foundation under Grant No. CHE-8411172.

**Supplementary Material Available:** Tables of crystal data, fractional atomic coordinates, anisotropic thermal parameters, and selected interatomic distances and angles for both structural analyses (14 pages); listings of structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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(9) Selected intramolecular distances (Å) and angles (deg) for 3 are as follows: Os(1)–Os(2) = 2.832 (1), Os(1)–Os(3) = 3.003 (1), Os(2)–Os(3) = 2.802 (1), Os(1)–C(1) = 2.17 (2), Os(2)–C(1) = 2.14 (2), Os(1)–C(2) = 2.91 (2), Os(2)–C(2) = 2.80 (2), Os(3)–C(2) = 2.10 (2), C(1)–C(2) = 1.43 (2), C(2)–N = 1.33 (2); Os(3)–C(2)–N = 133, Os(3)–C(2)–C(1) = 105 (1), C(1)–C(2)–N = 121 (2).

(10) This compound was recently prepared by another route[11] but has not yet been characterized crystallographically.

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(16) The reaction was performed in refluxing heptane solvent. for 4, $\nu$(CO) in hexane: 2101 (m), 2072 (vs), 2045 (vs), 2018 (sh), 2015 (vs), 2000 (s), 1982 (s), 1977 (w, sh), 1967 (m); $^1H$ NMR ($\delta$ in $CDCl_3$) 5.84 (s, 1 H), 3.48 (t, 2 H, $J$ = 8 Hz), 3.40 (t, 2 H, $J$ = 8 Hz), 1.66 (m, 4 H), 0.96 (t, 3 H, $J$ = 6 Hz), 0.94 (t, 3 H, $J$ = 7 Hz), −16.35 (s, br, 1 H), −18.90 (s, br, 1 H).

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# A Novel Dinuclear Tetrahydride-Bridged Ruthenium Complex, $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$

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*Summary:* The novel tetrahydride-bridged dinuclear ruthenium complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H)_4Ru(\eta^5\text{-}C_5Me_5)$ (**2**) has been synthesized by reaction of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ with $LiAlH_4$. X-ray crystal structure of complex **2** is reported.

Transition-metal hydrides are implicated in the variety of stoichiometric and catalytic organic transformations.[1] Di- and polyhydride complexes with electron-donating

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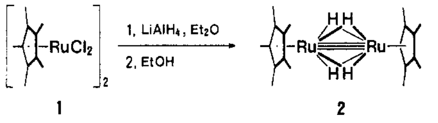
ligands have promoted the chemistry of activation of the carbon–hydrogen bonds in recent years.[2] In the previous papers, we reported that the reaction of $(\eta^5\text{-}C_5Me_5)RuCl_2(PR_3)$ with the hydridic agent such as $NaBH_4$ or $LiAlH_4$ afforded the corresponding trihydrides $(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)$ via the intermediacy of borohydrides or aluminohydrides.[3] Motivated by these results, we attempted to synthesize a new class of polyhydride complexes having only pentamethylcyclopentadienyl groups as the auxiliary ligands. We report here the preparation, the structure determination, and some reactions of a novel binuclear ruthenium hydride complex.

The suspension of $[(\eta^5\text{-}C_5Me_5)RuCl_2]_2$[4] (1) (1.01 g, 1.65 mmol) was stirred with $LiAlH_4$ (0.45 g, 11.9 mmol) in diethyl ether (30 mL) for 12 h at room temperature. After ethanolysis of the yellow intermediate at 197 K, the solvent was removed under reduced pressure. Extraction of the crude product with diethyl ether and purification by column chromatography on $Al_2O_3$ with toluene followed by recrystallization from toluene–pentane gave the binuclear tetrahydride $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}H)_4$ (2) in 30% yield as red plates (eq 1).



(1)

Complex 2 was also obtained even in lower yield (13%) by treatment of 1 with $NaBH_4$ in ethanol. Treatment of 1 with $LiAlD_4$ followed by the workup either with EtOH or with EtOD afforded the isotopomer $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}H)_2(\mu\text{-}D)_2$ (2-$d_2$) or $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}D)_4$ (2-$d_4$). To our knowledge, only three examples have been reported for the tetrahydride-bridged complexes $M\text{–}(\mu\text{-}H)_4\text{–}M$.[5-7] Complex 2 is the first binuclear tetrahydride-bridged complex having no phosphine or arsine ligands. The structure of 2 is unambiguously assigned on the basis of $^1H$ NMR, $^{13}C$ NMR, FD-MS, and elemental analysis.[8]

The $^1H$ NMR spectrum of 2 measured at room temperature showed two sharp singlet peaks at $\delta$ 1.87 ($C_5Me_5$) and −13.99 (Ru–H, $w_{1/2}$ = 2.2 Hz). The proton resonance for the hydride ligands of the isotopomer 2-$d_2$ was slightly broadened ($w_{1/2}$ = 6.0 Hz), but the apparent splitting due to the spin coupling with $^2H$ was not observed. The inversion-recovery $T_1$ determination for hydride ligands in 2 at 193 K was performed at 500 MHz by using standard JEOL programs. The $T_1$ value of 2.28 s and the $J_{HD}$ data above show the $\sigma$-bonded mode of the hydride ligands in 2, since they are not values consistent with H–H bonding.[9,17]

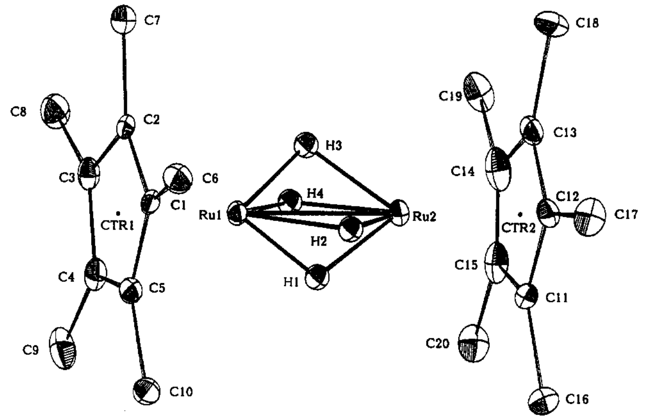


**Figure 1.** Molecular structure of $[(\eta^5\text{-}C_5Me_5)Ru]_2(\mu\text{-}H)_4$ (2). Bond lengths (Å) and angles (deg) of interest are as follows: Ru(1)–Ru(2), 2.463 (1); Ru(1)–H(1), 1.46 (7); Ru(1)–H(2), 1.78 (7); Ru(1)–H(3), 1.76 (7); Ru(1)–H(4), 1.51 (7); Ru(2)–H(1), 1.75 (7); Ru(2)–H(2), 1.68 (7); Ru(2)–H(3), 1.65 (7); Ru(2)–H(4), 1.63 (8); Ru(1)–CTR(1), 1.801 (1); Ru(2)–CTR(2), 1.817 (1); H(1)–H(2), 0.99 (8); H(3)–H(4), 0.84 (8); H(1)–H(4), 1.80 (8); H(2)–H(3), 2.23 (8); Ru(1)–H(1)–Ru(2), 99.7 (32); Ru(1)–H(2)–Ru(2), 90.9 (27); Ru(1)–H(3)–Ru(2), 92.5 (27); Ru(1)–H(4)–Ru(2), 103.3 (33); CTR(1)–Ru(1)–Ru(2), 178.7 (0); CTR(2)–Ru(2)–Ru(1), 179.0 (0). CTR indicates the centroid of a $C_5Me_5$ ring.

The magnetic equivalency of the hydride ligands in the $^1H$ NMR spectrum and the absence of the characteristic Ru–H absorption in the IR spectrum suggest that four hydride ligands are positioned on the mirror plane laid between two $(\eta^5\text{-}C_5Me_5)Ru$ units. In addition, the diamagnetism of 2 strongly indicates that two ruthenium centers are bound by a metal–metal bond. The 18-electron rule applied to the dimer 2 requires a triple bond between the ruthenium atoms.

A single-crystal X-ray diffraction study at low-temperature (118 K) has been carried out on 2 with the results shown in Figure 1.[10]

Two ruthenium centers of 2 are linked both by a metal–metal bond and by four bridging hydrides. The Ru–Ru distance of 2.463 (1) Å lies well within the values for the metal–metal triple bond. The average Ru–H distance of 1.65 (7) Å is comparable with the values of 1.69 (4) Å in $[(\eta^5\text{-}C_5Me_5)IrH(PMe_3)]_2(\mu\text{-}H)(PF_6)$,[11] 1.59 (7) Å in $[(\eta^5\text{-}C_5Me_5)IrH]_2(\mu\text{-}H)(\mu\text{-}BH_4)$,[12] 1.681 Å in $[[(C_6H_5)_2(p\text{-}ClC_6H_4)_2C_5O]Ru(\mu\text{-}H)(CO)_2]_2$,[13] and 1.62 (5) Å in $RuRh(\mu\text{-}H)(C_6H_5)(C_8H_{12})[C_6H_5PCH_2P(C_6H_5)_2][(C_6H_5)_2PCH_2P(C_6H_5)_2]$[14] but is shorter than the values for $[Ru(PMe_3)_3]_2(\mu\text{-}H)_3(BF_4)$ (1.91 Å),[15] $[RuH(PMe_3)_3]_2(\mu\text{-}H)_2$

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[8] **2**: IR (KBr) 2978, 2954, 2900, 1794 (vw), 1475, 1448, 1425, 1376, 1070, 1030, 1027, 585, 455 $cm^{-1}$; $^1H$ NMR ($C_6D_6$) $\delta$ 1.87 (s, 30 H), −13.99 (s, 4 H); $^{13}C$ NMR ($C_6D_6$) $\delta$ 88.2 (s, $C_5Me_5$), 12.5 (s, $C_5Me_5$); UV ($C_6H_5CH_3$) $\lambda_{max}$ 493 nm ($\epsilon$ 1270); mp 152 °C dec. Anal. Calcd for $C_{20}H_{34}Ru_2$: C, 50.39; H, 7.18. Found: C, 50.37; H, 7.27. Field-desorption mass spectrum was recorded on a Hitachi M-80 high-resolution mass spectrometer, and intensities of the obtained isotopic peaks for $C_{20}H_{34}Ru_2$ agreed well with the calculated values. The mass spectral data are available in the supplementary material.

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[10] X-ray crystallography. $(C_5Me_5)Ru(\mu\text{-}H)_4Ru(C_5Me_5)$ crystallizes from toluene–pentane in the monoclinic system, space group *Pa*, with $a$ = 12.291 (2) Å, $b$ = 8.521 (1) Å, $c$ = 10.053 (2) Å, $\beta$ = 108.519 (12)°, $V$ = 998.3 (3) $A^3$, and $Z$ = 2. From 4908 reflections collected at 118 K using Mo K$k\alpha$ radiation, the structure was solved and refined by standard methods to yield $R$ = 2.22% (2391 reflections, $F > 3\sigma(F)$). In a difference Fourier map, calculated following refinement of all non-hydrogen atoms with the anisotropic thermal parameters, the peaks corresponding to the positions of all hydrogen atoms including the hydridic hydrogens bound to the ruthenium atoms were found. Full structural details are available in the supplementary material.

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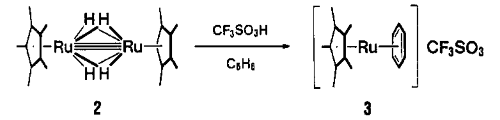
(1.954 (67) Å),[15] $Ru_2H(\mu\text{-}H)_3N_2(PPh_3)_4$ (1.89 Å),[16] and $[ReH_2(PEt_2Ph)]_2(\mu\text{-}H)_4$ (1.878 (7) Å).[5] The H–H distances, 0.99 (7) Å for H(1)–H(2) and 0.84 (8) Å for H(3)–H(4), are comparable to those of $\eta^2\text{-}H_2$ ligands,[17,18] but X-ray crystallography is not a good way to tell the H–H distances because the electron density maxima of the two-electron–three center (2e–3c) MHM bonds will be much closer than the nuclei themselves. We therefore conclude that 2 is not a $\eta^2\text{-}H_2$ complex but a σ-bonded metal hydride complex on the basis of the value of $J_{HD}$ and the $T_1$ data.

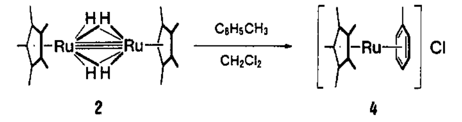
Transition-metal polyhydride complexes are known to have the potential for creating coordinative unsaturation by eliminating molecular hydrogen. While complex 2 is hardly decomposed upon irradiation of UV light, 2 evolves $H_2$ to generate the coordinatively unsaturated species by the addition of acid.

Treatment of 2 with 1.1 equiv of $CF_3SO_3H$ in benzene quantitatively afforded the cationic 18-electron complex $[(\eta^5\text{-}C_5Me_5)Ru(\eta^6\text{-}C_6H_6)](CF_3SO_3)$ (3) via the addition of benzene to the intermediary "$(\eta^5\text{-}C_5Me_5)Ru$" (eq 2).[19]

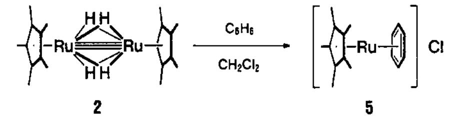


(2)

Cationic arene–ruthenium complexes 4 and 5 were also obtained in 99 and 91% yields, respectively, by reacting 2 with arenes in a halogenated solvent such as $CH_2Cl_2$ or $CHCl_3$ (eq 3 and 4).[20]



(3)



(4)

**Acknowledgment.** We thank the Instrument Center, Institute for Molecular Science, for the use of X-ray diffractmeter (Rigaku AFC-5). We are grateful to Drs. T. Inabe and T. Mori at Institute for Molecular Science for aid of X-ray structural analysis. Financial support for this work was generously provided in part by grants from the Kawakami Memorial Foundation and the Ministry of Education, Science and Culture of the Japanese Government (No. 62215009).

**Supplementary Material Available:** Tables of crystal data, bond distances and angles, positional parameters and isotropic temperature factors, and anisotropic temperature factors for 2 and field-desorption mass spectra and mass spectral data for $C_{20}H_{34}R_2$ (13 pages); a listing of structure factor amplitudes for 2 (6 pages). Ordering information is given on any current masthead page.

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(19) **3**: IR (KBr) 3072, 2981, 2909, 1258, 1170, 1041, 645, 581, 528 $cm^{-1}$; $^1H$ NMR ($CD_3COCD_3$) δ 5.97 (s, 6 H, $C_6H_6$), 2.04 (s, 15 H); $^{13}C$ NMR ($CD_3COCD_3$) δ 96.5 ($C_5Me_5$), 87.0 ($C_6H_6$), 9.7 ($C_5Me_5$). Anal. Calcd for $C_{17}H_{21}O_3F_3SRu$: C, 44.06; H, 4.57. Found: C, 43.96; H, 4.65.

(20) **4**: IR (KBr) 2987, 2941, 2899, 1616, 1473, 1451, 1385, 1129, 1072, 1033, 980, 860, 775 $cm^{-1}$; $^1H$ NMR ($CD_2Cl_2$) δ 5.95–5.80 (m, 3 H, aromatic), 5.33–5.32 (m, 2 H, aromatic), 2.23 (s, 3 H), 2.00 (s, 15 H); $^{13}C$ NMR ($CD_2Cl_2$) δ 100.6 (s), 96.6 (s, $C_5Me_5$), 88.8 (d, $J$ = 171.7 Hz), 88.1 (d, $J$ = 151.9 Hz), 87.4 (d, $J$ = 176.0 Hz), 19.0 (q, $J$ = 129.2 Hz), 11.1 (q, $J$ = 128.6 Hz). Anal. Calcd for $C_{17}H_{23}ClRu$: C, 56.11; H, 6.37; Cl, 9.74. Found: C, 55.85; H, 6.41; Cl, 9.53. **5**: IR (KBr) 3053, 3026, 2960, 2906, 1483, 1445, 1399, 396 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ 5.93 (s, 6 H, $C_6H_6$), 2.03 (s, 15 H); $^{13}C$ NMR ($CDCl_3$) δ 98.1 (s, $C_5Me_5$), 88.5 (d, $J$ = 176.4 Hz), 10.8 (q, $J$ = 128.0 Hz). Anal. Calcd for $C_{16}H_{21}ClRu$: C, 54.93; H, 6.05; Cl, 10.13. Found: C, 54.59; H, 6.29; Cl, 10.92.

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## Silaaziridines from the Reaction of Isonitriles with Stable Silenes

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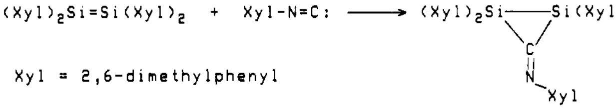
*Summary:* Stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ react with isonitriles $R'N{=}C{:}$ to yield unstable silacyclopropanimines which rapidly rearrange below room temperature to form the isomeric silaaziridines, as shown by the crystal structure of one of the compounds (R = Ad, R′ = *t*-Bu). These are the first reported examples of three-membered rings containing both silicon and nitrogen.

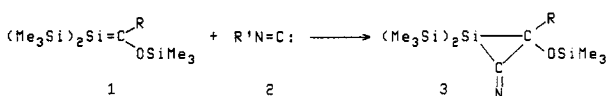
Silenes have been shown to undergo a variety of cycloaddition reactions,[1] including reactions with alkenes,[2,3] dienes,[2,3] aldehydes and ketones,[4,5] silylenes,[6] and imines[5] and diazenes.[5,7] We now report the cycloaddition reaction of stable silenes of the family $(Me_3Si)_2Si{=}C(OSiMe_3)R$ (1) with isonitriles $R'N{=}C{:}$ (2).

The reaction of an isonitrile with a disilene has recently been reported to yield a disilacyclopropanimine (eq 1), as



(1)

shown by the crystal structure of the product.[8,9] By analogy it might be expected that an isonitrile, 2, would react with a silene 1 to yield the related silacyclopropanimine 3 (eq 2), but this was not the structure of the compounds isolated at room temperature.



(2)

When members of our family of silenes 1 having R = *t*-Bu or Ad (1-adamantyl) were generated (by photolysis of the related acylsilane $(Me_3Si)_3SiCOR$ in $C_6D_6$ using 360-nm radiation at 10 °C) in the presence of an equivalent

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(1) For recent reviews on the chemistry of silenes see: Baines, K. M.; Brook, A. G. *Adv. Organomet. Chem.* **1986**, *26*, 1. Michl, J.; Raabe, G. *Chem. Rev.* **1985**, *85*, 419.

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(9) We are indebted to Prof. West for a preliminary communication on his studies of disilenes with isonitriles.

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