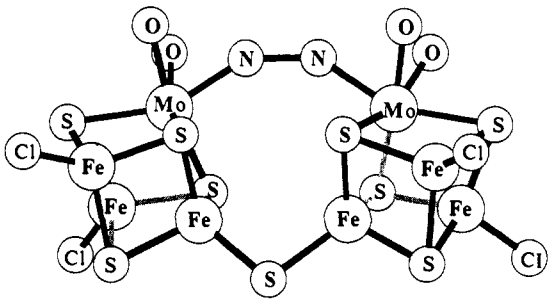

Figure 1. Preliminary structure[18] of the anion core in $[Et_4N]_4[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}N_2H_4)]\cdot CH_3CN$. The structure has been drawn from crystallographically determined coordinates with use of the program Molecular Editor, and the catecholate phenyl rings have been omitted for clarity.

data obtained from the best obtainable, albeit poor quality, crystals. The core structure in II (Figure 1) has been drawn on the basis of crystallographically determined coordinates and is presented with the intention of showing atomic connectivity. The anion has approximate C_{2v} symmetry and is located on a crystallographic mirror plane that contains the μ_2-S and the side-on, bridging N_2H_4 ligand and bisects the Mo-Mo and Fe-Fe intercube vectors. Most of the interatomic bond distances and angles in II and III are reasonable. Unfortunately the unacceptably high standard deviations of these values preclude a comparison of II or III to the structures of the μ_2-S or μ_2-OH analogues. A meaningful comparison can be made between the Mo-Mo distance in II (5.22 (1) Å) and that in I (4.248 (9) Å) and demonstrates the remarkable flexibility of the basic structure in accepting bridging ligands with differing steric demands.

The syntheses of II and III demonstrate the feasibility of introducing nitrogenase substrates in an "end-to-end" bridging mode within two μ_2-S-bridged cubane subunits and establish a methodology for the rational synthesis of analogous mixed-cubane clusters. Whereas II and III posess Mo-L-Mo bridges (L = CN^-, N_2H_4) and a stoichiometry of no direct consequence to the nitrogenase active site problem, mixed clusters analogous to II and III that contain $MoFe_3S_4$ and Fe_4S_4 as subunits could be biologically relevant. The latter will provide the first examples of molecules with Mo-L-Fe bridges, will have a biologically relevant Fe:Mo:S ratio, and will be potentially capable in the heterobimetallic coordination of nitrogenase substrates. A Mo-μ_2-S-Fe unit has been suggested previously[19] as a possible site for the activation and reduction of N_2 in nitrogenase.

An intriguing question arises as to whether, under strongly reducing conditions, clusters similar to I, II, and III or derivatives (perhaps with homocitrate[20] in place of the catechol ligands) can be obtained with N_2 as an intercube bridging ligand. Toward this goal the reactivity of I, II, and III, and of analogous "mixed" clusters[11] that contain Fe_4S_4 and $MoFe_3S_4$ subunits, currently is under investigation.

Acknowledgment. This research was supported by a grant from the National Institutes of Health (GM-33080).

(18) Black crystals of II·CH_3CN (MW 2042) are orthorhombic with space group *Pmcn* and a = 15.502 (6) Å, b = 19.661 (4) Å, c = 27.024 (6) Å, and Z = 4; d_{calc} = 1.64 g/cm^3; d_{obs} = 1.63 g/cm^3; MW_{calc} = 2020 ± 20. Single-crystal X-ray diffractometer data were collected for II and the structure was solved by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. All atoms in the anion were located, however, due to the poor quality of the crystal and limited data (II: Mo Kα, $2\theta_{max}$ = 35°, 1317 data with $I > 3\sigma I$); a satisfactory model for the disordered Et_4N^+ cations in the structure has not yet been found. At present with a complete anion refined but only parts of the Et_4N^+ cations included in structure factor calculations R = 0.16. All attempts to obtain better crystalline derivatives of II have failed. With the expectation that it will be possible to obtain high-quality data from better crystals, perhaps with different counterions, deposition of crystallographic data is not warranted at this time.

(19) Hardy, R. W. F.; Burns, R. C.; Parshall, G. W. In *Inorganic Biochemistry*; Eichhorn, G. L., Ed.; Elsevier: Amsterdam, 1973; pp 745-793.

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Nucleophilic Activation of Triruthenium Carbonyl Complexes by Semilabile Ancillary Ligands. Cluster-Assisted Codimerization of Alkynes and Ethylene To Give 1,2-Disubstituted 1,3-Butadienes

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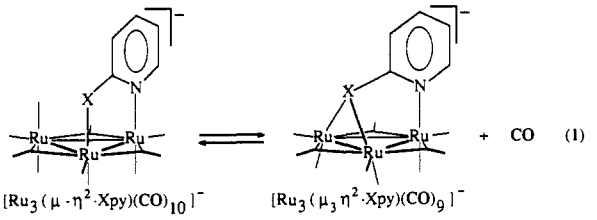
In connection with earlier observations that the variable hapticity of halides plays a "lightly stabilizing" role for coordination sites in some anion-promoted systems based on the complexes $[PPN][Ru_3(X)(CO)_n]$, (X = Cl, Br, I; n = 11, 10, 9),[1-4] we report that amido, mercapto, and alkoxy groups modified by a pyridyl substituent[5] give related activated species $[PPN][Ru_3(X\text{-}(C_5H_4N))(CO)_n]$ ([PPN][**1a-c**], n = 10; [PPN][**2a-c**], n = 9; $PPN^+ = (C_6H_5)_3PNP(C_6H_5)_3^+$; **a**, X = $N(C_6H_5)$; **b**, X = S; **c**, X = O) that are involved in the equilibrium shown in eq 1.[6,7]



$[Ru_3(\mu\text{-}\eta^2\text{-}Xpy)(CO)_{10}]^-$ $[Ru_3(\mu_3\eta^2\text{-}Xpy)(CO)_9]^-$ (1)

Furthermore, the corresponding hydrido amido complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N)(CO)_9$ (**3a**) is seen to activate alkynes selectively via the alkenyl complex **5a** and to promote an alkyne-ethylene codimerization[8] under mild conditions (Scheme I).

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(4) For recent reviews dealing with nucleophilic activation, see: (a) Ford, P. C.; Rokicki, A. *Adv. Organomet. Chem.* **1988**, *28*, 139-217. (b) Lavigne, G.; Kaesz, H. D. In *Metal Clusters in Catalysis*; Gates, B., Guczi, L, Knözinger, H., Eds.; Elsevier: Amsterdam, 1986; Chapter 4, pages 43-88. (c) Lavigne, G. In *The Chemistry of Metal Clusters*; Shriver, D., Adams, R. D., Kaesz, H. D., Eds.; Verlag Chemie: Weinheim, 1990; Chapter 5, pp 201-302.

(5) (a) Our interest in these ligands is related to our earlier work[5b] on phosphidopyridyl groups. (b) Lugan, N.; Lavigne, G.; Bonnet, J.-J.; Réau, R.; Neibecker, D.; Tkatchenko, I. *J. Am. Chem. Soc.* **1988**, *110*, 5369-5376.

(6) Experimental details for the preparation and characterization of the compounds are provided in the supplementary material.

(7) (a) [PPN][**1a**]: IR (ν(CO), cm^{-1}, THF) 2066 (m), 2035 (vw), 2007 (vs), 1985 (vs), 1951 (m), 1935 (m), 1925 (sh), 1855 (vw), 1811-1800 (s, br). (b) [PPN][**2a**]: IR (ν(CO), cm^{-1}, THF) 2021 (s), 2012 (sh), 1975 (vs), 1934 (ms), 1912 (m), 1842 (vw), 1793 (vs).

(8) Alkyne-alkene codimerization is unprecedented in cluster chemistry and rare for mononuclear complexes; see: (a) Heck, R. F. *Organo Transition Metal Chemistry*; Maitlis, P. M., Stone, F. G. A., West, R., Eds.; Academic Press: New York and London, 1974. (b) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York, 1985.

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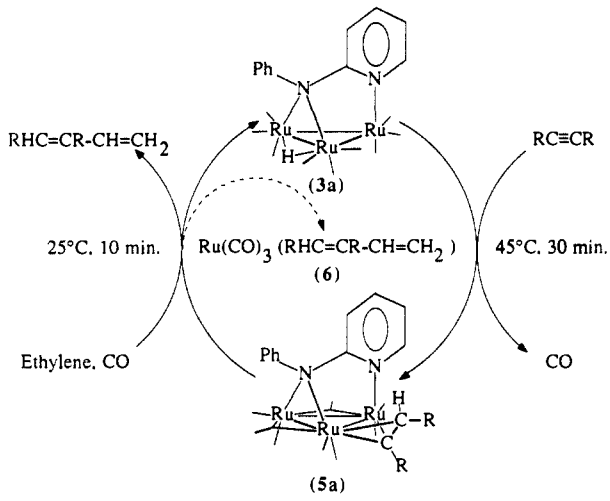
Scheme I



The complex [PPN][$Ru_3(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N))(CO)_9$] ([PPN][**2a**])[6,7] was prepared either (i) by treatment of $Ru_3(CO)_{12}$ with [K][$N(C_6H_5)(C_5H_4N)$], followed by metathesis with [PPN][Cl] (yield, 80–90%), or (ii) by reaction of 2-anilinopyridine with [PPN][$Ru_3(\mu\text{-}H)(CO)_{11}$] (THF, 60 °C, 2 h, 60% yield), or finally, (iii) by reaction of 2-anilinopyridine with $Ru_3(CO)_{12}$ (C_6H_6, 80 °C, 2 h) leading to $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)\text{-}(C_5H_4N))(CO)_9$ (**3a**)[6,9] (yield, 85%), followed by deprotonation of the latter with [PPN][BH_4] (yield, 90%). The complex [PPN][$Ru_3(\mu\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N))(CO)_{10}$] ([PPN][**1a**]) was quantitatively obtained in situ by bubbling CO into a solution of [PPN][**2a**] for 5–10 min at 25 °C. The anion route (i) is the most efficient process for the preparation of 2-mercaptopyridine derivatives. Routes i and ii are the only efficient ones for 2-hydroxypyridine, leading exclusively to [PPN][$Ru_3(\mu\text{-}\eta^2\text{-}O\text{-}(C_5H_4N))(CO)_{10}$] ([PPN][**1c**]) (60% yield).[6] The X-ray structures of [PPN][**1c**] and [PPN][**2a**] have been determined.[6]

The complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N))(CO)_9$ (**3a**) was found to react with PPh_2H at −40 °C over 2 min to give $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N))(CO)_8(PPh_2H)$ (**4a**).[10,11] The occurrence of a transient species involving a terminal amido group may account for the very low activation energy of this substitution, as observed in eq 1 and in few related systems.[4,12]

The high substitutional lability of the hydrido species **3a,b** was confirmed by the reaction with alkynes (40–50 °C, 30–45 min) giving *selectivity* the alkenyl derivative $Ru_3(\mu_3\text{-}\eta^2\text{-}X(C_5H_4N))\text{-}(\mu\text{-}\eta^2\text{-}(C_6H_5)CCH(C_6H_5))(CO)_8$ (**5a**, 90–95% yield; **5b**, 70–80% yield)[6,13] via cis insertion into the metal–hydride bond.[14] The retention of the trimetallic unit in this reaction is in sharp contrast with the behavior of related edge double bridged complexes $Ru_3(\mu\text{-}H)(\mu\text{-}X)(CO)_{10}$ (X = halide, C(O)R, $C(O)NMe_2$)[13a,b] that easily lose one metal center upon olefin insertion.

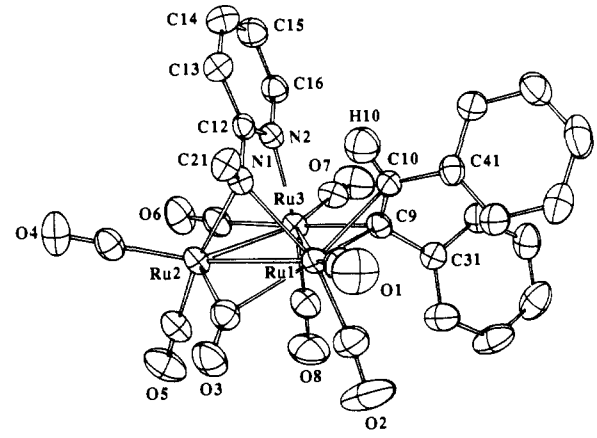


Figure 1. Perspective view of the alkenyl complex $Ru_3(\mu\text{-}N\text{-}(C_6H_5)(C_5H_4N))(\mu\text{-}(C_6H_5)CCH(C_6H_5))(CO)_8$ (**5a**). The phenyl substituent of the amido group has been omitted for clarity. Selected interatomic distances (Å) and bond angles (deg): Ru(1)–Ru(2) = 2.6786 (3), Ru(1)–Ru(3) = 2.8044 (4), Ru(2)–Ru(3) = 2.8198 (5), Ru(1)–N(1) = 2.242 (3), Ru(2)–N(1) = 2.207 (3), Ru(3)–N(2) = 2.166 (3), Ru(1)–C(9) = 2.276 (3), Ru(3)–C(9) = 2.114 (3), Ru(1)–C(10) = 2.306 (3), C(9)–C(10) = 1.397 (4), Ru(1)–N(1)–Ru(2) = 74.03 (9), Ru(1)–C(9)–Ru(3) = 79.3 (1).

The structure of **5a** (Figure 1)[15] consists of a triangular ruthenium unit supported by a face-bridging anilinopyridyl group. The bridging alkenyl group spans one lateral edge of the cluster, and the coordination shell is completed by six terminal, one bridging, and one semibridging carbonyl groups.

Instantaneous reductive elimination of the alkenyl group occurred upon addition of a hydride donor like [PPN][BH_4] to a solution of **5** (previously saturated with CO for 1 min), to produce the anion [PPN][**2**] quantitatively.[6] Catalytic hydrogenation of 1-phenyl-1-propyne to the corresponding *cis*-alkene was observed under hydrogen in the presence of **3a** as a catalyst precursor. It was followed by isomerization to the trans derivative under our nonoptimized reaction conditions.[6,18]

More surprisingly, the alkenyl complex **5a** was found to undergo fast reaction with ethylene (1 atm, 25 °C, 10 min) with recovery of the starting complex **3a** in up to 80% spectroscopic yield (see Scheme I). The only resulting organic product, 1,2-diphenyl-1,3-butadiene, was extracted by thin-layer chromatography on silica plates and identified by ^1H NMR and mass spectroscopy.[6,17] Its formation occurs likely by ethylene insertion into the metal–alkenyl bond, followed by β-hydrogen elimination. Small amounts of the colorless mononuclear η^4-butadiene complex $Ru(CO)_3\text{-}(\eta^4\text{-}(C_6H_5)CH{=}C(C_6H_5)CH{=}CH_2)$ (**6**) were eluted with hexane in the fast-moving band containing the free ligand.[17,18] This indicates that the elimination of free butadiene competes with a facile loss of the metal center on which this organic group is assembled (Scheme I, dashed path). At the present stage of our investigation, the cycle can be run up to three consecutive times in a stepwise manner, with progressive poisoning by accumulation of the side product **6**.

(9) **3a**: IR (ν(CO), cm^{-1}, cyclohexane) 2078 (m), 2050 (s), 2030 (vs), 2000 (m), 1993 (ms), 1971 (w), 1966 (w).

(10) **4a**: IR (ν(CO), cm^{-1}, THF) 2058 (s), 2024 (vs), 1999 (s), 1975 (m), 1956 (w).

(11) (a) **4a** undergoes rapid P–H bond activation to give the phosphido-bridged species $Ru_3(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N))(\mu\text{-}CO)_2(CO)_6(\mu\text{-}PPh_2)$.[5b] (b) Andreu, P. L.; Cabeza, J. A.; Riera, V.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1990**, *384*, C25–C28.

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(13) **5a**: IR (ν(CO), cm^{-1}, THF), 2062 (m), 2034 (vs), 2007 (vs), 1995 (s), 1974 (m), 1936 (s), 1822 (mbr).

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(15) Crystal data for **5a**: triclinic $P\bar{1}$, No. 2, a = 10.424 (a) Å, b = 18.795 (2) Å, c = 8.964 (1) Å, α = 93.97 (1)°, β = 105.09 (1)°, γ = 78.51 (1)°, V = 1661 (5) $Å^3$, Z = 2, μ(Mo Kα) = 13.76 cm^{-1}; R = 0.023, R_w = 0.025 for 5502 reflections and 436 variables.

(16) THF, 40 mL; T = 65 °C, $P(H_2)$ = 40 atm; catalyst, 0.012 mmol; substrate/catalyst ratio = 200; 100% conversion after 120 min with 99% selectivity in alkene; 100% cis/trans selectivity during the first 30 min.

(17) (a) ^1H NMR for 1,2-diphenyl-1,3-butadiene, $H_aPhC{=}CPhCH_b{=}CH_cH_d$ ($CDCl_3$): δ 7.3–6.8 (Ph), 6.74 (dd, 1, H_b, $J(H_bH_c)$ = 11 Hz, $J(H_bH_d)$ = 17 Hz), 6.60 (s, 1 H, H_a), 5.16 (d, 1 H, H_c), 4.83 (d, 1 H, H_d). Mass spectrum (EI): 206. (b) Spectroscopic data for **6**: IR (ν(CO), cm^{-1}, cyclohexane) 2061 (s), 2001 (vs), 1989 (s). Mass spectrum (EI), 392; ^1H NMR ($CDCl_3$) δ 7.3–6.8 (Ph), 5.44 (dd, 1 H, H_b, $J(H_bH_c)$ = 7 Hz, $J(H_bH_d)$ = 8 Hz), 2.28 (s, 1 H, H_a), 1.81 (dd, 1 H, H_c, $J(H_cH_d)$ = 3 Hz), 0.75 (dd, 1 H, H_d).

(18) For related butadiene complexes, see: (a) Gambino, O.; Valle, M.; Aime, S.; Vaglio, G. A. *Inorg. Chim. Acta* **1974**, *8*, 71–74. (b) Ruh, S.; von Philipsborn, W. *J. Organomet. Chem.* **1977**, *127*, C59–C61.

Curiously, this coupling reaction is only observed for the amido derivative.[19] There is a hint, here, that ruthenium carbonyl cluster complexes activated by nitrogen bases may be potential synthons for promoting carbon–carbon bond formation between different kinds of olefins. The next challenge will be to render the co-dimerization process catalytic.

Acknowledgment. This work was supported by the CNRS. We are grateful to Johnson-Matthey for generous loans of ruthenium trichloride, to Dr. Renê Mathieu for helpful discussions, and to Ms. Sylvie Segura for her contribution.

Supplementary Material Available: Details for the preparation and characterization of the complexes [PPN][**1a**,**c**], [PPN][**2a–c**], **3a**,**b**, **4a**,**b**, **5a**,**b**, and **6**, details of hydrogenation and codimerization reactions, preliminary crystallographic data for [PPN][**1c**] and [PPN][**2a**], and a listing of full crystallographic data for **5a** including atomic coordinates, thermal parameters, and selected interatomic distances and bond angles (17 pages); listing of observed and calculated structure factor amplitudes for **5a** (27 pages). Ordering information is given on any current masthead page.

(19) While we were in the process for submitting this work, a parallel report on vinyl ethylene combination appeared: Bruce, G. C.; Knox, S. A. R.; Phillips, A. J. *J. Chem. Soc., Chem. Commun.* **1990**, 716–718.

Intramolecular Reactions of Diazocyclobutanes. Synthesis of *trans*-Tricyclo[4.2.0.0^{1,3}]octane ([3.5.4]Fenestrane)†,[1]

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Small-ring carbenes, i.e., divalent carbons in three-[2] and four-membered rings,[3] respectively, have successfully been used for the construction of highly strained,[4] polycyclic compounds. While inter- and intramolecular additions of cyclopropylidenes and/or their corresponding carbenoids[2] are well-known, only *inter*molecular additions of cyclobutyliden(oid)s[5] to carbon double and triple bonds have been reported in the literature.[6]

The addition of 3-butenyl substituted cyclopropyliden(oid)s **3**, generated from the corresponding geminal dibromocyclopropanes

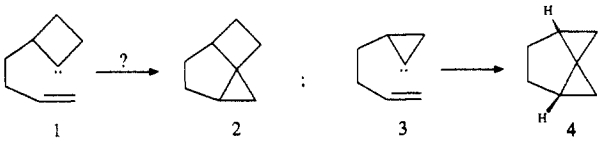

Figure 1.

on treatment with methyllithium, provides an easy access to *trans*-tricyclo[4.1.0.0^{1,3}]heptanes **4**.[7] Since an organometallic route to cyclobutyliden(oid)s **1** containing an additional double bond has not yet been uncovered, we chose to generate **1** via the corresponding diazo precursor.

Tricyclo[4.2.0.0^{1,3}]octane (**2**) resulting from the addition of the divalent carbon in **1** to the double bond represents a unique structure, comprising a three-, four-, and five-membered ring. In the literature besides a geminal dichloro-substituted ketone three pentasubstituted compounds with the carbon skeleton of **2** can be found.[8] The connection of the cyclopropane and the cyclobutane ring in **2** by the ethano bridge can be in either a cis or a trans fashion. The strain energy for *trans*-tricyclo[4.1.0.0^{1,3}]-heptane (**4**) and the corresponding cis isomer has been calculated to be 80 and 120 kcal/mol, respectively.[9] Of the five possible isomeric, unbridged, tricyclic carbon skeletons containing three-, four-, and five-membered rings sharing one common carbon atom, **2** comprises the highest computed strain energy (70.1 kcal/mol).[10]

For the synthesis of the unknown 2-(but-3-enyl)cyclobutanone, ethyl 3-chloropropanoate was converted to 1-ethoxy-1-(trimethylsiloxy)cyclopropane.[11] Treatment with phosphorus tribromide gave 1-bromo-1-ethoxycyclopropane,[12] which with 4-pentenal yielded 1-ethoxy-1-(1-hydroxy-4-pentenyl)cyclopropane. With HBF_4 (50%) this compound rearranged[13] to the required cyclobutanone. The corresponding cyclobutanone with two methyl groups on the terminal olefinic carbon was also prepared according to this methodology.

The flash pyrolyses[14] of the tosylhydrazone sodium salts of **5** and **6** each at 250 °C (10^{-5}–10^{-4} Torr) gave totally different results. While it is assumed that from both **5** and **6** the diazocyclobutanes **7** and **8** are formed, their reaction behavior differs strongly. In **7** preferentially a 1,3-dipolar cycloaddition[15] to **14** takes place which isomerizes to the more stable pyrazoline **16**. The loss of nitrogen in **7** and the generation of carbene **1** competes with the intramolecular 1,3-dipolar cycloaddition (ratio 3:7).

In carbene **1** the ring contraction reaction to **10** dominates over the 1,2-hydrogen migration to **12** (ratio 94:6); in addition, 2-(but-3-enyl)methylenecyclopropane, which seems to be a secondary thermal product of **10**, is formed. However, **2**, the product resulting from intramolecular addition of the divalent carbon in **1** to the double bond, is not found. In stark contrast to **7**, **8** liberates predominantly nitrogen to generate carbene **9**, while the 1,3-dipolar cycloaddition to **15** is only of minor significance (ratio 8:2). Not surprisingly, the reaction pattern of carbene **9** is almost identical

† Dedicated to Professor Wolfgang Kirmse on the occasion of his 60th birthday.

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(1) Carbene Rearrangements, Part 36. Part 35: Brinker, U. H.; Erdle, W. Heterocycloalkylidene, In *Houben-Weyl (Methoden der Organischen Chemie)*; Regitz, M., Ed.; Thieme: Stuttgart, 1989; Vol. E19b, pp 623–663.

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