Trapping the Dirhenium Alkynyl Fischer Type Carbene through Michael Addition. Unexpected Room-Temperature *E*/*Z* Isomerization of $(CO)_5Re(CO)_4Re({=}C(OMe)CH{=}C(NMe_2)TMS)$

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Summary: The reaction of $Re_2(CO)_{10}$ with LiC≡CTMS and $Me_3O^+BF_4^-$ results in a low-stability Fischer type alkynyl carbene complex, $(CO)_5Re(CO)_4Re(=C(OMe)C{\equiv}CTMS)$. This easily reacts with $HNMe_2$ to give the stable $(CO)_5Re(CO)_4Re(=C(OMe)CH{=}C(NMe_2)TMS)$ in 82% yield, which exhibits unrestrained rotation around the carbon−carbon "double bond", resulting in room-temperature E/Z isomerization. The aminolysis product $(CO)_5Re(CO)_4Re(=C(NMe_2)C{\equiv}CTMS)$ was also generated from $(CO)_5Re(CO)_4Re(=C(OMe)C{\equiv}CTMS)$ and could be desilylated to form the acetylene carbene $(CO)_5Re(CO)_4Re(=C(NMe_2)C{\equiv}CH)$.

Since the discovery by Fischer and Maasböl,[1] transition-metal-stabilized carbene complexes have been attracting attention from numerous fundamental and applied viewpoints. After a short period of their very limited applications, they became extremely attractive tools in organic and organometallic syntheses.[2] Today, due to a large diversity of the processes they are involved in, researchers have classified them as "chemically multitalented compounds".[3]

Among different types of metal carbenes the α,β-unsaturated alkenyl and alkynyl complexes are especially interesting. Much of this interest has been prompted by their potential to serve as C_2 and C_3 synthons for a large number of [2+] and [3+] cyclizations.[2f,4] This direction has been initiated by Dötz in the 1970s[5] and first led to the synthesis of numerous naphthoquinone derivatives via cycloaddition of alkynes to metal carbenes. Since then, a large number of other cycloaddition products have been obtained.[2f]

Although the chemistry of metal carbenes is very rich, it is mainly limited to group VI elements. Other Fischer type metal carbenes although well known[6] are—as reaction substrates—much less investigated. Mono- and dirhenium carbenes were synthesized in the 1960s and 1970s by Fischer.[7] Later, in 1982, Schubert and co-workers published the first structurally characterized carbene, *eq*-$(CO)_5Re(CO)_4(=C(OR)SiPh_3)$ (R = Me or Et), and a very interesting double carbene, *ax*,*eq*-$(Ph_3Si(OMe)C{=})Re(CO)_4Re(CO)_4(=C(OMe)SiPh_3)$.[8] In 1997, Gladysz described the first homopolymetallic $(CO)_5Re(CO)_4Re(=C(OMe)C{\equiv}C)(PPh_3)(NO)Re(\eta^5\text{-}C_5Me_5)$, which, under the influence of BF_3, rearranges via 1,3-sigmatropic shift to yield the $[(CO)_5Re(CO)_4Re(\mu\text{-}\eta^1{:}\eta^3{:}\eta^1\text{-}CCC)(PPh_3)(NO)Re(\eta^5\text{-}C_5Me_5)][BF_4]$ salt.[9] Other very interesting mono- and dirhenium carbenes have been reported by Casey[10a] and by Wojcicki.[10b,c] In the following communication the synthesis of dirhenium alkynyl(alkoxy)carbene and its reaction with $HNMe_2$ are described. On the basis of the crystallographic data the bonding within the carbonyl ligand is also discussed.

As shown in Scheme 1, $Re_2(CO)_{10}$ and freshly generated TMSC≡CLi were combined in THF/Et_2O at −78 °C. The reaction was allowed to warm to room temperature, and after 0.5 h it was cooled to −78 °C and $Me_3O^+BF_4^-$ was introduced. A chromatographic workup on deactivated Florisil gave the orange band containing diamagnetic $(CO)_5Re(CO)_4Re(=C(OMe)C{\equiv}CTMS)$ (**1**), as evidenced by ^1H NMR spectroscopy. The spectrum showed two siglets at 3.39 and 0.12 ppm that correspond to OMe and TMS groups, respectively. No other signals were observed, which suggested that a single isomer had been formed. The mass spectrum of **1** gave a strong

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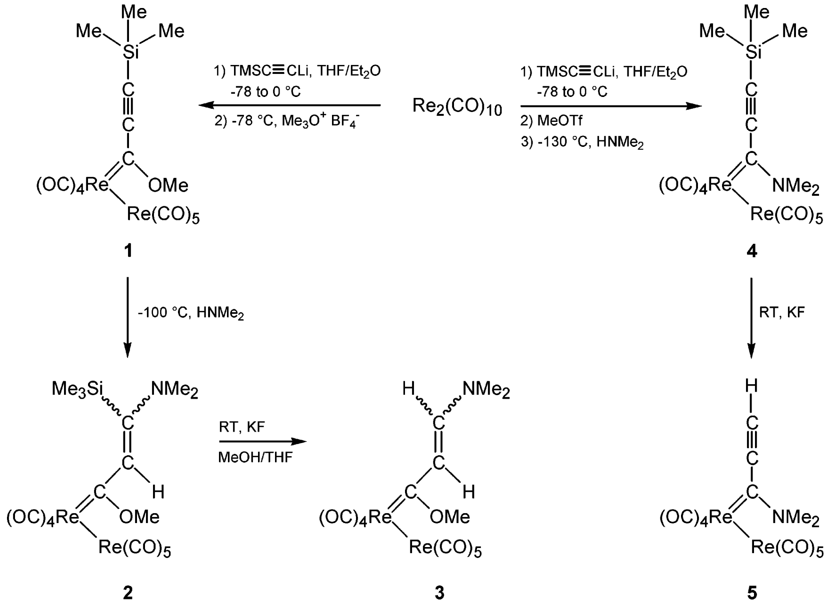
Scheme 1. Syntheses of Dirhenium Alkynyl and Alkenyl Carbenes



molecular ion peak and the IR spectrum exhibited a strong band at 2104 cm^{-1} from the C≡C stretching. Unfortunately the complex gave no correct microanalysis. A closer look at the IR spectrum revealed impurities of $Re_2(CO)_{10}$, which most probably formed due to the decomposition of **1** either at elevated temperature (rt) or during the workup. Low-temperature chromatography as well as workup that excluded Florisil (recrystallization, Celite) gave analogous results.

Despite its low stability compound **1** was tested in Michael addition to probe its potential as a synthetic tool for further transformations. Freshly generated **1** was treated at low temperature with $HNMe_2$, and the reaction was quenched with water. The red organic layer was chromatographed to give $(CO)_5Re(CO)_4Re({=}C(OMe)CH{=}C(NMe_2)TMS)$ (**2**) as an analytically pure red-orange solid in 82% yield. The structure of **2** was supported by a variety of data. The ^{1}H NMR spectrum (rt, CD_2Cl_2) showed four singlets at 6.25, 3.95, 3.13, and 0.32 ppm in a 1:3:6:9 ratio, suggesting the formation of a single diastereomer. The FAB-MS of **2** exhibited a peak at 809 with the correct isotope pattern. Interestingly, the ^{1}H NMR spectrum of the crude product showed only a minor (<5%) amount of the substitution product $(CO)_5Re(CO)_4Re({=}C(NMe_2)C{\equiv}CTMS)$ (**4**). The aminolysis of $(CO)_5M({=}C(OMe)C{\equiv}CTMS)$ (M = Cr or W) in similar conditions gave $(CO)_5M({=}C(NMe_2)C{\equiv}CTMS)$ in high yields.[11] No signs of the 1,4-addition−elimination cumulenic $(CO)_5Re(CO)_4Re({=}C{=}C{=}C(NMe_2)TMS)$ was observed, which is consistent with previous observations on similar chromium complexes.[11b,12]

Crystalline **2** can easily be obtained from a CH_2Cl_2/hexane mixture. The crystal structure was determined as described in the Supporting Information.[13] A little to our surprise it showed a 1:1 mixture of *Z*-**2** and *E*-**2**, which was in contrast with the ^{1}H NMR acquired from the crystalline material. It is also inconsistent with "the rule", which predicts exclusive formation of the *Z* diastereomer for the TMS substituent in **1**.[3,12] Both isomers are shown in Figure 1.

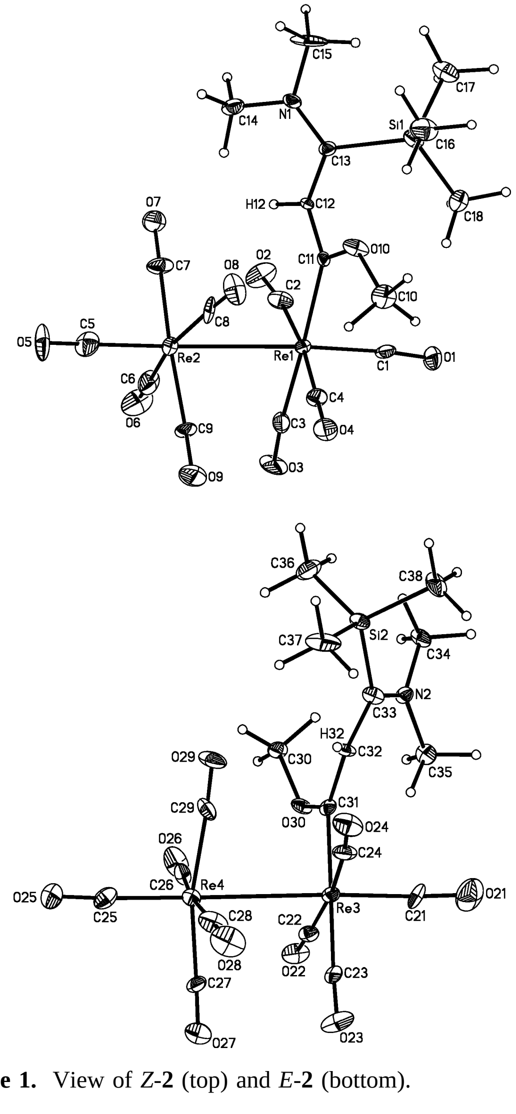


Figure 1. View of *Z*-**2** (top) and *E*-**2** (bottom).

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[13] Crystallographic data for **2**: $C_{18}H_{19}NO_{10}Re_2Si$, fw = 809.83, monoclinic, $P2_1/n$, a = 11.801(2) Å, b = 12.771(3) Å, c = 33.522(7) Å, β = 93.95(2)°, V = 5040.1(18) Å^3, Z = 8, ρ_{calc} = 2.134 g/cm^3, μ = 9.69 mm^{-1}, R_1 = 0.0429, wR_2 = 0.1609, GOF = 1.542.

As could be concluded from other data, both molecules have the carbene ligand in equatorial position. The Re═C bond lengths of 2.20(2) (isomer *Z*) Å and 2.14(2) (isomer *E*) Å are a little longer than the Re═C distances in *eq*-$(CO)_5Re(CO)_4Re(═C(OR)SiPh_3)$ (R = Me: 2.09(2) Å; R = Et: 2.08(5) Å),[8] *ax*,*eq*-$(Ph_3Si(OMe)C═)Re(CO)_4Re(CO)_4(═C(OMe)SiPh_3)$ (*eq* Re═C: 2.08(3) Å),[8] and *eq*-$(CO)_5Re(CO)_4Re(═C(OEt)CH_2CH_2CH═CH_2)$ (2.08(1) Å).[14] The carbon−carbon "double-bond" distances C12−C13 (*Z* isomer) and C32−C33 (*E* isomer) are 1.36(3) and 1.46(3) Å, respectively, which is a little too long for the double carbon−carbon bond (especially in the *E* isomer). Moreover, the N1−C13−C12−Si1 and C11−C12−H12−C13 planes in the *Z* isomer are twisted by 35.0° (the N1−C13−C12−C11 torsion angle is −148.8°). Analogous planes in the *E* isomer are slightly less twisted (16.9°; N2−C33−C32−C31 angle equals −23.4°), but in both molecules the carbene ligand is not planar. Careful search of the CCDC database showed ca. 20 structures of compounds of general formula M(═C(OMe)CH═CRR′). Comparable distortion was only present in the structure of the iron salt $[CpFe(CO)_2(═C(OMe)CH═C(t\text{-}Bu)NHPh][PF_6]$ reported by Rück-Braun and co-workers,[15] where analogous planes are twisted by 36.2° (torsion angle of 34.3°). Nevertheless the molecule was described as a *Z* diastereomer and no isomerization was mentioned/observed.

Considering the above compound, **2** does not seem to have a straightforward bond description. The lengthening of the "C═C" distance suggests reduced electron deficiency at these atoms. On the other hand the single C(OMe)−C(═C) bond did not significantly shorten to fully support the tautomeric shift toward the iminium structure $−C(OMe)═CC(═NMe_2)TMS$. Moreover the ^1H NMR suggests an unrestrained rotation around the N−C bond.

Partially concluding, the data suggest that unprecedented (to our knowledge) fast (on the NMR time scale) *E*/*Z* isomerization takes place in **2**. Similar *E*/*Z* isomerization was observed by Aumann in $(CO)_5Cr(═C(NMe_2)CPh═C(OEt)Ph)$.[16] Previously high-temperature isomerization was observed by Dötz,[17] but in both cases the process is quite slow (time scale from hours to days) and is better observed at elevated temperatures. From this perspective, the presented crystal structures should be viewed rather as structures of two conformers than as two separate diastereomers.

As shown in Scheme 1, desilylation of **2** gave after workup yellow $(CO)_5Re(CO)_4Re(═C(OMe)C(H)═C(NMe_2)TMS)$ (**3**) in 71% yield. The ^1H NMR (RT, CD_2Cl_2) revealed the disappearance of the TMS signal and four doublets between 8.83 and 5.78 ppm emerged. Also two signals in the methoxy region and four peaks from the NMe_2 group between 3.37 and 3.05 ppm have been observed. All this suggested that desilylated **3** had been obtained as an *E*/*Z* mixture of diastereomers. Their ratio was assigned as 30:70 on the basis of ^1H NMR integration. Also when crystalline **3** was observed under the microscope, yellow needles and yellow prisms could easily be noticed. The crystal structure for the *E* isomer has been solved, and its view is shown in Figure 2.[18]

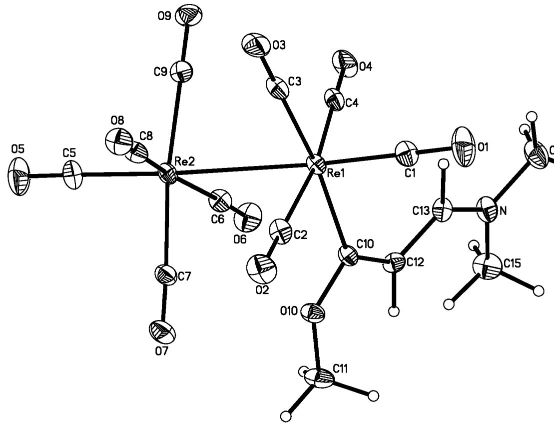

Figure 2. Crystal structure of **3**.

All the bond lengths in **3** are similar to those for **2**. The exchange of the bulky TMS group for hydrogen caused the carbene ligand to become planar (including both methyl groups of the amino substituent), allowing maximum conjugation with the lone pair of the nitrogen. Also in **3** the "double-bond" distance is long (1.413(11) Å), suggesting a tautomeric shift toward the iminium structure. An analogous situation was observed in $(CO)_5Cr(═C(OMe)CH═C(H)NMe_2$.[19]

It is noteworthy to look at the rhenium fragment in **2** and **3**. In both compounds the $Re(CO)_5$ moiety replaces one carbonyl group in the chromium or tungsten analogues. We have speculated if this much bulkier fragment can hinder or even block access to one of the faces of the carbon−carbon "double bond" in the carbene ligand. For both compounds the 3D graphics showed that the equatorial carbonyls of the $Re(CO)_5$ fragment are more or less coplanar with the carbon−carbon "double bond" (Figure 3 left). We tested the internal rotational barriers (rotation around the C(OMe)−CH═ single bond by 15° without any geometry optimization) for **3** in the gas phase at the B3LYP/LanL2DZ level of theory using the Gaussian 03 package.[20−22] Calculations showed a slight increase of the rotation barrier in **3** (from 0 to 28 kcal/mol difference in specific orientations), but we are sure that for compounds with a bulkier R substituent at the α-carbon of the "double bond" the rotation will be much more restricted. Moreover 3D views showed that despite the rotation the access from the direction of the axial carbonyl group (Figure 3) at the carbene rhenium is much easier than from the direction of the $Re(CO)_5$ fragment.

Desilylation at low temperature of the crude **1** using wet TBAF in THF or KI in MeOH/THF gave unidentified products and not even traces of the desired terminal alkynyl $(CO)_5Re$-

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[18] Crystallographic data for **3**: $C_{15}H_{11}NO_{10}Re_2$, fw = 737.65, triclinic, $P\bar{1}$, $a = 9.116(2)$ Å, $b = 9.691(4)$ Å, $c = 11.606(3)$ Å, $\alpha = 84.11(4)°$, $\beta = 84.02(3)°$, $\gamma = 82.64(3)°$, $V = 1007.2(6)$ Å^3, $Z = 2$, $\rho_{calc} = 2.432$ g/cm^3, $\mu = 12.06$ mm^{-1}, $R_1 = 0.0296$, $wR_2 = 0.0872$, GOF = 1.446.

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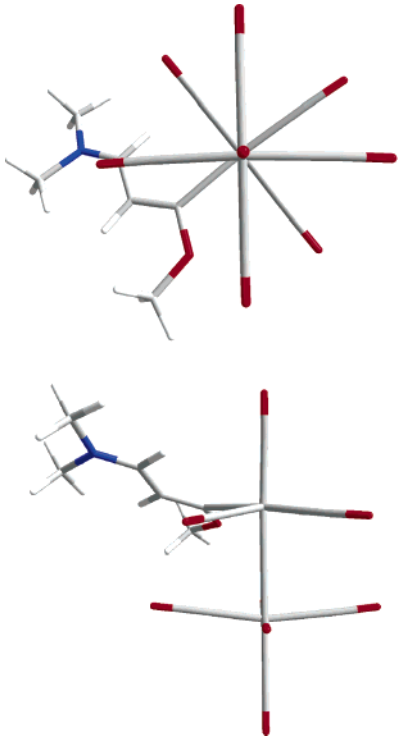

Figure 3. Compound **3**: view along Re−Re axis (top) and side view (bottom).

$(CO)_4(=C(OMe)C{\equiv}CH)$. Hence, more stable analogues of **1** were sought next. One of the methods of their stabilization is the substitution of the OMe group for the dimethylamino group at the carbene carbon. This method gave excellent results in the preparation of stable amino(ethynyl)carbenes $(CO)_5M{=}C(NMe_2)C{\equiv}CH$ (M = Cr or W) reported by Wulff.[11b] Thus, the $TMSC{\equiv}CLi$, $Re_2(CO)_{10}$, and MeOTf were combined as for **1**. After methylation, the solution was cooled to −130 °C (higher temperatures resulted in Michael additions) and $HNMe_2$ was applied. Chromatographic workup gave the yellow *eq*-$(CO)_5Re(CO)_4(=C(NMe_2)C{\equiv}CTMS)$, which in ^1H NMR showed signals at 0.21 (s, $SiMe_3$), 3.57 (s, 3 H from NMe_2), and 3.60 (s, 3 H from NMe_2) in a 9:3:3 ratio.[23]

Unfortunately **4** could also not be obtained in analytically pure form. Despite this, desililation was attempted. Freshly prepared **4** was treated with KF in a MeOH/THF mixture at room temperature. Workup gave **5**, as evidenced by ^1H NMR. The spectrum (rt, $CDCl_3$) shows three lines at 3.67 (s, 3 H from NMe_2), 3.63 (s, 3 H from NMe_2), and 5.28 (s, H from CCH) in 3:3:1 ratio.

In summary, we have shown that Fischer type dirhenium alkynyl and alkenyl(methoxy)carbenes can easily be obtained via original Fischer protocol and subsequent hydroamination. On the basis of the crystal structures and theoretical calculations we anticipate that alkenyl(alkoxo)carbenes of this type can be modified to other species with high selectivities. Additional applications of the presented compounds in organic synthesis will be described in future reports.

Crystallographic data for **2** and **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre (CCDC-293081 and -293082). Copies of this information can be obtained upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. E-mail: deposit@ccdc.cam.ac.uk.

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Supporting Information Available: Text and tables giving experimental procedures and characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) (a) Reactions started at −45 °C instead of −78 °C resulted in a mixture of axial and equatorial isomers. Their ratio, assigned on the basis of the ^1H NMR, was 1:4, which strictly corresponds to the ratio of axial and equatorial carbonyl groups. The ^1H NMR spectrum of the axial isomer (minor) shows signals at 3.67 and 4.02 ppm. (b) Garczynska, A. M.S. Thesis, University of Wrocław.