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Mono- and binuclear 3-amino cyclobuten-2-one complexes of tungsten—facile migration of pentacarbonylmetal fragments in carbene complexes

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Dedicated to Professor E.O. Fischer on the occasion of his 85th birthday

Abstract

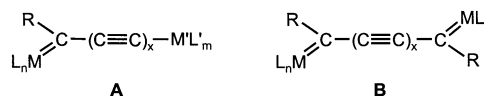
Reaction of $[(\text{CO})_5\text{W}=\text{C}(\text{NMe}_2)-\text{C}\equiv\text{CH}]$ (**1a**) with *n*-BuLi and $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{W}, \text{Cr}, \text{Mo}$) in THF and chromatography on silica affords the 3-dimethylamino cyclobuten-2-on-1-ylidene tungsten complex $[(\text{CO})_5\text{W}=\text{C}(\text{NMe}_2)-\text{C}(\text{NMe}_2)=\text{C}(\text{NMe}_2)-\text{C}(=\text{O})]$ (**2**). Complex **2** is also isolated, after chromatography, from the reaction of $[(\text{CO})_5\text{M}=\text{C}(\text{NMe}_2)-\text{C}\equiv\text{CH}]$ ($\text{M} = \text{Cr}$ [**1b**], Mo [**1c**]) with *n*-BuLi and $[\text{W}(\text{CO})_6]$ in THF. These results demonstrate the facile migration of carbonylmetal fragments along a carbon chain. When **1a** is sequentially treated with *n*-BuLi, $[\text{W}(\text{CO})_6]$, and water in $\text{Et}_2\text{O}-\text{THF}$ (5:1) a binuclear nonacarbonyl μ -3-dimethylamino-cyclobuten-2-on-1-ylidene complex $[(\text{CO})_5\text{W}\{\mu-\text{C}(\text{NMe}_2)=\text{C}(\text{NMe}_2)-\text{C}(=\text{O})\}\text{W}(\text{CO})_4]$ (**6**) is produced. In solution **6** decomposes to give **2**. The structures of the complexes **2** and **6** were established by X-ray structure analyses.

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Keywords: Carbene complexes; Cyclobutenylidene complexes; Binuclear complexes; Tungsten; Chromium

1. Introduction

Bi- and polynuclear organometallic complexes containing π -unsaturated conjugated bridging ligands have attracted considerable interest since these compounds are expected to exhibit potentially useful physical and chemical properties [1]. The electronic communication between the metal centers in such complexes can be mediated in different ways [2] and therefore various types of bridging ligands have been proposed. Recently synthetic routes to binuclear alkynyl–carbene complexes (**A**) and alkynediyl-bridged biscarbene complexes (**B**) have been developed [5].



Complexes of type **A** with various combinations of the metals M and M' are accessible by various routes:

- by reaction of deprotonated alkynyl complexes with metal carbonyls and subsequent alkylation of the resulting binuclear acylmetallates [3],
- by substitution of alkynylcarbene anions for the halide in metal halides [4,5], or
- by Pd-catalyzed coupling of C-stannylated alkynyl-carbene complexes with metal halides [5].

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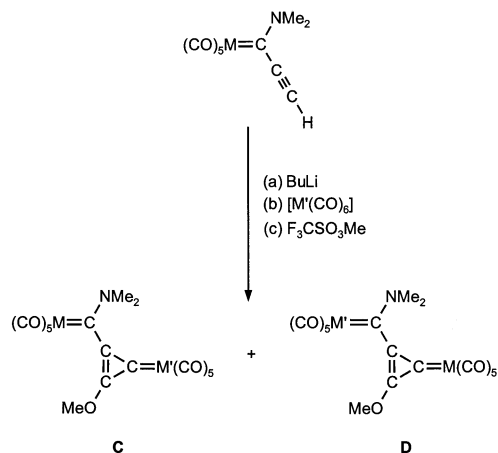
Binuclear bis(carbene) complexes with an alkynediyl fragment linking two $(\text{CO})_5\text{M}=\text{C}(\text{R})$ units (type **B**) can be prepared by Pd-catalyzed coupling of two $(\text{CO})_5\text{M}=\text{C}(\text{NR}_2)(\text{C}\equiv\text{C})_y$ units. By this method, biscarbene complexes $[(\text{CO})_5\text{M}=\text{C}(\text{NR}_2)-(\text{C}\equiv\text{C})_2]_2-(\text{NR}_2)\text{C}=\text{M}(\text{CO})_5$ ($\text{M} = \text{Cr}, \text{W}$) with 2, 4, and 6 $(\text{C}\equiv\text{C})$ fragments have been obtained [6]. Our attempts to synthesize the corresponding ethynediyl-bridged biscarbene complex by reaction of a lithiated amino(ethynyl)carbene complex $\text{Li}^+[(\text{CO})_5\text{M}=\text{C}(\text{NR}_2)-(\text{C}\equiv\text{C})]^-$ with a metal hexacarbonyl $[\text{M}'(\text{CO})_6]$ and subsequently with methyl triflate gave a rather unexpected result. Instead of the expected $[(\text{CO})_5\text{M}=\text{C}(\text{NR}_2)-(\text{C}\equiv\text{C})-(\text{MeO})\text{C}=\text{M}'(\text{CO})_5]$, binuclear complexes with a novel aminocarbene–cyclopropenylidene bridge were isolated as the major reaction products. In case of $\text{M} \neq \text{M}'$ two isomers were obtained (Scheme 1) [7].

The ratios of the isomers obtained by the two different reaction sequences were found to be similar. These results indicated that there is a facile migration of the carbonylmetal fragments along the carbon chain in an intermediate [7].

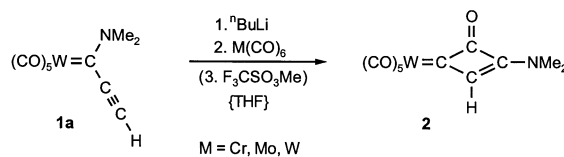
We now report that these reactions are strongly dependent on the solvent and the temperature and the type of products varies with these parameters.

2. Results

Diethyl ether was used as the solvent in the syntheses of the binuclear aminocarbene–cyclopropenylidene complexes (Scheme 1). Small amounts of THF were added to improve the solubility of the metal hexacarbonyl. When the ratio THF–diethyl ether was increased, the formation of a further complex in addition to that of the binuclear aminocarbene–cyclopropenylidene complexes was observed. Finally in neat THF the new complex (**2**) constituted the major reaction product. Complex **2** was also obtained when the last reaction step



Scheme 1.



Scheme 2.

of the sequence (addition of methyl triflate) was omitted. This indicated that **2** is formed from an intermediate that either gives rise to the formation of **2** or, by methylation, of **C/D**. The structure of **2** as shown in Scheme 2 was deduced from its mass spectra, elemental analysis, IR and NMR spectra and was additionally established by an X-ray structure analysis.

The IR spectrum of **2** exhibits one set of $\nu(\text{CO})$ absorptions only that, as expected, are at slightly higher wave numbers than those usually observed with other 3-amino-substituted pentacarbonyl–cyclobutenylidene complexes of chromium and tungsten [8]. From the observation of two methyl resonances in the ${}^1\text{H}$ - and ${}^{13}\text{C}$ -NMR spectra it follows that there is considerable double bond character in the C3–N bond. The resonance of the carbene carbon atom appears at $\delta = 281$ at the low-field end of the range characteristic for 3-aminocyclobutenylidene complexes of tungsten ($\delta = 245\text{--}280$ ppm) [8a,8b,8d] and is also at considerably lower field than the signal of the corresponding “metal-free” semisquaric dimethylamide **3** ($\delta = 190.1$ ppm) [9]. All other resonances in **2** agree reasonably well with those in **3** although $\delta(=\text{CH})$ and $\delta(=\text{C}=\text{O})$ in **2** are at somewhat lower field ($\delta(=\text{CH}) = 176.05$ versus 152.4 ppm and 9.20 versus 7.87 ppm).

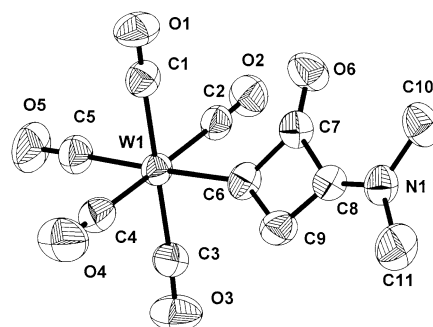
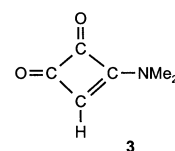
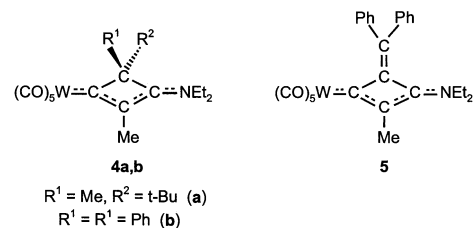


Fig. 1. Structure of complex **2** (hydrogen atoms omitted for clarity).

Table 1
Selected bond distances (Å) and bond angles (°) in **2** and **6**

| | 2 | 6 | 6 | 6 |
|-----------------------|-----------|-----------|------------------|------------|
| <i>Bond distances</i> | | | | |
| W(1)–C(1) | 2.076(8) | 2.074(19) | W(1)–W(2) | 3.1933(18) |
| W(1)–C(2) | 2.064(8) | 2.07(2) | W(2)–C(6) | 2.268(15) |
| W(1)–C(3) | 2.037(8) | 2.106(18) | W(2)–C(9) | 2.387(13) |
| W(1)–C(4) | 2.048(8) | 2.05(2) | W(2)–C(24) | 2.00(2) |
| W(1)–C(5) | 2.051(8) | 2.107(19) | W(2)–C(22) | 2.041(16) |
| W(1)–C(6) | 2.176(6) | 2.197(15) | W(2)–C(21) | 2.059(19) |
| C(1)–O(1) | 1.148(9) | 1.12(2) | W(2)–C(23) | 2.089(18) |
| C(2)–O(2) | 1.153(8) | 1.14(2) | | |
| C(3)–O(3) | 1.177(9) | 1.14(2) | | |
| C(4)–O(4) | 1.163(9) | 1.17(2) | | |
| C(5)–O(5) | 1.150(9) | 1.12(2) | | |
| C(6)–C(9) | 1.419(10) | 1.46(2) | | |
| C(6)–C(7) | 1.523(10) | 1.54(2) | | |
| O(6)–C(7) | 1.215(9) | 1.225(18) | | |
| C(7)–C(8) | 1.534(10) | 1.54(2) | | |
| C(8)–C(9) | 1.449(10) | 1.47(2) | | |
| N(1)–C(8) | 1.329(8) | 1.322(19) | | |
| <i>Bond angles</i> | | | | |
| C(1)–W(1)–C(6) | 86.5(3) | 81.3(7) | C(6)–W(1)–W(2) | 45.2(4) |
| C(3)–W(1)–C(6) | 92.0(3) | 113.4(6) | C(22)–W(2)–C(6) | 147.0(6) |
| C(5)–W(1)–C(6) | 177.2(3) | 167.4(6) | C(24)–W(2)–C(6) | 121.0(6) |
| C(7)–C(6)–C(9) | 88.8(5) | 89.4(12) | C(22)–W(2)–C(9) | 164.4(6) |
| C(9)–C(6)–W(1) | 142.1(6) | 139.3(12) | C(24)–W(2)–C(9) | 90.7(6) |
| C(7)–C(6)–W(1) | 129.1(5) | 131.3(11) | C(21)–W(2)–C(9) | 108.3(6) |
| O(6)–C(7)–C(6) | 137.0(7) | 137.1(16) | C(23)–W(2)–C(9) | 78.4(6) |
| O(6)–C(7)–C(8) | 134.8(7) | 134.6(15) | C(6)–W(2)–C(9) | 36.4(6) |
| C(6)–C(7)–C(8) | 88.1(6) | 87.9(12) | C(24)–W(2)–W(1) | 164.4(5) |
| N(1)–C(8)–C(9) | 136.4(7) | 138.6(16) | C(22)–W(2)–W(1) | 104.1(5) |
| N(1)–C(8)–C(7) | 136.2(7) | 132.6(16) | C(6)–W(2)–W(1) | 43.5(4) |
| C(9)–C(8)–C(7) | 87.3(8) | 88.6(13) | C(9)–W(2)–W(1) | 74.5(4) |
| C(6)–C(9)–C(8) | 95.7(6) | 93.7(14) | C(9)–C(6)–W(2) | 76.3(9) |
| W(1)–C(3)–O(3) | 177.6(7) | 166.6(15) | C(7)–C(6)–W(2) | 100.5(9) |
| C(1)–W(1)–W(2) | | 126.5(5) | W(1)–C(6)–W(2) | 91.3(6) |
| C(3)–W(1)–W(2) | | 68.3(5) | C(6)–C(9)–W(2) | 67.3(8) |
| C(5)–W(1)–W(2) | | 147.4(5) | C(8)–C(9)–W(2) | 97.1(9) |
| C(6)–W(1)–W(2) | | 45.2(4) | W(2)–C(22)–O(22) | 178.4(16) |

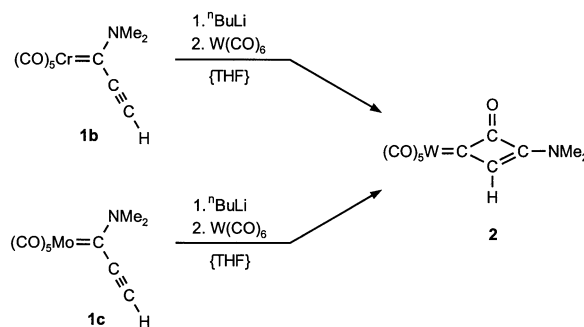
The solid-state structure of **2** is shown in Fig. 1 and relevant data are compiled in Table 1. Bond distances and bond angles are similar to those in **4a** [10], **4b** [10], and **5** [11].



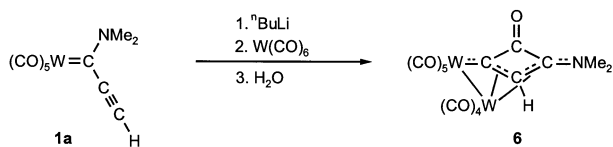
The four-membered ring is planar (**2**: torsion angle C(6)–C(7)–C(8)–C(9) 1.3(5)°) and staggered with respect to the *cis*-CO ligands (C(1)–W(1)–C(6)–C(7): –41.0(6)°). Like in **4a,b** and **5**, the nitrogen atom is planar coordinated. The atoms N(1), C(10), and C(11) are in the plane of the ring (torsion angle C(10)–N(1)–C(8)–C(7): –0.9(12)°). This arrangement allows for optimal π -interaction of the lone electron pair at nitrogen with the ring. In accord with that the N(1)–C(8) distance is short and both CC-bonds, C(6)–C(9) and C(8)–C(9), are nearly equal in length. The “single bond” C(6)–C(9) is even slightly shorter than the “double bond” C(8)–C(9) [1.419(10) Å versus 1.449(10) Å]. The same is true for **4a** and **4b** the difference in bond lengths being somewhat more pronounced whereas in complex **5** C(8)–C(9) is slightly shorter than C(6)–C(9). The W–C(6) distance in **2** is shorter and the mean W–CO distance is longer than the corresponding bond lengths in **4a,b** and **5** indicating that the donor properties of the cyclic ligand in **2** are less than those in **4a,b** and **5**.

Surprisingly, the tungsten complex **2** is also formed when, instead of the tungsten carbene complex **1a**, the corresponding chromium or molybdenum carbene complexes **1b** or **1c** are employed in the reactions with *n*-BuLi and [W(CO)₆] in THF (Scheme 3). Likewise, complex **2** was obtained when [W(CO)₆] was replaced by [Cr(CO)₆] or [Mo(CO)₆] in the reactions with lithiated **1a**. The formation of chromium and molybdenum cyclobutenonylidene complexes related to **2** was in neither if these reactions observed.

Although **2** was obtained after chromatography and recrystallization in a pure form, the spectra taken from the eluate after chromatography only indicated the presence of various amounts of an additional binuclear



Scheme 3.

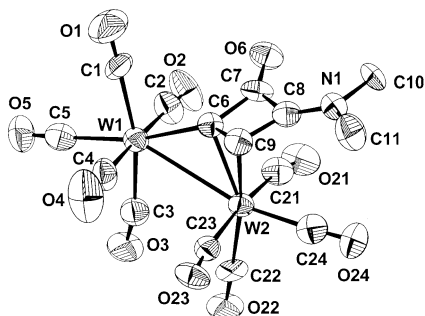


Scheme 4.

complex (**6**). It was possible to isolate and characterize pure compound **6** through modification of the reaction procedure. When water was added to the mixture obtained from the reaction of **1a** with *n*-BuLi and {W(CO)₆} in Et₂O–THF (5:1), a vigorous evolution of a gas was observed. Chromatographic purification of the reaction mixture yielded, in addition to **2**, complex **6**. After recrystallization **6** was obtained in a pure form. Its structure was deduced from its mass spectra, elemental analysis, IR and NMR spectra and was additionally established by an X-ray study (Scheme 4).

The IR spectrum of **6** exhibits seven $\nu(\text{CO})$ absorptions. The N–Me groups are inequivalent giving rise to two singlets in the ¹H-NMR spectrum indicating restricted rotation around the C3–N bond. The resonance of the hydrogen atom bonded to the ring ($\delta = 6.18$ ppm) is at significantly higher field than that of **3** ($\delta = 7.87$ ppm) [9] and **2** ($\delta = 9.22$ ppm) due to the coordination of the ring to the W(CO)₄ fragment. The ¹³C-NMR spectrum shows all in all six resonances for the nine CO ligands indicating a rather rigid structure. The influence of the coordination of W(CO)₄ to **2** (to give **6**) on the ¹³C-NMR resonances of the various ring carbon atoms differs strongly. The peaks of the W-bonded carbon atom and the C(H) atom are shifted towards higher field by about 90 ppm [in **6**: $\delta = 186.26$ ppm (WC) and 88.53 ppm (CH)] whereas the remaining two atoms C3 and C4 are less strongly affected (shift of 10–15 ppm towards higher field).

The solid-state structure of **6** is shown in Fig. 2. A detailed discussion of the influence of the W(CO)₄ fragment on the structure of the pentacarbonyl-ring part of the molecule is not feasible due to the rather large standard deviations in **6**. In general, distances and angles of comparable bonds in **2** and **6** (Table 1) are very similar although the distances W(1)–C(3) and W(1)–

Fig. 2. Structure of complex **6** (hydrogen atoms omitted for clarity).

C(5) are longer in **6** than in **2**. As expected, coordination of C(6)–C(9) to W(CO)₄ results in a bond elongation. The W(1)–W(2) bond in **6** (3.193(2) Å) compares well with that in other (CO)₉W₂L complexes {e.g. 3.119(1) Å (L = C(H)C₆H₄OMe [12]), 3.119(1) Å (L = CH–C(Ph)=C(H)Ph [13]), and 3.189(1) Å (L = CH–CH=CMe₂ [14])}. The two carbonyl ligands C(3)–O(3) and C(22)–O(22) are located in the plane of the dimetalla-cycle formed by the atoms W(1), W(2), and C(6). The fragment W(1)–C(3)–O(3) is bent at C(3) [angle: 166.6(15)°] and is bent towards W(2) [C(3)–W(1)–W(2): 68.3(5)°, O(3)–W(2): 3.108 Å]. Conversely, W(2)–C(22)–O(22) is linear (178.4(16)°) and bent away from W(1) [W(1)–W(2)–C(22): 104.1(5)°].

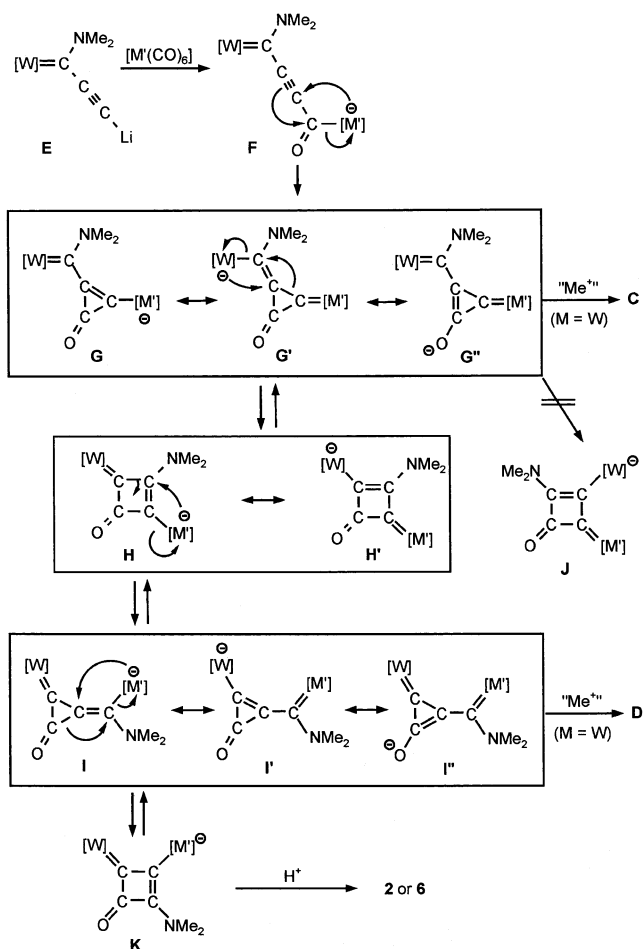
In solution, complex **6** slowly decomposes to give **2** obviously by decooordination of the W(CO)₄ fragment. It is at present unknown whether **2** is formed exclusively by decomposition of **6** or from a common intermediate leading in parallel pathways to **2** and **6**.

The IR spectra of the reaction mixtures of the heterometallic reactions of lithiated **1a** with [Cr(CO)₆] and [Mo(CO)₆] as well as those of Scheme 3 indicate the presence of binuclear complexes, presumably related to **6**. However, it was not possible to isolate these compounds in a pure form due to their instability.

Product formation (C/D versus cyclobutenonylidene complexes **2/6**) in these reaction systems seems to be not only solvent-dependent but also strongly temperature-dependent. When all steps in the reactions of **1b** with *n*-BuLi, [Cr(CO)₆], and methyl triflate were carried out below –30 °C (reaction of lithiated **1b** with [Cr(CO)₆] in THF at –60 °C, methylation in CH₂Cl₂ at –30 °C), the aminocarbene–cyclopropenylidene complex **C** (M=M′=Cr) was isolated. In contrast, no aminocarbene–cyclopropenylidene complex **C** was obtained from the same reactions at room temperature. Possibly a cyclobutenonylidene complex is formed under these circumstances but quickly decomposes again.

3. Discussion

These results in combination with those previously reported demonstrate that the type of product obtained from the reactions of lithiated alkynylcarbene complexes with metal hexacarbonyl strongly depend on the reaction conditions. In diethyl ether isomeric mixtures of aminocarbene–cyclopropenylidene complex **C** and **D** are formed the ratio of isomers being essentially independent of the two possible reaction sequences employed (Scheme 1). In contrast, the reaction in THF affords the cyclobuten-2-onylidene tungsten complex **2** independent of whether the tungsten complex **1a**, the chromium complex **1b**, or the molybdenum complex **1c** is used in the reaction with *n*-BuLi/[W(CO)₆]/silica. In **2**, the tungsten atom is bonded to the terminal carbon



atom of the alkynylcarbene ligand of the starting carbene complex. The tungsten compound **2** is also the only cyclobuten-2-onylidene complex to be detected when **1a** is treated with *n*-BuLi/[M(CO)₆]/silica (M = Cr, W). In neat THF at room temperature complex **2** is also obtained when the methylating agent methyl triflate is added to the reaction solution. The formation of a methylated derivative of **2** was not observed. From all these observations and the failure to interconvert the isomers **C** and **D** it follows that in one or several intermediates in the reaction sequences, the pentacarbonylmetal fragment must be highly mobile and that the intermediates in these reactions readily rearrange. Since homobinuclear complexes are not formed when complexes with different central metals M and M' are employed, the rearrangement must proceed by an intramolecular process. The solvent- and temperature-dependence indicates that there is at least one common intermediate in the formation of **2**, **6**, **C**, and **D**. A possible mechanistic scheme that is in accord with all experimental results is shown in Scheme 5.

Nucleophilic addition of lithiated **1a** (E in Scheme 5) at a carbonyl ligand of [M'(CO)₆] affords the acyl-

carbene metallate **F** which rapidly rearranges to **G/H/I**. **G** and **I** are in rapid equilibrium via the pseudosymmetric intermediate **H**. Alkylation of **G** yields complex **C**, methylation of **I** gives **D** (Schemes 1 and 5). Rearrangement of **I** into **K** (the “unsymmetric” isomer of **H**) and reaction with H⁺/SiO₂ and H₂O gives **2** and **6**, respectively. Complex **2** is either formed by protonation of M and reductive elimination or by direct protonation at carbon and elimination of “M(CO)₅”. Alternatively, protonation of **K** yields, after loss of one CO ligand, complex **6** which then transforms by loss of “W(CO)₄” into **2**.

The rearrangement of **I** into **H** (and **G**) is reversible, however, that of **I** into **K** is very likely irreversible. The irreversibility is in accord with the following observations:

- Complex **2** is formed from **K** independent of whether methyl triflate is added to the reaction solution or not. Obviously, **K** is not methylated by methyl triflate but only adds H⁺.
- When solvent mixtures with low THF content are used the yields of the cyclopropenylidene complexes **C** and **D** on the one hand and of **2** on the other hand depend on the reaction times. Increasing the reaction times leads to decreasing yields of **C** and **D** and simultaneously increasing yields of **2**.

The temperature-dependence indicates that its activation barrier for **I**→**K** rearrangement is considerably higher than that for the transformation of **I** into **H**. When similar reaction conditions are applied the yields of **2** increase with increasing ratio THF–diethyl ether of the solvent mixture (dielectric constant of diethyl ether: 4.2, of THF 7.4). From this it follows that the transition state leading to **K** is more polar than to **I**.

Chromatography on silica plays an essential role in the formation of **2** from **K**. Water adsorbed at silica is obviously the source of the hydrogen bonded to the ring carbon atom. In accord with that complex **2** is not obtained when solutions of the reaction mixture are chromatographed on florisil (activated magnesium silicate). When the deuterated complex [(CO)₅W=C(NMe₂)-C≡CD] is used instead of **1a**, non-deuterated **2** is isolated. Likewise, when the reaction of **1a** with *n*-BuLi and [Cr(CO)₆] is carried out in THF-*d*₈ instead of THF, again complex **2** isolated after chromatography on silica is non-deuterated.

Addition of water to the reaction mixture gives the binuclear complex **6** albeit, after chromatography, in only modest yield. In solution **6** slowly decomposes to form **2**. Very likely on chromatography of **I** on silica, **6** is initially formed which then slowly decomposes to **2** and “W(CO)₄” adsorbed on silica. The observation that the eluate of **2** is usually contaminated with small amounts of **6** is in accord with that.

Until now, complexes derived from **J** have not been isolated. At present it is not known whether chromium or molybdenum complexes analogous to **2** and **6** are unstable and rapidly decompose or **G** does not rearrange into **J**. Presumably, migration of “W(CO)₅” (to form **K**) is less favorable compared to migration of “Cr(CO)₅” and “Mo(CO)₅” (to form **J**). The assumption agrees with the observation that the yield of **2** is considerably higher from the reaction of **1a** (M = W) with [Cr(CO)₆] than with [W(CO)₆].

In summary the results reported here together with those previously described [7] demonstrate that pentacarbonylmetal fragments in such anionic binuclear carbene complexes readily migrate along the “bridging” carbon chain and that the migration can proceed reversible or irreversibly.

4. Experimental

4.1. General

All operations were carried out under Ar by using conventional Schlenk techniques. Solvents were dried by refluxing over sodium-benzophenone ketyl (pentane, Et₂O, THF) or CaH₂ (dichloromethane) and were freshly distilled prior to use. The stationary phase used for chromatography [silica gel for flash chromatography (J.T. Baker), florisil, 60–100 mesh (Acros)] was Ar saturated. The yields refer to analytically pure compounds and were not optimized. The complexes [(CO)₅M=C(NMe₂)-C≡CH] [M = W (**1a**), Cr (**1b**)] were prepared by a slight modification [4] of the procedure reported in Ref. [15]. Complex **1c** (M = Mo) was synthesized analogously. The compounds [M(CO)₆] and *n*-BuLi were commercial products and were used without further purification. IR: FTIR spectrophotometer (FTS70), Bio-Rad. All IR measurements were carried out at 298 K. ¹H-NMR, ¹³C-NMR: Bruker AC 250, Bruker DRX 600. NMR spectra were recorded at room temperature (r.t.). Chemical shifts are reported in ppm relative to the residual solvent peaks. UV-vis: Hewlett-Packard diode array spectrophotometer 8453. MS: Finnigan MAT 312. Elemental analysis: CHN-Analyser (CHN-O-RAPID) Heraeus.

4.2. Pentacarbonyl[3-(dimethylamino)cyclobut-2-en-4-on-1-ylidene]tungsten (**2**)

4.2.1. Reactions of **1a** with [M(CO)₆]

At –80 °C, a solution of 1.00 mmol of *n*-BuLi (0.63 ml of a 1.6 M solution in *n*-hexane) was added to a yellow–orange solution of 1.00 mmol (0.41 g) of **1a** in 20 ml of THF. The solution was stirred for 30 min at –60 °C. The color changed to orange–red. Then, 1.00 mmol (0.35 g) of [W(CO)₆] in 5 ml of THF was added.

The solution was allowed to warm to r.t. Stirring was continued for 45 min. The solvent was removed in vacuo. The red–brown residue was dissolved in 10 ml of CH₂Cl₂ and chromatographed on silica at –40 °C. With CH₂Cl₂ an orange band was eluted. Removal of the solvent in vacuo and recrystallization from 3 ml of CH₂Cl₂ at 4 °C affords orange–red crystals of complex **2**. Yield: 0.19 g (44% relative to **1a**). M.p. (dec.) above 116 °C. IR (Et₂O, cm⁻¹): ν(CO) 2062 w, 1976 vw, 1937 vs, 1923 sh. ¹H-NMR: δ 3.16 (s, 3H, NCH₃), 3.38 (s, 3H, NCH₃), 9.22 (s, 1H, C=CH). ¹³C-NMR: δ 39.85, 41.04 (NCH₃), 176.05 (C²), 184.78, 190.07 (C³, C⁴), 197.57 [*J*(WC) = 125.8 Hz, *cis*-CO], 207.95 [*J*(WC) = 123.3 Hz, *trans*-CO], 281.09 (W = C). UV-vis (nm, lg ε): pentane: 244 (4.816), 361 (3.723), 446 (4.486); CH₂Cl₂: 218 (4.689), 246 (4.838), 361 (3.806), 432 (4.455). MS (EI, 70 eV, 170 °C): *m/z* (%) = 433 (42) [M⁺], 377 (34), 321 (100) [M⁺ – *n* CO, *n* = 2, 4], 291 (83) [M⁺ – 4 CO – 2 Me], 278 (11) [M⁺ – 5 CO – Me], 263 (74) [M⁺ – 5 CO – 2 Me], 248 (34) [M⁺ – 5 CO – NMe₂ – H]. Anal. Found: C, 30.76; H, 1.73; N, 2.91. Calc. for C₁₁H₇NO₆W (433.02): C, 30.51; H, 1.63; N, 3.23%.

The analogous reactions of **1a** with 0.22 g of [Cr(CO)₆] and 0.26 g of [Mo(CO)₆] and (instead of 0.35 g of [W(CO)₆]) gave 0.26 g (60%) and 0.20 g (46%) of **2**, respectively.

4.2.2. Reactions of **1b** and **1c** with [W(CO)₆]

The sequential reactions of 1.00 mmol (0.27 g) of **1b** [1.00 mmol (0.32 g) of **1c**] with 1.00 mmol of *n*-BuLi and 1.00 mmol (0.35 g) of [W(CO)₆] in 5 ml of THF were carried out analogously to those of Section 4.2.1. Chromatography and recrystallization of the product from 3 ml of CH₂Cl₂ gave orange–red crystals of **2**. Yields: 0.19 g (44% relative to **1b**) [0.20 g (46% relative to **1c**)].

4.3. (Pentacarbonyl[3-(dimethylamino)cyclobut-2-en-4-on-1-ylidene]tungsten)tetracarbonyl-tungsten (**6**)

At –80 °C, a solution of 2.50 mmol of *n*-BuLi (1.56 ml of a 1.6 M solution in *n*-hexane) was added to the yellow–orange solution of 2.50 mmol (1.01 g) of **1a** in 25 ml of Et₂O. Within about 30 min at –60 °C a yellow precipitate formed. 2.50 mmol (0.88 g) of [W(CO)₆] and 3 ml of THF were added. On stirring for 45 min at r.t. the suspension turned red–brown. Then 20 ml of H₂O were added leading to a rapid gas evolution. After stirring for 5 min at r.t. the organic phase was separated and the solvent was removed in vacuo. The black–brown residue was dissolved in 15 ml of CH₂Cl₂ and chromatographed at –40 °C on silica. With CH₂Cl₂–THF (19:1) the red–orange band was eluted. Removal of the solvent in vacuo and recrystallization from 3 ml of CH₂Cl₂ at 4 °C affords complex **6** as red crystals. Yield: 0.23 g (13% relative to **1a**). M.p. (dec.) above 134 °C. IR

(Et₂O, cm⁻¹): $\nu(\text{CO})$ 2084 w, 2033 m 2008 vw, 1975 vs, 1963 m,sh, 1936 vw, 1907 w. ¹H-NMR (DRX 600): δ 3.21 (s, 3H, NCH₃), 3.48 (s, 3H, NCH₃), 6.18 (s, 1H, C=CH). ¹³C-NMR (DRX 600): δ = 39.53 (NCH₃), 41.29 (NCH₃), 88.53 (C²), 175.51, 176.63 (C³, C⁴), 186.26 [$J(\text{WC}) = 71.9$ and 31.5 Hz, C¹], 195.07 [$J(\text{WC}) = 120.6$ Hz, *cis*-CO, W(CO)₅], 197.62 [$J(\text{WC}) = 130.8$ Hz], 199.27 [$J(\text{WC}) = 122.5$ Hz], 203.95 [$J(\text{WC}) = 112.5$ Hz], 208.55 [$J(\text{WC}) = 152.0$ Hz], 209.94 [$J(\text{WC}) = 180.2$ Hz, *trans*-W(CO)₅ and W(CO)₄]. MS (FAB, CH₂Cl₂/NBA): m/z (%) = 729 (82) [M⁺], 702 (19) [MH⁺ - CO], 673 (75), 645 (64), 617 (52), 589 (41), 561 (25) [M⁺ - *n* CO, *n* = 2–6], 433 (100) [M⁺ - W(CO)₄], 405 (34), 377 (51) [M⁺ - W(CO)₄ - *n* CO, *n* = 1, 2]. Anal. Found: C, 24.66; H, 1.15; N, 1.70. Calc. for C₁₅H₇NO₁₀W₂ (728.92): C, 24.72; H, 0.97; N, 1.92%.

4.4. X-ray structural analyses of 2 and 6

Single crystals of **2** and **6** suitable for an X-ray structural analyses were obtained from CH₂Cl₂ at -30 °C. The measurements were performed with a crystal mounted in a glass capillary on a Siemens P4 diffractometer (graphite monochromator, Mo-K α radiation, $\lambda = 0.71073$ Å). For the data collection the Wyckoff technique was used. Semiempirical absorption correction (ψ scan with 10 reflections) was performed. The structures were solved by direct methods using the SHELXTL-97 program package [16]. The positions of the hydrogen atoms were calculated by assuming ideal geometry, and their coordinates were refined together with those of the attached carbon atoms as “riding model”. All other atoms were refined anisotropically.

2: C₁₁H₇NO₆W, molecular mass 433.03, crystal size 0.3 × 0.3 × 0.3 mm³, crystal system monoclinic, space group *P*2₁/*c*, $a = 12.942(9)$ Å, $b = 6.753(7)$ Å, $c = 15.574(10)$ Å, $\beta = 90.25(5)^\circ$, $V = 1361.1(19)$ Å³, $Z = 4$, $D_{\text{calc}} = 2.113$ g cm⁻³, temperature 248(2) (K), 2θ range 4.08–53.98°, absorption coefficient 8.507 mm⁻¹, min. (max.) transmission 0.0415 (0.0717), $F(000)$ 808, collected reflections 3944, unique reflections 2976 (all), 2444 ($I > 2\sigma(I)$); index range -1/+16, -1/+8, ± 19 ; 173 refined parameters, R_1 (all data) = 0.0455, wR_2 (all data) = 0.0916, R_1 ($I > 2\sigma(I)$) = 0.0340, wR_2 ($I > 2\sigma(I)$) = 0.0838, res. electron density +0.945/-1.634 e Å⁻³.

6: C₁₅H₇NO₁₀W₂, molecular mass 728.92, crystal size 0.3 × 0.2 × 0.1 mm³, crystal system orthorhombic, space group *Pbca*, $a = 16.437(10)$ Å, $b = 13.304(10)$ Å, $c = 18.367(11)$ Å; $V = 4016(5)$ Å³, $Z = 8$, $D_{\text{calc}} = 2.411$ g cm⁻³, temperature 240(2) (K), 2θ range 4.44–53.98°, absorption coefficient 11.497 mm⁻¹, min. (max.) transmission 0.1230 (0.1846), $F(000)$ 2656, collected reflections 7962; unique reflections 4369 (all), 2631 ($I > 2\sigma(I)$), index range: ± 20 , -16/+15, ± 23 ; 253 refined parameters, R_1 (all data) = 0.1210, wR_2 (all data) =

0.1997, R_1 ($I > 2\sigma(I)$) = 0.0743, wR_2 ($I > 2\sigma(I)$) = 0.1704, res. electron density: +1.887/-5.029 e Å⁻³.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 204585 (**2**) and 204586 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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