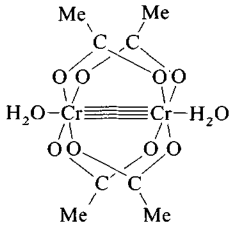
New Discoveries in the Realm of Metal–Metal Multiple Bonds: $[\eta^5\text{-}C_5Me_5)_2Co_2]$, the First Organometallic Multiple-Bond Complex without Bridging Ligands

By *Joachim Wachter**

Every advanced chemistry student should be clearly aware of the significance of the following experiment, which is relatively easy to perform, provided that it is carried out under inert gas atmosphere: If a light blue aqueous Cr^{II} solution is allowed to react with sodium acetate, red crystals of Cr^{II} acetate precipitate out. However, the path leading from the first synthesis of this compound in 1844 by *E. Peligot*[1] to the correct interpretation of its structure[2] (dimeric, extremely short Cr–Cr bonds) has been long. Only X-ray structure analysis was capable of revealing that the M–M distances in such compounds are much shorter than those in the corresponding metals. Hence, defined multiple-bond orders (2 for $[Re_3Cl_{12}]^{3\ominus}$[3] and 4 for $[Re_2Cl_8]^{2\ominus}$[4]) were first formulated in 1964.

Further examples were reported soon thereafter and led, in turn, to theoretical investigations and interpretations (for example, the involvement of d orbitals in the bonding system). An almost immediate consequence was the distinction between bridged and nonbridged systems, as exemplified by the two historical protagonists **1** and **2**, respectively.



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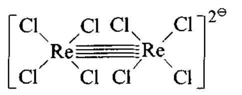

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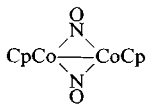
The significance of this classification only becomes clear when the chemistry of transition-metal carbonyl complexes and their derivatives is examined. It is immediately apparent that "... even today no unequivocal case of multiple M–M bonding (i.e., a bond without bridges) has ever been found in a metal carbonyl type system..."[5] This statement, made in 1982 by the grand master of the M–M bond, *F. A. Cotton*, is still valid today.

Numerous examples of double- and triple-bond systems involving π-acceptor ligands are known for elements of groups 3–8 of the periodic table. Although the diverse reactivity of these complexes has attracted much interest, the determination of defined bond orders has proven to be very problematic. For example, the distances in complexes **3** and **4** are equal despite differing bond orders.[6] Thus, bridging ligands complicate the matter. Similar relationships are found in the important class of compounds $[Cp_2M_2(CO)_4]$ (**5**; M = Cr, Mo, W).[7] On the basis of the 18-electron rule and the experimentally found M–M distances, an M–M triple bond has been postulated for these d^5–d^5 systems. In order to understand the overall system, however, it is necessary to consider the electronic situation of the CO bridges (σ + π bond, referred to as semi-bridging) and even that of the Cp ligands.



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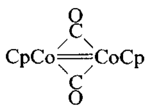

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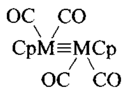

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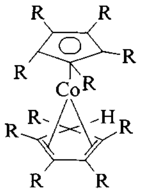
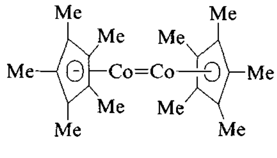
But how does one synthesize organometallic multiple-bond systems without bridging ligands? The answer, recently found by *J. J. Schneider* et al.,[9] is to cocondense a potential π ligand with cobalt atoms in a metal vaporization reactor. *G. A. Ozin* et al. have already had a similar idea, namely, the addition of naked metal atoms to benzene-derived ligands with the formation of bis(arene)metal complexes, but they were unable to isolate weighable amounts of a corresponding substance.[10]

Since the synthesis of dibenzenechromium from chromium vapor and benzene by *P. L. Timms* in 1969,[11] the cocondensation method has been continually developed in order to obtain organotransition-metal complexes.[12] For instance, the cocondensation of metal vapors with a wide range of substituted cyclopentadienes has usually afforded metallocene hydrides of the type $[Cp_2MoH_2]$ or $[Cp_2ReH]$.[13] Cobalt atoms, on the other hand, react with unsubstituted cyclopentadiene to give the mononuclear compound $[(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_5H_6)Co]$ (**6a**) as the sole isolable product.[14]

The decisive turn of events leading to a binuclear cobalt complex, as reported by *Schneider* et al., was brought about by increasing the proportion of metal to about 33% and using pentamethylcyclopentadiene (Cp*H). In this way, complex **7**, the first nonbridged organometallic multiple-bond complex, was obtained in 5–15% yield. At the same time, the permethylated sandwich complex **6b**, analogous to **6a**, and the complex **8** were formed; **8** is only the fifth structurally characterized homoleptic triple-decker complex and is thus a noteworthy rarity.



R = H: **6a**
R = Me: **6b**



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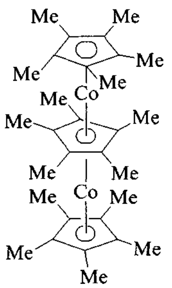

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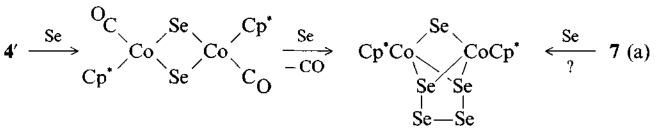
The structure of **7** is characterized by two parallel Cp* rings; the distance between the two Co atoms (2.253(1) Å) is 0.08 Å shorter than in $[Cp_2^*Co_2(\mu\text{-}CO)_2]$.[15] This finding and the effective atomic number (EAN) rule indicate the presence of a nonbridged M–M double bond, for which, on the whole, only one example has been established.[16] The relationship to **4** merely involves the addition of two CO bridges. These conclusions are contradicted, however, by the ^1H NMR spectrum of **7** ($\delta = 61.3$), which supports a marked paramagnetic component. Clearly, theoretical chemists have much to look into here! Similarly, a certain resistance of **7** toward C_2H_4 and Co (at least under the normal conditions used so far) seems not to support the presence of a Co–Co double bond.

The question now is whether relationships to the reactivity of **4′**, the pentamethylated derivative of **4**, can be established. A salient feature of ligand-bridged multiple-bond complexes is that, usually, they readily undergo addition reactions involving opening of the bridge and only afterwards do they undergo substitution reactions [Eq. (a)]; the analogous transformation could occur directly from **7**, starting with addition.[17]



The prospect of being able to investigate the bonding and reactivity of nonbridged organometallic multiple-bond systems is why the successful synthesis of **7** is so significant. A sure goal will be to extend the preparation to other transition metals.

German version: *Angew. Chem. 103* (1991) 1140

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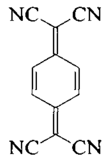
Novel Building Blocks for the Synthesis of Organic Metals

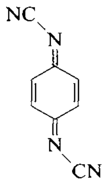
By *Volker Enkelmann**

Organic crystals with special electrical, optical or magnetic properties are attracting increasing interest as "unconventional materials".[1] The special properties alluded to are not determined alone by the electronic structure of the individual molecule, but are only manifested upon interaction of many molecules in the solid state. It therefore does not suffice just to master the synthesis of suitable building blocks, an important step is obtaining the desired interactions in certain crystal structures. This has led to interest being always concentrated on a few model systems in which all steps, from the synthesis of the starting components up to and including reproducible crystallization, have been perfected.

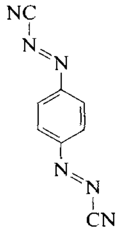
High electrical conductivities in organic metals are, independently of the nature of the building blocks, always associated with certain structural principles. The crystal structure of the long known charge transfer (CT)-salt TTF/TCNQ (TTF = tetrathiafulvalene, TCNQ = tetracyanoquinodimethane, Fig. 1)[2] exhibits the most important features:[3] 1) crystallization of donor and acceptor molecules in segregated stacks with 2) uniform interstack distances; 3) formation of mixed valence states, i.e. only partial charge transfer between the stacks of the redox partners. The charge transport takes place along the stacks, whereby in TFF/TCNQ the two stacks contribute to the total conductivity independently of each other.



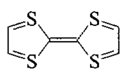
TCNQ



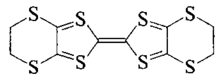
DCNQI



DCNAB



TTF



BEDT-TTF

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