Abstract: For linear and cyclic coupling reactions of CO, among other products, the formation of the hexapotassium salt of hexahydroxybenzene is of particular interest. The interaction of metallic potassium and CO offers, via the assumed K[OC=C=CO] as the result of several carbon monoxide coupling reactions, the formation of K[OK] among other products. To date, only speculations exist about the reaction pathway for these products, which were first described by Liebig in 1834. A novel concept is suggested here, which consists of the single steps (i) reductive coupling of CO, (ii) formation of dihetero-metallacyclopentynes (cis-2,5-diheterobutatriene as formal ethynediene O=C=C=O complexes), (iii) formation of its dinuclear 1-metalla-2,5-dioxo-cyclopentene complexes by external coordination of the triple bond, (iv) insertion of CO into the M–C bond of the formed metallacyclopropene, and (v) the reductive elimination of C[OK]. The novel aspect of this concept is the formation of dihetero-metallacyclopentynes (in analogy to the well characterized all-C-metallacyclopentynes), which have not been considered in the mechanism of reductive CO coupling reactions. It is expected that the presence of transition-metal impurities would promote the reaction.

Introduction

A long time ago, in a classical work, Liebig described reactions of metallic potassium with carbon monoxide in which a dark-colored mixture was formed, which consists of [KOC] giving after hydrolysis hexahydroxybenzene (Scheme 1).

This was followed by an argument from Brodie, that the mixture contains the hexapotassium salt of hexahydroxybenzene K[OK]. Since investigations from Nietzki and Benckiser, the compound of the formula [KCO] is considered as K[OC=C=CO] without any information about the formed amounts, supported by a paper by Kröger and co-workers. Weygandt et al. estimated yields of 15% for the hexahydroxybenzene K[OH] Sager, Fatadi, and co-workers published that, in these reactions, at first a black product [KOC] is formed, which reacts with CO to give K[OCO] as the product at the melting point of potassium. It is assumed that only at higher temperatures this compound is converted to the hexapotassium salt of hexahydroxybenzene K[OCO] because at the melting temperature of potassium 0% of K[OCO] was obtained. Fatadi described yields of 35% at temperatures of 150–200 °C. Later, Weiss and co-workers reported in a series of very detailed investigations about this and similar systems the result that K[OCO] is not formed from KOC=COK and at temperatures higher than 180 °C the hexapotassium salt of hexahydroxybenzene K[OCO] predominates. Additionally, Schuschunov and Weiss published some kinetic results indicating an induction period and exothermic absorption of carbon monoxide. It is worth mentioning that product formation starting from carbon monoxide is an important part of C chemistry and that the product hexahydroxybenzene is an interesting compound for several applications. The reductive coupling of carbon monoxide, CO, to acetylenedioxolates and of isocyanides, RNC, are interesting processes of C–C bond formation, which are attractive for several synthetic prospects. This was investigated and calculated by Hoffmann, Lippard, Templeton, and co-workers in detail. Also, Filipou and co-workers described many examples of metal-induced C–C coupling reactions of isocyanides to bis(amine)acetylenes.

Later, the unusual coupling of alkyn groups to all-C-metallacyclocumulenes (as 1,3-butadiyne complexes) was described and it was found that the products coordinate a second metal fragment under formation of dinuclear complexes (as cycloolefin complexes). Also, the all-C-metallacyclopentynes (as butatriene complexes) coordinate a second metal to form dinuclear complexes (as cycloalkyne complexes; Scheme 3).

The formation of C-metallacyclopentynes (as complexes of butatriene HRC=C=C=CHR with R =tBu and Me) was first described by Suzuki and later extended to the unsubstituted compounds of HRC=C=C=CH. Also, dihetero-metallacyclo-
Based on this, for the oxidative coupling of CO to acetylene, the assumption of dioxo-butatriene, the corresponding symmetric di-dioxo-dinuclear complexes (Scheme 7) were mentioned as a possible product. These results for dihetero-metallacyclopentynes (in analogy with the well characterized all-C-metallacyclopentynes) offer novel aspects for the presented concept of CO coupling.

Additionally, these results show several similarities to reactions of all-C-metallacyclopentynes (complexes of butatrienes H$_2$C$_5$C$_5$C$_5$CH$_3$) with dioxo-metallacyclopentynes (complexes of ethynediolide O=C=C=O) as a product of the proposed and discussed reductive coupling of CO (Scheme 6).

This symmetric all-C-dinuclear products were isolated and characterized for M = Ti and M = Zr.

In a series of excellent papers, Cloke, Green and co-workers described the reductive cyclo(trimethylene oxide) and RNC analogous dinuclear complexes, isolated from all-C-metallacyclopentynes (complexes of butatrienes H$_2$C$_5$C$_5$C$_5$CH$_3$) with dioxo-metallacyclopentynes (complexes of ethynediolide O=C=C=O) as a product of the proposed and discussed reductive coupling of CO (Scheme 6).

Additionally, there exist some very interesting mechanistic studies from this group and computational studies to gain a computational insight into the reductive coupling reactions of CO. In the last paper, the corresponding symmetric dioxo-dinuclear complexes (Scheme 7) were mentioned as a possible product. This is very similar to the dinuclear complexes, isolated from all-C-metallacyclopentynes (Scheme 7).

It should be noted that Berry and Bercaw described the first example of a C–C bond-forming reaction by direct coupling of two carbonyl ligands to a dinuclear complex. In the reaction of [Cp*Mn(CO)$_3$] with [CpFe(CO)$_2$]$_2$, a compound was obtained in which a Zr$_2$O$_2$C$_2$ unit (as a dioxo-zirconacyclooctane) bridges two iron atoms. In this study, it was mentioned that this reaction resembles the reduction of CO by potassium to CO to CO$^-$ and its oligomers as published by Weiss and co-workers previously.

Additionally, more specific methods to obtain other examples for such dinuclear dihetero-metallacyclopentynes complexes, including acetylenediiodolate, R$_2$PC$_{11}$CPR$_{11}$ or [Si(Me)$_2$C$_2$Si(Me)$_2$]$_{11}$ ligands, are known. Additionally, the formation of further bridged alkylene complexes is possible (Scheme 5).

Uwe Rosenthal studied chemical oceanography (1968–1972), received his Ph.D. under the supervision of E. Kuras (1976), and completed his habilitation (1991) at the University of Rostock. After postdoctoral work at the INEOS of the Russian Academy of Sciences in Moscow with M. E. Volpin and V. B. Shur (1988) and a visiting research scientist at the MPI of Kohlenforschung in Mulheim/Ruhr with G. Wilke and K. Porschke (1990–1991), he headed the Max Planck Research Group “Complex Catalysis” (1992–1996) and became Professor of Inorganic Chemistry at the University of Rostock (1993). As Deputy Director of the Leibniz Institute of Catalysis (2003–2016), his scientific interests were the fundamentals of organometallic chemistry, such as unusual metallocycles for applications in homogeneous catalysis for the selective oligomerization of ethene.
there are “substructural parts” (in red), which would support the concept of $\eta^2$ coordinated ethyne diolates as intermediates. In a very recent paper, Kong and Crimmin summarized cooperative strategies for CO homologation. Nevertheless, this possibility was not considered in all these papers. Treatment of $\text{Cp}_2^*\text{ZrN}_2^\text{II}_2$ ($\text{Cp}^*=\text{C}_5\text{Me}_5$) with $[(\text{C}_5\text{H}_4\text{R})\text{Fe(CO)}_2\text{L}_2]$ ($\text{R}=\text{H}, \text{R}=\text{Me}$) results in the formation of $\text{Cp}_2^*\text{Zr(CO)}_4\text{Fe}_2(\text{C}_5\text{H}_4\text{R})_2$. Scheme 8.

Scheme 5. Examples of dinuclear dihetero-metallacyclopentynes complexes together with other bridged alkyne complexes.

This was the first example of a new type of carbon–carbon bond-forming reaction by direct coupling of two carbonyl ligands of a dinuclear transition-metal complex. Additionally, for coupling reactions of isocyanides, some similarities can be found. So far, no investigations exist for the coupling of six CO molecules to hexahydroxybenzene.

The main point of all these considerations is that for the formed transition-metal metallacycloprenes (as complexes of dihetero-metallacyclopentynes) typical insertions of further molecules of CO or isocyanides into the $\text{M}^\text{II}_\text{C}$ bonds should be possible, thus giving different linear or cyclic oligomers (Scheme 9).

With respect to the formation of the hexapotassium salt of hexahydroxybenzene $\text{C}_6(\text{OK})_6$ that was mentioned in the Introduction, Serratosa described several other aromatic oxocarbon dianions $\text{C}_6\text{O}_2^{2-}$ like acetylene diolate, deltaxate, suarate, crocenate, and rhodizanate, which were described, depending on different reaction conditions (Scheme 10).

Until now, the mechanism for formation of all these products has not been clear. Coming back to the main results from Weiss et al. mentioned in the Introduction, only at temperatures higher than 180 °C, the hexapotassium salt of hexahy-
droxybenzene $K_6O_6C_6$ predominates in the obtained products. If this is true, the addition of transition metals as catalysts to the reaction mixture should lower the reaction temperature for its formation considerably, because the discussed dinuclear species could enable further insertions of CO. This aspect is supported by the existence of metallacyclopentyne transition-metal complexes and should be a matter of more detailed investigations and by the fact that distilled and not totally pure alkali metals were used for these investigations. Additionally, the pressure of CO and the polarity of solvents could have an influence, but there are no systematic investigations of this and the reactions were realized directly with metallic potassium without any solvents.

It is worth mentioning that according to the calculations of Hoffmann, Lippard, Templeton, and co-workers, some linear and cyclo-trimerization reactions of CO were published for main group and transition-metal organometallics.

**Conclusion**

For some special carbon monoxide coupling reactions, up to now only speculations exist about the reaction pathway and product formation. One example is the formation of the hexapotassium salt of hexahydroxybenzene through interaction of metallic $K$ and CO. Based on this, a novel concept is presented based on metalla-dioxo-cyclobutadiynes. It consists of five single steps: the reductive coupling of CO, the formation dihetero-metallacyclopentynes ($cis$-$2,5$-dihetero-butatriene as ethylene-dione complexes), the coordination to its dinuclear 1-metalla-$2,5$-dioxo-cyclopentyne complex, several insertions of CO into the M–C bond of the formed metallacyclopene, and the reductive elimination of the products. The novel aspect of this concept is the well-documented experience for diheterometallacyclopentynes (in analogy to the well-characterized all-C-metallacyclopentynes). Other insertion reactions would give aromatic oxocarbon dianions $C_nO_n^2@$ like acetylene diolate, deltate, square, croconate, and rhodizanate. This has not been considered in all papers published so far about the mechanism of such reductive CO coupling reactions. Some calculations support the first steps of CO coupling. It is expected that these single steps are possible at lower temperature, either by catalysis or if transition-metal impurities are present in the system based on metallic potassium because the metallacyclopentynes react with transition-metal complexes. A hint in this direction could be the very recently published preprint from Paparo, Cameron and coworkers in which the reductive hexamerization of CO by the cooperativity between magnesium(I) reductants and $[Mo(CO)_6]$ to well-defined magnesium benzene-hexolate complexes was described.

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**Conflict of interest**

The authors declare no conflict of interest.
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