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Carbon Monoxide Coupling Reactions: A New Concept for the Formation of Hexahydroxybenzene

Uwe Rosenthal*[a]

Abstract: For linear and cyclic coupling reactions of CO, among other products, the formation of the hexapotassium salt of hexahydroxybenzene is of particular interesting. The interaction of metallic potassium and CO offers, via the assumed K[OC≡CO]K as the result of several carbon monoxide coupling reactions, the formation of $C_6(OK)_6$ 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 ethylenedione O≡C=C≡O complexes), (iii) formation of its dinuclear 1-metalla-2,5-dioxo-cyclopentyne 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 $C_6(OK)_6$. 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 $[KCO]_n$,[1] giving after hydrolysis hexahydroxybenzene (Scheme 1).[1]

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This was followed by an argument from Brodie, that the mixture contains the hexapotassium salt of hexahydroxybenzene $C_6(OK)_6$.[2a,b] Since investigations from Nietzki and Benckiser, the compound of the formula $[KCO]_n$ is considered as $K_6O_6C_6$ without any information about the formed amounts,[3a] supported by a paper by Kröger and co-workers.[3b] Weygandt et al. estimated yields of 15% for the hexahydroxybenzene $C_6(OH)_6$.[4] Sager, Fatiadi, and co-workers published that, in these reactions, at first a black product $[K_3C_2O_2]_n$ is formed, which reacts with CO to give $K_4C_4O_4$ as the product at the melting point of potassium.[5] It is assumed that only at higher temperatures this compound is converted to the hexapotassium salt of hexahydroxybenzene $K_6O_6C_6$ because at the melting temperature of potassium 0% of $K_6O_6C_6$ was obtained.[5] Fatiadi described yields of 35% at temperatures of 150–200°C.[6] Later, Weiss and co-workers reported in a series of very detailed investigations about this and similar systems[7] the result that $K_6O_6C_6$ is not formed from KOC≡COK and at temperatures higher than 180°C the hexapotassium salt of hexahydroxybenzene $K_6O_6C_6$ predominates.[7d] Additionally, Schuschunow[8] and Weiss[7d] published some kinetic results indicating an induction period and exothermic absorption of carbon monoxide.
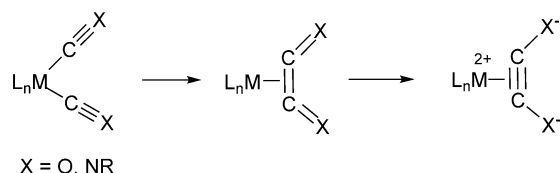
It is worth mentioning that product formation starting from carbon monoxide is an important part of C_1 chemistry[9] and that the product hexahydroxybenzene is an interesting compound for several applications.[10] The reductive coupling of carbon monoxide, CO, to acetylenedioxolates $^-[OC≡CO]^-$ and 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 (Scheme 2).[11] Also, Filippou and co-workers described many examples of metal-induced C−C coupling reactions of isocyanides to bis(amino)acetylenes.[11d]

Later, the unusual coupling of alkynyl groups to all-C-metallacyclocumulenes (as 1,3-butadiyne complexes) was described[12] and it was found that the products coordinate a second metal fragment under formation of dinuclear complexes (as cycloolefin complexes).[13] Also, the all-C-metallacyclopentynes (as butatriene complexes) coordinate a second metal to form dinuclear complexes (as cycloalkyne complexes; Scheme 3).[14]

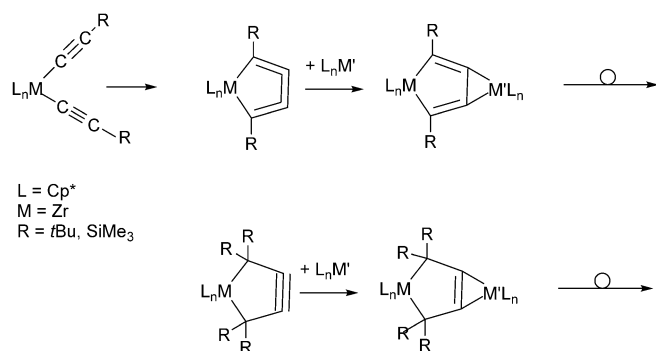The formation of C-metallacyclopentynes (as complexes of butatriene HRC=C=C=CHR with R = tBu and Me₃Si) was first described by Suzuki[15a,b] and later extended to the unsubstituted compounds of $H_2C=C=C=CH_2$.[15c,d] Also, dihetero-metallacyclo-

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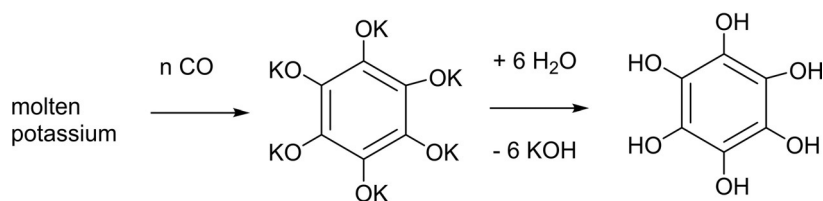
Scheme 1. Reactions of metallic potassium with carbon monoxide to give hexahydroxybenzene.

Scheme 2. Reductive coupling of CO and RNC with transition metals.

L = Cp*
M = Zr
R = tBu, SiMe$_3$

Scheme 3. Reductive coupling of alkynyl groups to metallacyclocumulenes and its coordination of transition-metal complexes as well as the analogous external coordination of metallacyclopentynes to dinuclear complexes.

pentadienes (as complexes of Me$_2$Si=C=C=SiMe$_2$) were published.[15e] Based on this, for the oxidative coupling of CO to acetylenedioxolates $^-$OC≡CO$^-$ and isocyanides RNC analogous dihetero-metallacyclopentynes are assumed (Scheme 4) as alternative intermediates in addition to those mentioned in Scheme 2.[15f] Regarding the assumed dioxo-butatriene, the question to understand this molecule as ethylenedione O=C=C=O or ethyne diolide $^-$OC≡CO$^-$ still remain.[15g]

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.[16] In the reaction of [Cp*$_2$Zr] with [CpFe(CO)$_2$]$_2$, a compound was obtained in which a ZrO$_2$C$_2$ unit (as a dioxo-zirconacyclopenane) bridges two iron atoms. In this study, it was mentioned that this reaction resembles the reduction of CO by potassium to K$^+$ $^-$OC≡CO$^-$K$^+$ and its oligomers as published by Weiss and co-workers previously.[7]

Additionally, more specific methods to obtain other examples for such dinuclear dihetero-metallacyclopentyne complexes, including acetylenedithiolate $^-$[SC≡CS]$^-$,[17a] R$_2$PC≡CPR$_2$,[17b] or $^-$[Si(Me)$_2$C≡CSi(Me)$_2$]$^-$[17c] ligands, are known. Alternatively, the formation of further bridged alkyne complexes is possible (Scheme 5).[17d] 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=C=C=CH$_2$) with dioxo-metallacyclopentynes (complexes of ethylenedione O=C=C=O) as a product of the proposed and discussed reductive coupling of CO (Scheme 6).

Such symmetric all-C-dinuclear products were isolated and characterized for M=Ti[15c] and M=Zr.[15g]

In a series of excellent papers, Cloke, Green and co-workers described the reductive cyclotrimerization of carbon monoxide to different coupling products.[18] The deltate dianion was formed by the reductive cyclotrimerization by an organometallic uranium complex.[18a] The formation of a squarate by a U^{III} complex by the reductive cyclotrimerization was later reported, too.[18b] Steric effects in the reductive coupling of CO by mixed-sandwich uranium(III) were published with the result of alternatives for different sizes of the oxocarbons in the obtained products. Cloke later discussed mechanistic investigations for the formation of oxocarbons (Scheme 7).[18c]

Additionally, there exist some very interesting mechanistic studies from this group[18d] and computational studies[18e] to gain a computational insight into the reductive coupling reactions of CO.[18f] In the last paper, the corresponding symmetric dioxo-dinuclear complexes (Scheme 7) were mentioned as a possible product.[18f] This is very similar to the dinuclear complexes, isolated from all-C-metallacyclopentynes (Scheme 7)[18f,g]

Uwe Rosenthal studied chemistry (1968–1972), received his Ph.D. under the supervision of E. Kurras (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. Vol'pin and V. B. Shur (1988) and a visiting research scientist at the MPI of Kohlenforschung in Mülheim/Ruhr with G. Wilke and K. Pörschke (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 metallacycles for applications in homogeneous catalysis for the selective oligomerization of ethene.
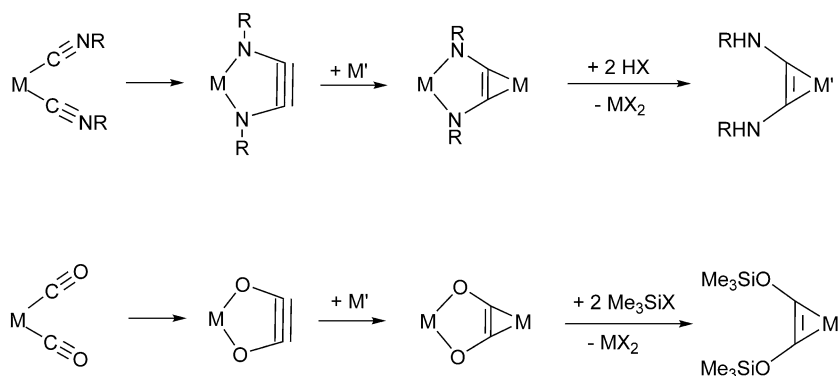
Scheme 4. Oxidative coupling of isocyanides RNC and CO to dihetero-metallacyclopentynes, its complexation, and the formation to metallacyclopropenes (as alkyne complexes).

X = O^-, RN^-, S^-, R_2P, $SiMe_2$
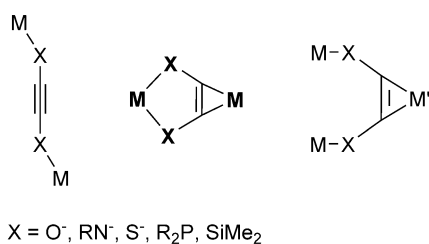
Scheme 5. Examples of dinuclear dihetero-metallacyclopentyne complexes together with other bridged alkyne complexes.
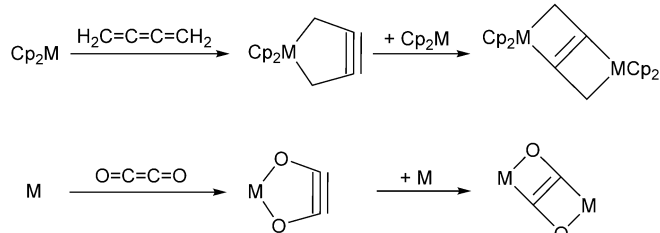
Scheme 6. Reactions of all-C-metallacyclopentynes ($H_2C=C=C=CH_2$ complexes) and dioxo-metallacyclopentynes (complexes of ethylenedione $O=C=C=O$) with metal fragments to give similar dinuclear products.
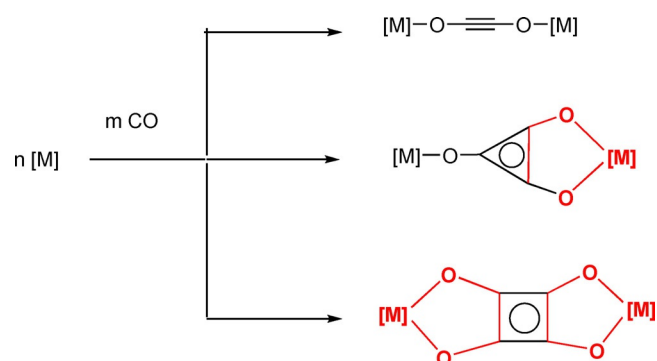

Scheme 7. Formation of η^2 coordinated ethyne diolates for oxocarbons.

and could give a hint for the existence of dioxo-metallacyclopentynes. In the isolated deltate and squarate compounds,

there are "substructural parts" (in red), which would support the concept of η^2 coordinated ethyne diolates as intermediates. In a very recent paper, Kong and Crimmin summarized cooperative strategies for CO homologation.[18] Nevertheless, this possibility was not considered in all these papers.[18]

Treatment of $|Cp_2^*ZrN_2|_2N_2$ ($Cp^* = C_5Me_5$) with $[(C_5H_4R)Fe(CO)_2I_2$ (R=H, R=Me) results in the formation of $Cp_2^*Zr(CO)_4Fe_2(C_5H_4R)_2$ (Scheme 8).[16]
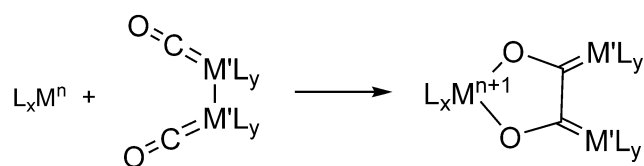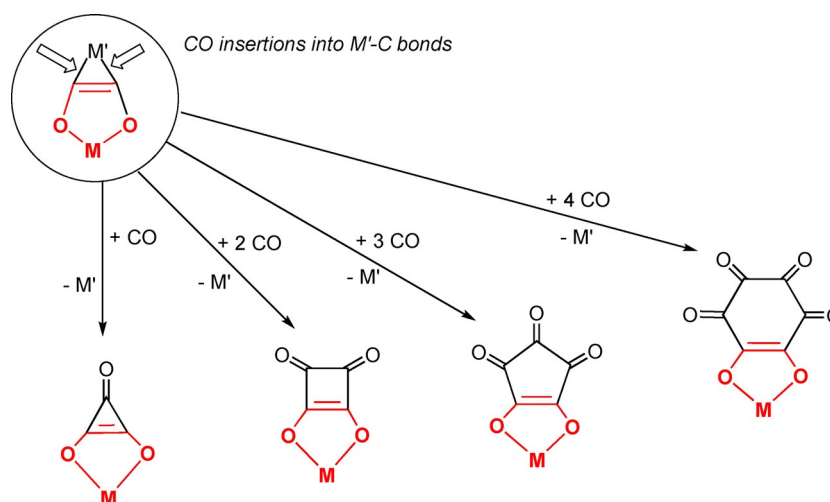

Scheme 8. General scheme of CO coupling via dioxo-dinuclear complexes.

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.[19] So far, no investigations exist for the coupling of six CO molecules to hexahydroxybenzene.
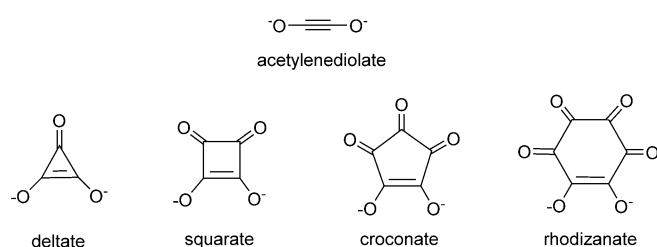
The main point of all these considerations is that for the formed transition-metal metallacyclopropenes (as complexes of dihetero-metallacyclopentynes) typical insertions of further molecules of CO or isocyanides into the M'−C bonds should be possible, thus giving different linear or cyclic oligomers (Scheme 9).

With respect to the formation of the hexapotassium salt of hexahydroxybenzene $C_6(OK)_6$ that was mentioned in the Introduction, Serratosa described several other aromatic oxocarbon dianions $C_nO_n^{2-}$ like acetylene diolate, deltate, suarate, croconate, and rhodizanate, which were described, depending on different reaction conditions (Scheme 10).[20]

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,[7] only at temperatures higher than 180 °C, the hexapotassium salt of hexahy-

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Scheme 9. Multiple insertions of CO could give different cyclic oligomers.

Scheme 10. Formation of aromatic oxocarbon dianions $C_nO_n^{2-}$ like acetylene diolate, deltate, squarate, croconate, and rhodizanate.

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.[7f] 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,[11] some linear- and cyclo-trimerization reactions of CO were published for main group and transition-metal organometallics.[20]

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 hexa-potassium 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 dihe-tero-metallacyclopentynes (*cis*-2,5-dihetero-butatriene as ethyl-enedione complexes), the coordination to its dinuclear 1-met-alla-2,5-dioxo-cyclopentyne complex, several insertions of CO into the M—C bond of the formed metallacyclopropene, and the reductive elimination of the products. The novel aspect of this concept is the well-documented experience for dihetero-metallacyclopentynes (in analogy to the well-characterized all-C-metallacyclopentynes). Other insertion reactions would give aromatic oxocarbon dianions $C_nO_n^{2-}$ like acetylene diolate, del-tate, squarate, 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 cataly-sis or if transition-metal impurities are present in the system based on metallic potassium because the metallacyclopen-tynes react with transition-metal complexes. A hint in this di-rection could be the very recently published preprint from Paparo, Cameron and coworkers in which the reductive hex-amerization of CO by the cooperativity between magnesium(I) reductants and $[Mo(CO)_6]$ to well-defined magnesium benzene-hexolate complexes was described.[18j]

Conflict of interest

The authors declare no conflict of interest.

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