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Chemistry–A European Journal

Research Article
doi.org/10.1002/chem.202500489

Chemistry Europe
European Chemical Societies Publishing

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Isolation and Characterization of $[MnFe(CO)_{10}]^+$: The Missing Link in the 3*d* Dimetal Decacarbonyl Series

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The heterodinuclear dimetal decacarbonyl cation $[MnFe(CO)_{10}]^+$ has been synthesized by combining the metalloradical $[Fe(CO)_5]^{+\cdot}$ with half an equivalent of $Mn_2(CO)_{10}$. The complex was subsequently isolated and characterized using single-crystal X-Ray Diffraction (scXRD), as well as IR, Raman, NMR and Mössbauer spectroscopy. Experimental results, complemented by DFT calculations of the relaxed force constants and an analysis of the electron density, reveal that the interaction between the two $\{M(CO)_5\}$ fragments in $[MnFe(CO)_{10}]^+$ is in between a covalent and a dative bond, representing a borderline case between the 2x17 VE and the 16 + 18 VE electron counting. Additionally, the known isoelectronic anion $[CrMn(CO)_{10}]^-$ was prepared as its $[PPN]^+$ salt and characterized for the first time by scXRD. These finding complete the series of structurally characterized isoelectronic dimetal decacarbonyls, spanning from $[Cr_2(CO)_{10}]^{2-}$ to $[Fe_2(CO)_{10}]^{2+}$, the characteristics of all of which are compared based on experiment and theory.

Introduction

Carbon monoxide (CO), owing to its excellent π-acceptor and moderate σ-donor properties, is a quintessential ligand in organometallic chemistry, playing a key role in photochemistry,[1] catalysis[2] and medical applications.[3] The unusually good π-acceptor properties of this ligand have not only facilitated the stabilisation of a wide variety of binary $M_x(CO)_y$ complexes (TMCs) but have also enabled the isolation of carbonylmetalates $[M_x(CO)_y]^{z-}$ (TMCAs), where the metals can exhibit formal oxidation states as low as –IV, exemplified by $[W(CO)_4]^{4-}$.[4] In contrast, the relatively weaker σ-donor properties of CO pose challenges for the isolation of homoleptic transition metal carbonyl cations (TMCCs).[5] Isolating such complexes requires stringent exclusion of nucleophiles, strongly limiting the choice of the solvent and counterions.[6,7] Superacidic conditions, such as those provided by the mixture HF/SbF_5 or similar systems, have proven particularly effective, enabling the isolation of various TMCCs with formal oxidation states of the metals reaching up to + III.[8,9] Building on this foundation, methodologies and reagents developed in our group that induce *pseudo gas-phase conditions*[6,10] have expanded the scope of TMCCs also to the first paramagnetic or clustered examples and to mononuclear heptacarbonyl complexes.[11] Hence, for each transition metal in the groups 5–11 now at least one structurally characterized TMCC is known, with the exception of vanadium (Table 1).

Most homometallic TMCCs are mononuclear, structurally characterized examples (*via* scXRD) of homomultinuclear TMCCs are limited to group 8 complexes.[15,23,24] Beyond gas-phase studies,[31] there are only two additional examples of homomultinuclear TMCCs outside group 8: $[Pt_2(CO)_6]^{2+}$ and $[Hg_2(CO)_2]^{2+}$. However, these complexes have unfortunately not been structurally characterized using scXRD.[32] In contrast, numerous metal-only Lewis-pairs (MOLPs)[33] have been synthesized by the reaction of coinage- or post transition metals and binary TMCs yielding clusters of the formula $[M'\{TMC\}_2]^{z+}$ (M' = Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^{2+}).[34] This class of MOLPs displays a high variety of TMC fragments, extending up to $Ir_4(CO)_{12}$.[11,24,35] Additionally, reactions of TMCAs $[M_x(CO)_y]^{z-}$ with silver(I) salts yields a versatile series of larger clusters, which may also carry a positive overall charge, as exemplified by $[Ag_6\{Nb(CO)_6\}_4]^{2+}$.[20,36]

For the more stable TMCAs, a much larger variety of homo- and heteromultinuclear[37] complexes has been isolated, extending to examples such as $[Os_{20}(CO)_{40}]^{2-}$.[38] Due to carbon monoxide being a strong-field ligand, the 18 valence electron (VE) rule is particularly strict, especially in small clusters. As a result, some clusters can be directly derived from binary TMCs.

Dimetal Decacarbonyls

Similar to $Mn_2(CO)_{10}$, also $[Cr_2(CO)_{10}]^{2-}$ exists as a 2x17 VE complex stabilized by a metal-metal bond.[39] While substitution of both metal atoms with isoelectronic, negatively charged metal atoms straightforwardly leads to two 17 VE fragments

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/chem.202500489

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Table 1. Overview of the structurally characterized (scXRD) homometallic TMCCs from groups 5–11.

Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11
–	$[Cr(CO)_6]^{+}$[12]	$[Mn(CO)_6]^{+}$[13]	$[Fe(CO)_5]^{+}$[14] $[Fe_2(CO)_{10}]^{2+}$[15] $[Fe(CO)_6]^{2+}$[16]	$[Co(CO)_5]^{+}$[17]	$[Ni(CO)_4]^{+}$[18]	$[Cu(CO)_4]^{+}$[19]
$[Nb(CO)_7]^{+}$[20]	$[Mo(CO)_6]^{+}$[21]	$[Tc(CO)_6]^{+}$[22]	$[Ru_2(CO)_{10}]^{2+}$[23] $[Ru_3(CO)_{14}]^{2+}$[24] $[Ru(CO)_6]^{2+}$[9]	$[Rh(CO)_4]^{+}$[25]	$[Pd(CO)_4]^{2+}$[26]	$[Ag(CO)_2]^{+}$[27]
$[Ta(CO)_7]^{+}$[20]	$[W(CO)_6]^{+}$[21]	$[Re(CO)_6]^{+}$[28]	$[Os_3(CO)_{14}]^{2+}$[24] $[Os(CO)_6]^{2+}$[9]	$[Ir(CO)_6]^{3+}$[29]	$[Pt(CO)_4]^{2+}$[26]	$[Au(CO)_2]^{+}$[30]

{$[Cr(CO)_5]^-$}, replacing only one fragment towards $[CrMn(CO)_{10}]$ creates a more complex electronic situation. The $[CrMn(CO)_{10}]^-$ complex can be formulated either as a metal-only Lewis-pair (MOLP) containing the Lewis-acidic 16 VE {$Cr(CO)_5$} complex fragment and the Lewis-basic 18 VE {$[Mn(CO)_5]^-$} complex fragment or as covalently bonded system of two 17 VE fragments, {$[Cr(CO)_5]^-$} and {$Mn(CO)_5$}. And, while the 3*d* heterodinuclear transition metal carbonyl anions $[CrMn(CO)_{10}]^-$, $[MnFe(CO)_9]^-$ and $[FeCo(CO)_8]^-$ have been already synthesised in the 1960s–1970s,[40] their unique electronic properties have been investigated in depth only for $[FeCo(CO)_8]^-$, driven by the unusual *semi*-bridging binding motif of one carbonyl ligand,[41] while a scXRD study of a $[CrMn(CO)_{10}]^-$ salt is still missing. On the other hand, heterodinuclear TMCCs have until recently only been observed in the gas-phase.[42] Still, the advances of Malischewski *et al.* and our group in the isolation of homomultinuclear TMCCs are leaving a clear gap for isoelectronic heterodinuclear TMCCs.[15,23] To address this, we targeted in this work the isolation of $[MnFe(CO)_{10}]^+$ thereby completing the series of the $[MM'(CO)_{10}]^z$ complexes (Figure 1).

Hence, the first extended 34 VE series is established that complements several well-known 18 VE series including $[M(CO)_6]^z$ (M = Hf^{-II} to Ir^{III}),[29,43] $[M(CO)_5]$ (M = V^{-III} to Co^{I})[17,44] and $[M(CO)_4]^z$ (M = Cr^{-IV} to Cu^{I}).[4,19]

Results and Discussion

To prepare the elusive cationic heterodinuclear TMCC, we combined the mononuclear 17 VE metalloradical salt $[Fe(CO)_5]^{+\cdot}[WCA]^-$[14] (WCA = $[Al(OR^F)_4]^-$ & $[F\{Al(OR^F)_3\}_2]^-$; $R^F = C(CF_3)_3$) with the 2x17 VE dimer $Mn_2(CO)_{10}$ in 1,2,3,4-tetrafluorobenzene (4FB) as a non-nucleophilic and non-basic, but polar solvent[45] (ε_r = 12.6; eq. 1).* Slow diffusion of the solution with *n*-pentane yielded yellow crystals suitable for single-crystal X-ray diffraction (scXRD) of $[MnFe(CO)_{10}]^+[Al(OR^F)_4]^-$ and $[MnFe(CO)_{10}]^+[F\{Al(OR^F)_3\}_2]^-\cdot$(4FB) in 77% and 71% yield respectively. Bulk purity and the 1:1 Mn:Fe ratio in $[MnFe(CO)_{10}]^+[F\{Al(OR^F)_3\}_2]^-\cdot$(4FB) were confirmed by SEM-EDX (ESI). Unfortunately, the crystals of $[MnFe(CO)_{10}]^+[Al(OR^F)_4]^-$ diffracted poorly (ESI), so only $[MnFe(CO)_{10}]^+[F\{Al(OR^F)_3\}_2]^-\cdot$(4FB) is further discussed and has been uploaded to the CCDC.

$$2\ [Fe(CO)_5]^{+\bullet}[WCA]^- + Mn_2(CO)_{10} \xrightarrow{(1)} 4FB \rightarrow 2\ [MnFe(CO)_{10}]^+[WCA]^-$$

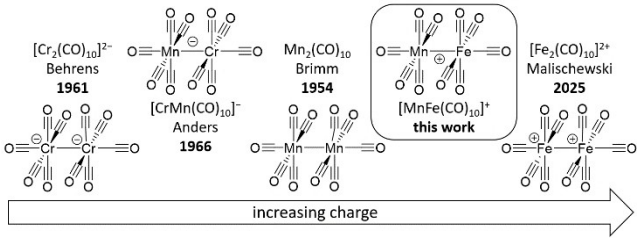

Figure 1. Isoelectronic row of 3*d* dimetal decacarbonyl complexes.

Molecular Structures

As expected, $[MnFe(CO)_{10}]^+$ exhibits near C_{4v} symmetry. The Mn–Fe distance of 290.1(1) Å is comparable to the Mn–Mn distance observed in $Mn_2(CO)_{10}$, which measures 290.3(2) Å.[46] Unfortunately, the complex cation is disordered, and due to the close proximity of both parts, a reliable modelling of the full disorder of the entire $[MnFe(CO)_{10}]^+$ moiety could not be achieved. Consequently, the manganese and iron atoms were modelled with mixed site occupancy, preventing a detailed discussion of the M–C or C≡O bond lengths, as DFT calculations predict these distances to differ between the {$Fe(CO)_5$} and {$Mn(CO)_5$} fragments.

The attempted syntheses of $[FeCo(CO)_9]^+$ and $[CoNi(CO)_8]^+$ by the combination of $[Fe(CO)_5]^{+\cdot}$ and $\frac{1}{2}$ $Co_2(CO)_8$ and $[Ni(CO)_4]^{+\cdot}$ and $\frac{1}{2}$ $Co_2(CO)_8$ respectively, have only led to the isolation of $[Co(CO)_5]^+$. Different stoichiometries of $Mn_2(CO)_{10}$ and $[Fe(CO)_5]^{+\cdot}$ did not yield any different complexes, but rather left over unreacted $Mn_2(CO)_{10}$ or $[Fe(CO)_5]^{+\cdot}$. $[MnFe(CO)_{10}]^+$ decomposes at room temperature in solution over days to $[Mn(CO)_6]^+$ under precipitation of solid iron and evolution of carbon monoxide.

Nevertheless, to discuss the differences of the {$M(CO)_5$} geometries of a heterodinuclear decacarbonyl, we prepared the isoelectronic TMCA $[PPN]^+[CrMn(CO)_{10}]^-$ ($[PPN]^+ = [N\{P(C_6H_5)_3\}_2]^+$) according to literature procedures[47] and determined its missing solid-state structure. Indeed, the {$Cr(CO)_5$} fragment

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displays a nearly linear C–Cr–C angle of 176.9°, whereas the {Mn(CO)$_5$} fragment shows a more bent geometry with a C–Mn–C angle of 164.8°. This observation aligns with the DFT-calculated structure (B3LYP(D3BJ)/def2-TZVPP) and suggests that the HOMO, which also contributes to the M–M bond, is more localized on the {Mn(CO)$_5$} fragment than on the {Cr(CO)$_5$} fragment. A similar geometry is expected for [MnFe(CO)$_{10}$]$^+$, as supported by the DFT-optimized structure. In this calculated structure, rather related structural parameters to the anion are found: the C–Mn–C angle is nearly linear at 177.2°, while the C–Fe–C angle deviates more significantly from linearity at 166.1° (Figure 2).

IR and Raman Spectra

The vibrational spectra of [MnFe(CO)$_{10}$]$^+$ are in good agreement with the DFT simulated spectra on the B3LYP(D3BJ)/def2-TZVPP level of theory (Figure 3). The average C–O stretching frequency $\tilde{\nu}$(CO)$_{av}$ weighted according to their degeneracies is at ca. 2085 cm^{-1}. As this is red-shifted relative to free carbon monoxide at 2143 cm^{-1}, the [MnFe(CO)$_{10}$]$^+$ cation clearly counts to the group of classical carbonyl complexes (Table 2).[48]

NMR-Spectroscopy

The ^{13}C NMR spectrum of [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$ in *ortho*-difluorobenzene shows four peaks in the typical metal carbonyl region with an intensity pattern of 1:4:4:1 (Figure 3C). The two broadened peaks at 210.4 and 208.7 ppm have been assigned to the one axial and the four equatorial manganese bound carbonyl ligands, while the sharper peaks at 202.1 and 191.7 ppm have been assigned to the four equatorial and the one axial iron bound carbonyl ligands. A stronger low-field shift

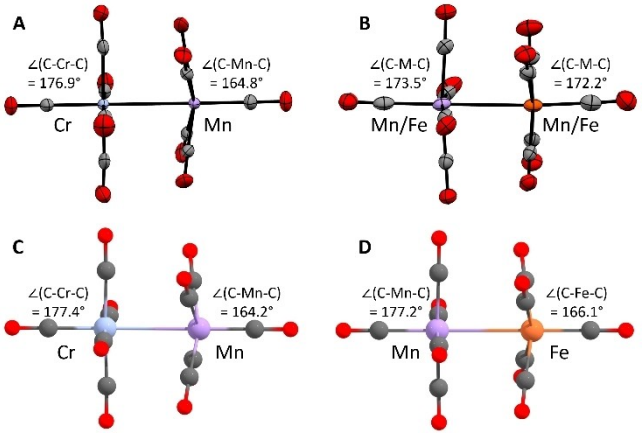

Figure 2. Molecular structures of the carbonyl complexes in [PPN]$^+$[CrMn(CO)$_{10}$]$^-$ (**A**) and (disordered) [MnFe(CO)$_{10}$]$^+$[F{Al(OR^F)$_3$}$_2$]$^-$·(4FB) (**B**) in the solid-state and in comparison, to the DFT optimized structures of [CrMn(CO)$_{10}$]$^-$ (**C**) and [MnFe(CO)$_{10}$]$^+$ (**D**) at B3LYP(D3BJ)/def2-TZVPP level of theory. Colour code: iron – orange, manganese – lavender, chromium – blue, oxygen – red, carbon – grey. Thermal ellipsoids depicted at 50% probability in **A** and **B**.

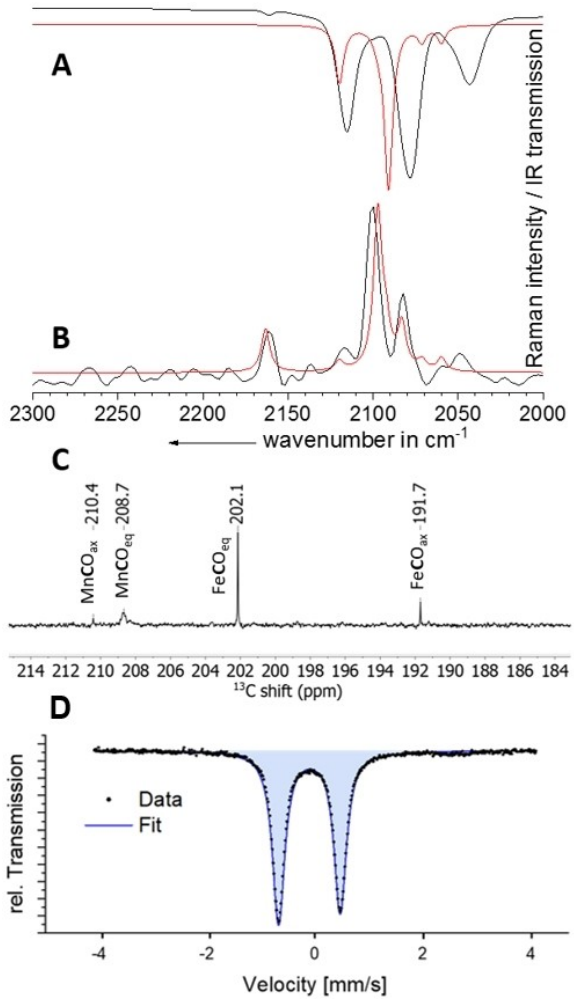

Figure 3. Spectroscopic data for [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$. Top: ATR-IR (**A**, black line, dried solution) and Raman (**B**, black line, crystals) spectrum of [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$ in comparison to the respective simulated spectra of [MnFe(CO)$_{10}$]$^+$ (red lines, B3LYP(D3BJ)/def2-TZVPP level of theory, scaled by 0.968 according to Duncan *et al.*).[49] **C**: ^{13}C NMR spectrum of [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$ in *ortho*-difluorobenzene at room temperature. **D**: Zero-field ^{57}Fe Mössbauer spectrum of crystalline [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$ at 80 K (data – black dots, fit – blue line).

in the ^{13}C NMR is indicative for more π-backdonation, although this comparison can be only made comparing carbonyl ligands attached to the same element.[11] Following this reasoning, the equatorial carbonyl ligands in the {Fe(CO)$_5$} fragment experience more π-backdonation than the axial one, while the opposite is the case for the {Mn(CO)$_5$} fragment. This underlines the unusual electronic properties of the heterodinuclear transition metal carbonyl complexes. Note that the DFT calculated ^{13}C NMR shifts are in line with this finding, although they differ strongly in both offset and relative position (ESI).

Mössbauer Spectroscopy

To further investigate the anisotropy of the electron density around the iron atom, we measured a zero-field ^{57}Fe Mössbauer spectrum of [MnFe(CO)$_{10}$]$^+$[Al(OR^F)$_4$]$^-$. The spectrum yields a

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Table 2. DFT calculated (B3LYP(D3BJ)/def2-TZVPP) vibrational modes and the IR intensities of the C–O stretches with the Mulliken symbols scaled by 0.968 according to Duncan *et al.*[49] in comparison to the experimentally observed bands. All numbers are given in wavenumbers (cm^{-1}). The intensities are reported as follows: ≥0.8 = very strong (vs), ≥0.6 = strong (s), ≥0.4 = medium (m), ≥0.2 = weak (w), <0.2 = very weak (vw).

DFT	IR	Raman
2163 (vw, A_1)	2161 (vw)	2161 (m)
2120 (w, A_1)	2115 (s)	2117 (w)
2097 (A_1)	–	2100 (vs)
2093 (B_2)	–	–
2091 (vs, E)	2078 (vs)	–
2083 (B_1)	–	2083 (s)
2071 (vw, A_1)	2056 (sh)	2059 (sh)
2060 (vw, E)	2043 (m)	2049 (w)

quadrupole splitting (ΔE_Q) of 1.14 mm s^{-1} with an isomeric shift of $\delta_{is} = -0.11$ mm s^{-1} (Figure 3). Although in many series of compounds, the isomeric shifts can be often correlated to the formal/physical oxidation state of the iron atoms, especially for +II, +III and +IV systems,[50] this is not the case for the $Fe(CO)_5$ series (Table 3) with 0 and +I.

The quadrupole splitting on the other hand is more helpful here, showing to which extent the Lewis-basic HOMO is located at the iron atom, as this orbital strongly contributes to the anisotropy in this fragment. While the parent $Fe(CO)_5$ has the highest quadrupolar splitting in this series, it gets halved upon the coordination of a proton or the formal {$[Mn(CO)_5]^+$} fragment. The deelectronation (one-electron oxidation)[53] of the $Fe(CO)_5$ moiety to $[Fe(CO)_5]^{+\cdot}$ yields a further reduction of the quadrupolar splitting as well as the Fe–Fe bond formation to $[Fe_2(CO)_{10}]^{2+}$. The removal of the second electron and subsequent coordination of an additional carbonyl ligand yields no quadrupole splitting at all (Table 3). In context of both Mössbauer parameters, the $[MnFe(CO)_{10}]^+$ ion is most related to $[HFe(CO)_5]^+$, but not the isoelectronic $[Fe_2(CO)_{10}]^{2+}$, underlining the importance of the MOLP resonance structure for $[MnFe(CO)_{10}]^+$.

Covalent or Lewis-Pair?

To test, if the covalent or the coordinative MOLP formulation is better suited, we calculated the dissociation of $[MnFe(CO)_{10}]^+$ under both a heterolytic and homolytic bond cleavage in the vacuum at the B3LYP(D3BJ)/def2-TZVPP level of theory (eq. 2ab). While the heterolytic cleavage is with $\Delta_{diss,g}G^o = +97$ kJ mol^{-1} less energy demanding, the difference between these two dissociation pathways is with a $\Delta(\Delta_{diss,g}G^o) = 8$ kJ mol^{-1} small. According to this test, the classification of $[MnFe(CO)_{10}]^+$ as a MOLP is only slightly preferred. In the condensed phase, the reaction energies are getting less predictable, as $[Mn(CO)_5]^+$ is expected to be a strong Lewis acid, thus a comparison is omitted here. Yet, the Gibbs energy of the reaction towards $[MnFe(CO)_{10}]^+$ in solution is with $\Delta_{rxn,4FB}G^o = -32$ kJ mol^{-1} significantly lower, due to the breaking of the Mn–Mn bond in $Mn_2(CO)_{10}$ and solvation effects (eq. 2c).

$$\Delta_{diss,g}G^o = +97 \text{ kJ mol}^{-1}$$
$$[MnFe(CO)_{10}]^+ \longrightarrow Fe(CO)_5 + [Mn(CO)_5]^+ \quad (2a)$$

$$\Delta_{diss,g}G^o = +105 \text{ kJ mol}^{-1}$$
$$[MnFe(CO)_{10}]^+ \longrightarrow [Fe(CO)_5]^{+\bullet} + Mn(CO)_5^{\bullet} \quad (2b)$$

$$\Delta_{rxn,4FB}G^o = -32 \text{ kJ mol}^{-1}$$
$$[Fe(CO)_5]^{+\bullet} + 0.5\ Mn_2(CO)_{10} \longrightarrow [MnFe(CO)_{10}]^+ \quad (2c)$$

Table 3. Zero-field ^{57}Fe Mössbauer isomeric shifts (δ_{is}) and quadrupole splittings (ΔE_Q) of a selection of $Fe(CO)_5$ containing complexes with calculated values in parentheses.

Molecular Entity	δ_{is} (sim.)	ΔE_Q (sim.)
$Fe^0(CO)_5$	−0.08[a] (−0.08)	2.55[a] (2.30)
$[HFe^I(CO)_5]^+$	−0.08[b] (−0.07)	1.40[b] (−1.74)
$[MnFe(CO)_{10}]^+$	−0.11 (0.08)	1.14 (−1.06)
$[Fe^I(CO)_5]^{+\cdot}$	0.17[a] (0.18)[c]	0.53[a] (−0.45)[c]
$[Fe^I_2(CO)_{10}]^{2+}$	0.03[b] (0.06)	0.23[b] (0.31)
$[Fe^{II}(CO)_6]^{2+}$	0.00[d] (0.07)	0.00[d] (0.12)

[a] taken from Ref. [14]; [b] taken from Ref. [15]; [c] taken from Ref. [51]; [d] taken from Ref. [52].

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To investigate the charge distribution in $[MnFe(CO)_{10}]^+$, we performed (QT)AIM analyses on the B3LYP(D3BJ)/def2-TZVPP level of theory, yielding $\{[Mn(CO)_5]\}^{q+}$ and $\{[Fe(CO)_5]\}^{(1-q)+}$ ($q = +0.50$). In line with the calculations on the dissociation energies of $[MnFe(CO)_{10}]^+$, nearly equal distribution of the charge does not show a strong preference for either the 2x17 VE or the 16 + 18 VE electron count.

Topology of the Electron Density

The nature of a bond can be additionally analysed by the properties of its bond critical point (BCP). AIM analyses of the entire series from $[Cr_2(CO)_{10}]^{2-}$ to $[Fe_2(CO)_{10}]^{2+}$ show that the Laplacian of the electron density at the bond critical points ($\nabla^2\rho(r_c)$) are higher in the heterodinuclear complexes than in the homodinuclear complexes, indicating a more polar bond. The difference between the M–M bonds of these homo- and heterodinuclear metal carbonyls is exemplified by the comparison of the Laplacian of the electron density $\nabla^2\rho(r)$ in $Mn_2(CO)_{10}$ and $[MnFe(CO)_{10}]^+$ in Figure 4.

While not intended by the concept of electron counting by Langmuir,[54] an accurate formulation of the heterodinuclear decacarbonyls $[CrMn(CO)_{10}]^-$ and $[MnFe(CO)_{10}]^+$ would be as "16.5 VE" and "17.5 VE" fragments. Although this formulation is clearly exaggerated, it showcases the borderline case between the covalent 2x17 VE and the coordinative 16 + 18 VE formulation.

Relaxed Force Constants

As important as the analysis of vibrational normal modes might be per se, by definition these modes are delocalized. In order to shed some light on the local bonding situation we therefore calculated individual relaxed force constants[55] for all $[MM'(CO)_{10}]^z$ systems (Table 4).

As the M–M distances are very sensitive to the choice of the basis set, the trends in the relaxed force constants will not be discussed within the $[MM'(CO)_{10}]^z$ series. All complexes in this series have a M–M force constant between 45 and 66 $N\,m^{-1}$ and are thus in the expected range for a metal-metal single-bond. For comparison: the formal M=M double bond in the unbridged $Fe_2(CO)_8$ prepared as a transient species by Poliakoff and Turner in 1971[56] has a relaxed force constant of 104 $N\,m^{-1}$. The general softness of the M–M potential is visible in all our studied $[MM'(CO)_{10}]^z$ systems (Table 4). The equilibrium metal-metal distance might therefore be easily affected by crystal packing or other external forces.

On the other side, the calculated relaxed force constant of the carbonyl C–O bond seems to be an extremely sensitive descriptor for the electronic situation in general. Going from the $[Cr_2(CO)_{10}]^{2-}$ dianion with a pronounced back donation to the electron poor $[Fe_2(CO)_{10}]^{2+}$ the value for the C–O bond increases by 42% from 1369 $N\,m^{-1}$ to 1962 $N\,m^{-1}$, respectively (Table 4).

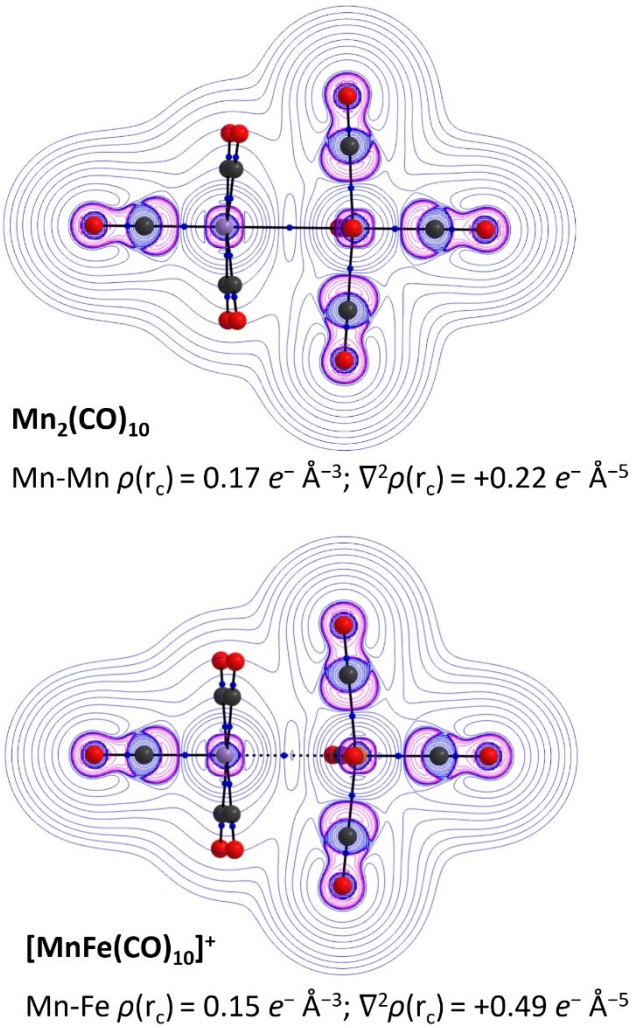

Figure 4. Laplacian of the electron density $\nabla^2\rho(r)$ in the M–M–C plane in $Mn_2(CO)_{10}$ (top) and $[MnFe(CO)_{10}]^+$ (bottom) calculated at the B3LYP(D3BJ)/def2-TZVPP level. $\nabla^2\rho(r) > 0$ – blue lines, $\nabla^2\rho(r) < 0$ – pink lines; blue dots represent bond critical points.

Nonetheless, the carbonyl C–O force constant (or frequency) is only a proxy for the actual bond of interest, the metal-carbonyl bond, while our calculated full compliance matrix allows the determination of the relevant M–CO force constants directly. Looking at the relevant values in Table 4, the pronounced π-back-bonding in $[Cr_2(CO)_{10}]^{2-}$ indeed leads to a strong metal-carbon bond with a relaxed force constant of 337 $N\,m^{-1}$ while the M–CO bond in the $[Fe_2(CO)_{10}]^{2+}$ dication drops down to 198 $N\,m^{-1}$ due to a minimized back-donation of electron density.

Conclusions

In conclusion, we isolated the first heterodinuclear TMCC $[MnFe(CO)_{10}]^+[Al(OR^F)_4]^-$ and characterized it by vibrational, NMR and Mössbauer spectroscopy as well as scXRD. The complimentary and first structural characterization of the $[CrMn(CO)_{10}]^-$ anion yields the complete structurally character-

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Table 4. Comparison of the key experimental data and calculated properties surrounding the isoelectronic 34 VE $[MM'(CO)_{10}]^z$ (M, M' = Cr^-, Mn^0, Fe^+) series. Properties of the BCPs and QTAIM charges calculated at the B3LYP(D3BJ)/def2-TZVPP level of theory. Force constants calculated at the TPSSH/def2-TZVPP of theory.

	$[Cr_2(CO)_{10}]^{2-}$	$[CrMn(CO)_{10}]^-$	$Mn_2(CO)_{10}$	$[MnFe(CO)_{10}]^+$	$[Fe_2(CO)_{10}]^{2+}$
$\tilde{\nu}$(CO) (IR) in cm^{-1}	1917[a] 1890 1793	2065[b] 1991 1952 1927 1894 1865	2044[c] 2013 1983	2161 2115 2078 2056 2043	2208[d] 2160 2127 2107
$\tilde{\nu}$(CO) (Raman) in cm^{-1}	2008[a] 1879 1809	2065[b] 1991 1941 1927 1894 1865	2111[e] 2009 1981	2161 2117 2100 2083 2059 2049	2207[d] 2184 2170 2156
d(M–M) in pm	299.5(1)[f]	294.1(1)	290.3(2)[g]	290.1(1)	282.7(3)
k(M–M)/N m^{-1}	52	56	66	50	45
$\rho_{BCP,M-M}/e^-$ $Å^{-3}$	0.13	0.14	0.17	0.15	0.18
$\nabla^2\rho_{BCP,M-M}/e^-$ $Å^{-5}$	+0.28	+0.44	+0.22	+0.48	+0.05
$q(M(CO)_5)/e^-$	−1.00	−0.49 (Cr) −0.51 (Mn)	0.00	+0.50 (Mn) +0.50 (Fe)	+1.00
$q(CO)_{av}/e^-$	−0.423	−0.302	−0.184	−0.072	+0.034
$k(C–O)_{av}$/N m^{-1}	1369	1492	1666	1851	1960
$k(M–C)_{av}$/N m^{-1}	337	319	294	245	198

[a] in dimethylsulphoxide from Ref. [57] [b] from Ref. [58] [c] in cyclohexane from Ref. [59] [d] as powder from Ref. [15] [e] from Ref. [60] [f] in $([PPN]^+)_2[Cr_2(CO)_{10}]^{2-}$ from Ref. [61] [g] from Ref. [46].

ized 3*d* series of 34 VE dimetal decacarbonyls from $[Cr_2(CO)_{10}]^{2-}$ to $[Fe_2(CO)_{10}]^{2+}$. The metal-metal bond shortening gradually increases within the series and the calculated AIM partial charges in all complexes are equally distributed over both $\{M(CO)_5\}$ fragments. Still, through the different electron count, the heterodinuclear complexes are containing more polar M–M bonds, yielding strong differences in the force constants and polarization of the carbonyl ligands as well as the relevant M–C bonds (Table 4).

Author Contributions

MS performed all the synthetic and analytical work and wrote the manuscript together with IK. HK measured and analysed the SEM-EDX spectra. TE measured and analysed the Mössbauer spectra. JG performed the DFT calculations for the determination of the force constants. HK, TE and JG helped actively writing the respective passages discussing their results.

Acknowledgements

The authors would like to thank Harald Scherer for the NMR measurements. This work was supported by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – Project number 350173756 and the ERC Advanced Grant InnoChem (101052935). M. S. is grateful for a PhD fellowship from the "Fonds der Chemischen Industrie FCI". The authors thank Felix Tuczek for measurement time on his Mössbauer spectrometer. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interests

The authors declare no conflicts of interest

Data Availability Statement

Full experimental details and additional drawings of the spectra as well as computational details are deposited with the Supporting Information. Crystallographic data for $[MnFe(CO)_{10}]^+$ $[F\{Al(OR^F)_3\}_2]^-$ and $[PPN]^+[CrMn(CO)_{10}]^-$ has been deposited at the CCDC with deposition numbers 2151904 and 2408047.

Keywords: Carbonyl ligands · Cations · Donor-acceptor systems · Heterometallic complexes · Metal-metal interactions

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Manuscript received: February 7, 2025
Accepted manuscript online: February 24, 2025
Version of record online: March 11, 2025

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