Completing the triad: synthesis and full characterization of homoleptic and heteroleptic carbonyl and nitrosyl complexes of the group VI metals†‡

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Abstract

Oxidation of MICO₆ (M = Cr, Mo, W) with the synergistic oxidative system Ag[WCA]/0.5 I₂ yields the fully characterized metalloradical salts [M(CO)₆][⁺[WCA]⁻ (weakly coordinating anion WCA = [F-{Al(ORF)₃}₂]⁻, R¹ = C(CF₃)₂). The new metalloradical cations with M = Mo and W showcase a similar structural fluidity as the previously reported [Cr(CO)₆][⁺⁺]. Their reactivity increases from M = Cr < Mo < W and their syntheses allow for in-depth insights into the properties of the group 6 carbonyl triad. Furthermore, the reaction of NO⁺[WCA]⁻ with neutral carbonyl complexes MICO₆ gives access to the heteroleptic carbonyl/nitrosyl cations [M(CO)₆(NO)]⁺ as salts of the WCA [Al(ORF)₃]⁻, the first complete transition metal triad of their kind.

Introduction

Although personal and professional preferences do definitively differ, having a ‘chemical playground’ at hand and being able to explore fundamentally new compounds is one of the great appeals of chemical research. Especially so, when decade- or century-long questions and problems can be answered or solved. The peculiar compound family of carbonyl complexes is part of this century-long research: even about 130 years after the discovery of Ni(CO)₄, new ‘milestones’ of homoleptic carbonyl complexes are still to be revealed today (Fig. 1).2 And after lying dormant for well over a decade, the synthesis of novel homoleptic transition metal carbonyl complexes has risen anew.

Fig. 1. (a) Timeline of the milestones in the synthesis of homoleptic carbonyl complexes; (b) Overview to literature-known and fully characterized homoleptic carbonyl cations (green; our work: green-hatched)†−¹² and this work (pale blue).
most promising approach in the past decades, which yielded the majority of the homoleptic carbonyl cations known today\(^{1,2}\) (Fig. 1), was the use of superacidic media such as SbF\(_5\), HF–SbF\(_5\) or HSO\(_3\)F.\(^{21}\) However, the limiting factor was and still is the quality of the [SB\(_6\)F\(_7\)]\(^{--}\)/[SB\(_2\)F\(_{11}\)]\(^{++}\) anions as a WCA: if the carbonyl cation is electron deficient (e.g. does not fulfill the 18-electron rule) and is coordinatively unsaturated, the lone pair orbitals of the fluorine atoms can still be Lewis-basic enough to bind to the metal center. Especially for the group 6 carbonyl cations this is the case, as the tendency to an increased coordination number 7 for Mo and W led to a coordination polymer or fluorine-bridged adducts with the [SB\(_6\)F\(_7\)]\(^{--}\) anion with the respective metals in the oxidation state of VII (Fig. 2).\(^{18}\) Apparently, despite many synthesis attempts, the [SB\(_6\)F\(_7\)]\(^{--}\)/[SB\(_2\)F\(_{11}\)]\(^{++}\) system is not suitable for the synthesis of truly homoleptic group VI carbonyl cations.

Our approach is an oxidative one starting from the commercially available neutral carbonyl complexes Mo(CO)\(_6\) and W(CO)\(_6\) and the Ag\(^+/0.5\) Halogen\(_2\) or [NO\(^+\)]\(^{--}\) oxidants as salts of the WCAs [Al(OR\(_5\))]\(^{++}\) and [F–Al(OR\(_5\))]\(^{--}\) (R\(^=\)C\(_{6}F_{14}\)). Both anions have proven their value in the stabilization of numerous reactive cations.\(^{18}\) The larger and even less coordinating [F–Al(OR\(_5\))]\(^{--}\) anion has a higher stability towards strong electrophiles\(^{19}\) and was essential for the stabilization of [W(CO)\(_6\)]\(^{++}\). Furthermore, we make use of standard Schlenk-techniques as well as easy-to-handle solvents and reagents, which should increase the accessibility to a broad scientific community.

## Results and discussion

### Previous findings on [Cr(CO)\(_6\)]\(^{++}\)

Recently, we published our discovery of the surprising formation of [Cr(CO)\(_6\)]\(^{++}\)/[WCA] when Cr(CO)\(_6\) was oxidized with NO [WCA].\(^{2}\) Although thermodynamically favored by about 180 kJ mol\(^{-1}\), the heteroleptic substitution product [Cr(CO)\(_5\)/NO]/[WCA] is only quantitatively gained after one to two weeks of stirring in a closed vessel. The NO/CO exchange therefore is slow enough for the kinetic product [Cr(CO)\(_6\)]\(^{++}\) to be selectively synthesized at −78 °C under removal of the evolving NO\(_{2}\). By assuming an associative reaction mechanism, an energetically highly disfavored transition state with a coordination number of >6 for Cr may account for this. The [Cr(CO)\(_6\)]\(^{++}\) radical cation features the same structural fluctuation as the isoelectronic vanadium hexacarbonyl V(CO)\(_6\); the D\(_{2d}\) ground state with a low-lying (~1 kJ mol\(^{-1}\) barrier) D\(_{2h}\) transition state leads to a fluctuating structure even at low temperatures. This is reflected in a broad F\(_{g}\) CO vibration in Raman spectroscopy as well as a (pseudo-)isotropic EPR signal at 100 K. Only at 4 K, the D\(_{2d}\) ground state manifests itself by a rhombic EPR spectrum. Now, the question arose, whether the synthetic methodology could be expanded to the heavier group 6 metal carbonyls of Mo and W, or if other oxidants than [NO\(^+\)] had to be used.

[NO\(^+\)]\(^{--}\) as oxidant: ternary carbonyl/nitrosyl cations

Since the gas-phase ionization energies (IE) of the heavier homologues are similar to that of Cr(CO)\(_6\) (8.2 eV Cr(CO)\(_6\)), 8.25 eV Mo(CO)\(_6\); 8.0 eV W(CO)\(_6\),\(^{28}\) the use of [NO\(^+\)]\(^{--}\) as oxidant (IE: 9.26 eV)\(^{21}\) was our starting point. However, already on physical contact of Mo(CO)\(_6\)/W(CO)\(_6\) with the solid NO [Al(OR\(_5\))]\(^{++}\), the distinctive reactivity of the heavier group 6 homologues became apparent. The orange substitution products [Mo(CO)\(_5\)/NO][Al(OR\(_5\))]\(^{1}\) (1) or [W(CO)\(_5\)/NO][Al(OR\(_5\))]\(^{2}\) (2) were immediately generated, even without solvent or also in inert solvents (such as perfluorohexane, C\(_{6}F_{14}\)) at −78 °C in a dynamic vacuum. This observation is in accordance with our above-mentioned assumption of the kinetic hindrance of Cr(CO)\(_6\) towards a preferred associative CO/NO substitution mechanism via a seven-coordinate transition state.\(^{2}\) Because of the ready tendency of Mo and W to adopt a coordination number of 7, it was not surprising that the reaction to the mere oxidation products [Mo/W(CO)\(_6\)]\(^{2+}\) was not observed. Instead, the CO/NO exchange is inevitable and only the heteroleptic carbonyl/nitrosyl cation salts 1 and 2 were obtained according to eqn (1).

\[
{\text{[NO]}^{+}\text{[Al}^{(OR_{5})_{3}]^{\text{2+}}} + \text{Mo(CO)_{6}} \xrightarrow{\text{dDB}} \text{[Mo(CO)_{5}\text{NO}]}^{+}\text{[Al}^{(OR_{5})_{3}]^{\text{2+}}} + \text{CO} \] (1)

By vapor diffusion of n-pentane into an ortho-difluorobenzene (dDB) solution of 1 and 2, the complexes can be crystallized in yields of around 90%.\(^{2}\) They are isostructural to their lighter homologue [Cr(CO)\(_{6}\)][NO][Al(OR\(_5\))]\(^{1}\) and the cations feature the same undistorted local \(C_{4v}\) symmetry in the solid state. This reflects in good agreement of the experimental vibrational spectra with the simulation from the respective calculated gas-phase cations (Fig. 3).

Fully characterized ternary transition metal carbonyl/nitrosyl cations are surprisingly scarce in literature.\(^{22}\) The only example, apart from [Cr(CO)\(_{6}\)][NO]\(^{+}\) recently reported by us,\(^{2}\) is the [Co(CO)\(_{6}\)][NO]\(^{+}\) cation reported in 2006.\(^{23}\) For structurally characterized ternary Mo and W carbonyl/nitrosyls, no entry is found in the CCDC to date (neither anionic, neutral, nor cationic).\(\|\)
The synergistic oxidative system Ag+/0.5 I2 and its complications

Obviously, a different oxidant than [NO]⁺ was necessary here. It should be noted as a side that the reaction of [Cr(CO)₆][Al(ORF)₄] with the neutral W(CO)₆ in TFB (¼ 1,2,3,4-tetrafluorobenzene) did not yield any apparent reaction (e.g. color change of the homogeneous solution) over the course of several weeks, despite the about 0.2 eV lower IE of the tungsten compound. Only [Cr(CO)₆][Al(ORF)₄] was visible after work up by IR spectroscopy.

Note that related studies with the isoelectronic V(CO)₆ showed its capability to oxidize carbonyl anions such as [Mn(CO)₅]/CO and [Co(CO)₄]/CO²⁴ or Nb(mes)₂ to [Nb(mes)₂(CO)][V(CO)₆] (mes: C₉H₁₂).²⁵

Since also Ag[WCA] showed no reaction with Cr(CO)₆, the additional use of halogens seemed promising. The resulting synergistic Ag⁺/0.5 Hal₂ (Hal = Cl₂, Br₂, I₂) system is known to be very strongly oxidizing²⁶,²⁷ and the respective silver halides should simply precipitate after the oxidation took place as in eqn (2).

\[
\text{Ag[WCA]} + 1/2 \text{Hal₂} \quad \rightarrow \quad \text{[Substrate][WCA]} + \text{AgHal}_1^+ + \text{Substrate}
\]

In terms of reactivity, it did not matter, whether the (Ag⁺)₂/Hal₂ complex was formed in situ or was isolated prior to use – indicating that the same active species is present in solution. The exact 2 : 1 stoichiometry of 2Ag⁺/Hal₂ is crucial to prevent any excess halogen from reacting with the desired products. In terms of practicability, this meant that the heavy diiodine was the dihalogen of choice, since (a) [Ag₂I₂][Al(ORF)₄]₂, shown in Fig. 4, is the only one of the Cl₂/Br₂/I₂ triad to be stable enough to be isolated and stored as starting material and (b) the in situ generation of 2Ag⁺/Hal₂ with an exact 2 : 1 stoichiometry is more tedious (to say the least) with small amounts of gaseous Cl₂ and volatile Br₂.** Furthermore, it should be noted that already†† the 2Ag⁺/I₂ mixture is strongly oxidizing enough to react with solvents up to an IE of 11.4 eV such as oDFB or CH₂Cl₂, as indicated by the immediate precipitation of yellow AgI.²⁷

Impact of anion and solvents

The limitations of the [Al(ORF)₄]⁻ anion became clear when we switched from Cr(CO)₆ to the Mo(CO)₆ system. Ag[Al(ORF)₄]₀.5 I₂ reacted with Cr(CO)₆ according to eqn (3) cleanly and quantitatively to [Cr(CO)₆][Al(ORF)₄] and AgI precipitate in any

![Fig. 4 Molecular structure of the known²⁷ [Ag₂I₂][Al(ORF)₄]₂ oxidant.](image-url)

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solvent that we used (SO₂, oDFB, C₆F₁₄). Thus, this new route is the most convenient and preferred one for its synthesis.

\[
\text{Ag[Al(ORF)₄] + 1/2 I₂ + Cr(CO)₆ \rightarrow oDFB \rightarrow [Cr(CO)₆][Al(ORF)₄] + AgI.}
\]

(3)

However, the accessibility of the coordination number 7 for Mo became evident: when applying the same reaction conditions to Mo(CO)₆, always an inseparable orange mixture of the as [Al(ORF)₄]⁻ salts co-crystallizing cations [Mo(CO)₆]⁺ and [Mo₂(CO)₆I₄]⁻ obtained. Leftover Ag[Al(ORF)₄] contaminated the product and proved difficult to be separated by crystallization (Scheme 1). It soon became apparent that the solvent played a crucial role. In ‘well-dissolved’ systems (such as CH₂Cl₂, oDFB, TFB or SO₃), the formation of different Mo(II) species could never be satisfyingly suppressed. In low polarity inert solvents (perfluorohexane C₆F₁₄ or perfluorobenzene C₆F₆), the reaction mixture was a suspension, which induced long reaction times (e.g. several days in C₆F₁₄), but at the same time also little or no iodide-containing side products (vide infra). In C₆F₆, an inseparable mixture of [Mo(CO)₆][Al(ORF)₄]⁺, [Mo(CO)₆][Mo(CO)₄I][Al(ORF)₄]⁻, and [[Mo(CO)₆]₂][F{-[Al(ORF)₃]}₂] was gained upon crystallization. The presence of [F{-[Al(ORF)₃]}₂] was demonstrated for the decomposition of the [Al(ORF)₄]⁻ ion, and the anion of choice. Depending on the solvent (oDFB, C₆F₆), either only seven-coordinate [W(CO)₆I]⁺ or decomposition products of the [Al(ORF)₄]⁻ ion such as [W(CO)₆I(ORF)]⁻ and [W(CO)₄(ORF)₂][F{-[Al(ORF)₃]}₂] and a grey precipitate were obtained (Scheme 2). All of those include W in oxidation state +II or +III. However, the last reaction also showed traces of the desired [W(CO)₆][F{-[Al(ORF)₃]}₂].

It became more and more apparent that the synthesis would be even more fickle for the heavier homologue W(CO)₆.

In order to evaluate the role of the halogen in the Ag⁺/0.5 Hal₂ oxidant and its ability to coordinate to the metal center, we reacted Ag[F{-[Al(ORF)₃]}₂]/0.5 Cl₂ with W(CO)₆ in perfluorohexane. Solely the chlorido-bridged tungsten(II) salt [W₂(CO)₈Cl₂][F{-[Al(ORF)₃]}₂] could be isolated and crystallized (Scheme 3), underlining the importance of I₂ as an oxidant – especially since with gaseous Cl₂ and liquid Br₂ the spatial separation of dihalogen and the volatile carbonyl substrate is difficult to realize in the reaction vessel. Thus, it is not clear, if the neutral carbonyl already reacts with the dihalogen without presence of the silver salt.

Scheme 1 Impact of the solvent on the formation of [Mo(CO)₆]⁺; bottom: molecular structures of [Mo(CO)₆]⁺ (d(Mo-C) = 212.2(3) pm, d(C-O) = 111.8(4) pm); [Mo₂(CO)₆I₄]⁻ (d(Mo-Mo) = 355.0(1) pm, d(Mo-C) = 203.7(3) pm, d(C-O) = 112.5(4) pm, d(Mo-I) = 287.1(3) pm; av.); co-crystals and [Mo₂(CO)₆I₄]⁻ (d(Mo-Mo) = 312.4(1) pm, d(Mo-C) = 208.0(9) pm, d(C-O) = 112.5(10) pm, d(Mo-I) = 271.5(1) pm; av.) were identified by single-crystal XRD (scXRD); thermal ellipsoids were drawn at 50% probability level; note that the “+...” stands for additional (unidentified) side-products; AgI was formed in all reactions, leftover Ag[Al(ORF)₄] was also commonly observed, albeit not for the best reaction in C₆F₁₄.

Scheme 2 Impact of the solvent on the formation of the undesired (side-)products [W(CO)₆]⁺ (d(W-C) = 209.3(7) pm, d(C-O) = 112.5(8) pm, d(W-I) = 276.7(1) pm), [W(CO)₆(ORF)]⁺ (d(W-C) = 210.3(3) pm, d(C-O) = 113.5(3) pm, d(W-O) = 201.4(2) pm) and [W(CO)₄(ORF)₂]⁺ (d(W-C) = 214.5(3) pm, d(C-O) = 114.5(3) pm, d(W-O) = 189.6(2) pm; av.) as well as their molecular structures (anions are omitted for clarity); all complexes marked with [*] were identified by single-crystal XRD (scXRD); thermal ellipsoids were drawn at 50% probability level; note that the “+...” stands for additional (unidentified) side-products; AgI was formed in all reactions, which turned to a grey precipitate after some time.
The conclusions from these insights were that (a) \( \text{F-}[\text{Al(ORF)}_3]_2/C_0 \) was our anion of choice, (b) iodine was the most viable halogen and (c) the reaction was best carried out in an inert solvent. We believe that the solvation of the molecular complex \([\text{WCA}]\text{Ag}--\text{I}--\text{I}--\text{I}--\text{Ag}[\text{WCA}]\) (Fig. 4), (\([\text{Ag}_2\text{I}_2][\text{WCA}]_2\)) plays a crucial role in the reaction behavior: ideally, to ensure a mere oxidation, an intact \(\text{Ag}_2\text{I}_2\)-moiety is necessary. This is only the case for an inert solvent (such as \(\text{C}_6\text{F}_{14}\) or 1,2,3,4-tetrafluorobenzene, see eqn (4a)), since coordinating solvents (such as oDFB) solvate \(\text{Ag}^+\) and therefore promote an asymmetric dissociation of the \([\text{Ag}_2\text{I}_2][\text{WCA}]_2\) complex. The resulting molecular \(\text{WCA}\text{Ag)--I}--\text{I}--\text{I}--\text{Ag}[\text{WCA}]\) species, which was crystallographically characterized with the WCA \([\text{Al(ORF)}_3]_4^-\), can then act as an I source upon formation of AgI, which eventually leads to the mixed carbonyl/halide side-products as in eqn (4b). We believe this behavior to be similar for both WCAs \([\text{Al(ORF)}_3]_4^-\) and \(\text{F-}[\text{Al(ORF)}_3]_2\).

When carrying out the reaction in \(\text{C}_6\text{F}_{14}\), in order to separate the desired products from the precipitated AgI, the crude reaction mixture needs to be dissolved, extracted and then crystallized for purification. The dissolution in oDFB or TFB then often led to precipitation of grey solids, presumably due to incomplete reactions even after numerous days, which also complicated reproducibility.

### Best reaction conditions towards \([\text{M(CO)}_6]^+\)

A number of diverse reaction conditions led us to the conclusion that the best oxidizer is \([\text{Ag}_2\text{I}_2][\text{F-}[\text{Al(ORF)}_3]_2]\) in the solvent TFB, since especially \([\text{W(CO)}_6]^+\) is not stable in oDFB. Furthermore, all manipulations in solution were carried out at lower temperatures (\(\sim 0^\circ\text{C}\)) due to the temperature-sensitive nature of \([\text{W(CO)}_6]^+\) and the side-products. This led to the curious point, where crystallization at room temperature was actually beneficial, due to the decomposition and precipitation of undesired by-products, which otherwise would have contaminated the crystalline \([\text{W(CO)}_6][\text{F-}[\text{Al(ORF)}_3]_2]\). Overall,

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**Scheme 3** Use of \(\text{Cl}_2\) as oxidant and the molecular structure of the \([\text{W}_2(\text{CO})_6\text{Cl}]^+\) cation (\(d(\text{W}\cdots\text{W}) = 350.7(1)\text{pm}, d(\text{W}\cdots\text{O}) = 203.1(3)\text{pm}, d(\text{C}\cdots\text{C}) = 113.0(3)\text{pm}, d(\text{W}\cdots\text{Cl}) = 251.1(3)\text{pm}\); av.: anions are omitted for clarity) identified by single-crystal XRD. Note that the “+…” stands for additional (unidentified) side-products.
the best procedure was to stir the crude reaction mixture over
night thawing from 0 °C to room temperature (RT), after which
the color of the suspension changed from green to grey and
after filtration, a clear yellow TFB solution was obtained in the
W(CO)6 case given in eqn (5). Unfortunately, this precipitation
of undesired side products also led to a partial decomposition
even of the robust [F-{Al(ORF)3}2]- anion and the reproducible
formation of [W(CO)6(ORF)]{F-{Al(ORF)3}2} was observed as a
side product. Again, this was difficult to separate from
[W(CO)6][F-{Al(ORF)3}2] by crystallization – especially, since both
species are of similar yellow color and equally soluble in TFB.
Careful manual sorting of the two crystalline species is neces-
sary, leading to a quite low total yield (35%) for M = W.
However, the procedure for M = Mo given in eqn (5) yields
a rather clean product at 78% yield.

\[
\text{Ag}[[\text{F-Al(ORF)}_3]_2] + 1/2 \text{I}_2 + \text{Mo(CO)}_6 \rightarrow \text{TFB, o.n.} \rightarrow [\text{Mo(CO)}_6][\text{F-Al(ORF)}_3]_2 \quad (3)
\]

\[
[W(CO)_6][\text{F-Al(ORF)}_3]_2 \rightarrow [W(CO)_6][\text{F-Al(ORF)}_3]_2 + \text{I}_2 \quad (4)
\]

\[
[W(CO)_6][\text{F-Al(ORF)}_3]_2 \rightarrow [W(CO)_6][\text{F-Al(ORF)}_3]_2 \quad (5)
\]

Both [F-{Al(ORF)3}2]- salts 3 and 4 crystallize isostructural to
the [Cr(CO)6]2+ analogue in the cubic space group Pa3 (Fig. 5).
The M atoms of the [M(CO)6]+ cation reside on a –3 position
and feature only one symmetry-independent CO ligand. They
exhibit crystallographic D3d symmetry – as in the undistorted
gas phase and thus underlining the claim of the [F-{Al(ORF)3}2]-
anion being “least-coordinating” and providing exceptional
pseudo gas phase conditions.18

In summary, a completely satisfying route to the heavier
group VI carbonyl cations is still to be found. By principle, our
system allows access to and first insights of the properties of
these compounds. However, the limitations of the synergistic
2Ag[WCAl]/Hα2 oxidant are also clear: if the coordination
number of seven is somewhat easily attainable, coordination
of a halide to the Lewis acidic metal center is always
problematic.

It also has to be noted here that all the identified and
structurally characterized side-products were previously
unknown from the literature and should – in principle – be
accessible selectively. However, an extensive study of the novel
mixed group 6 carbonyl/halide cations was not part of our
project and would by far exceed the scope of this report.

Fig. 6 Temperature dependence of the CW X-band EPR spectra of 3 (top left) and 4 (bottom left) in frozen TFB. Experimental and simulated EPR
spectra of 3 (top right) and 4 (bottom right) at 4 K. Simulation parameters for 3: \(g_1 = 2.374, g_|| = 1.800\); simulation parameters for 4: \(g_1 = 1.722, g_|| = 2.427\). The asterisk (*) denotes an impurity (see ESI Fig. 22†).
Comparison of the [M(CO)₆]⁺ and [M(CO)₆(NO)]⁺ triad (M = Cr, Mo, W)

For the first time, it is possible to study a complete isostructural triad of homolecate radical carbonyl and heteroleptic carbonyl/nitrosyl cations for their properties.

**EPR spectra.** To confirm the radical character of the isolated cations we recorded CW X-band EPR-spectra of 3 and 4 in frozen TFB solutions at temperatures between 100 K and 4 K (Fig. 6).

As for the [Cr(CO)₆]⁺ [WCA]⁻ spectra, at higher temperatures (100 K) we detected only weak (pseudo)isotropic signals indicating a fluctuating structure of the radical cations. At lower temperatures we could clearly detect an anisotropic signature of the EPR signals of both radical cations in agreement with an axial Jahn–Teller distortion of the d⁵ complexes as it was already seen in the crystal structure of 3 and 4 and described for the isoelectronic [Cr(CO)₆]⁺ and V(CO)₆. In contrast to [Cr(CO)₆]⁺ and [Mo(CO)₆]⁺, where gₗ > gₜ, for [W(CO)₆]⁺ it is opposed, i.e. gₜ > gₗ. Reports on the EPR spectra of isoelectronic Nb(CO)₆⁺ and Ta(CO)₆⁺ generated in CO matrix at 2 K reveal that these complexes also adopt a linear distorted octahedral structure, however, their specific molecular symmetry could not be determined yet. DFT studies suggest the neutral Ta(CO)₆⁺ radical should not exist as a monomer but form CO-bridged dimeric structures. Interestingly, the hypothetic Ta(CO)₆⁺ monomer is predicted to take a C₃₄ symmetric structure in contrast to the D₃d structure found for [Mo(CO)₆]⁺ and [W(CO)₆]⁺, which is not even a local minimum structure in the case of Ta(CO)₆⁺.

We performed SA–CAS–SCF calculations on the isolated radical cations both in D₃d and D₄h symmetry and compared the obtained g values with the experimentally determined ones (Table 1). Although there are deviations between calculated and experimental values, the results show that the axial EPR signature of the radical cation [Mo(CO)₆]⁺ is rooted in a D₃d symmetric ground state analogously to [Cr(CO)₆]⁺. For [Mo(CO)₆]⁺, our calculations predict a smaller g-anisotropy of the hypothetic D₄h symmetric state compared to the D₃d symmetric one, whilst the opposite is true for [Cr(CO)₆]⁺.

For [W(CO)₆]⁺, the calculations predict the gₜ > gₗ like for the other cations, however, we were not able to get an acceptable fit of the EPR spectrum of 4 using this g factor ratio. Instead, only a ratio gₜ < gₗ led to reasonable accordance of experimental and simulated EPR spectra. We were not able to uncover the underlying reasons for this difficult to calculate heavy element and avoid speculative proposals.

**Vibrational analysis.** The wavenumber, shape and quantity of the observed CO bands enables conclusions to be drawn with respect to the symmetry and bonding situation of the complexes. All three complexes feature one (slightly broadened) overlapping A₁u and E₁u vibration in IR spectroscopy, as well as two characteristic bands in Raman spectroscopy. The sharp, totally symmetric A₁g stretching vibration in the Raman spectrum is of the same energy for all three salts (2173 cm⁻¹, Fig. 7 right), since the metal atoms remain motionless during the vibration and thus its frequency is independent of the mass of the metal atom. On the other hand, in the IR spectrum, the vibrational frequencies decrease from 2096 cm⁻¹ (Cr) over 2089 cm⁻¹ (Mo) to 2075 cm⁻¹ (W) for the asymmetric vibrations (Fig. 7 left) - here influenced by the increasing mass of the central atom. Both trends are in accordance with the DFT calculations as well as their similar fluoride ion affinities (FIA’s) speaking for similar acceptor properties (Table 2). Yet, those effects on the asymmetric vibrations are small, as already noted for the Raman spectra of the neutral M(CO)₆ triad. Within the resolution of the measurement of 4 cm⁻¹, they are nearly identical (see S.I. for their experimental spectra).

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**Table 1** Experimental (Exp.) g values compared to calculated (calc.) ones as well as relative electronic energies of the investigated radical cations with different point groups and comparison to the already reported [Cr(CO)₆]⁺.

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<th></th>
<th>[Cr(CO)₆]⁺</th>
<th>[Mo(CO)₆]⁺</th>
<th>[W(CO)₆]⁺</th>
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</tbody>
</table>

ᵃ For details of the g-value calculations please refer to the ESI. Values for [Cr(CO)₆]⁺ taken from ref. 2.ᵇ Electronic energies (in cm⁻¹, in brackets: kJ mol⁻¹) were calculated at the DLPNO-CCSD(T)/def2-TZVPP level of theory using structures optimized with TPSSH-D3BJ/def2-TZVPP. g₁₀₀₀ = (2gₗ + gₜ)/3. ｃ g₁₀₀₀ = (gₕ + 2g₁)/3. ｄ The better accordance of the isotropic gvalue of D₄h with experiment must not be misinterpreted: deviations in the calculation of the perpendicular component gₜ enter twofold.

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**Fig. 7** Comparison of the IR (left) and Raman (right) spectra of the [M(CO)₆][F-(Al(OOR)₃)₂] triad. All three Raman spectra feature the same sharp A₁g CO vibration at 2173 cm⁻¹ and a broad E₂g vibration indicating a fluctuating structure, even more so for [W(CO)₆]⁺ where two very broad bands spanning over more than 300 cm⁻¹ are visible between 1800 and almost 2200 cm⁻¹.
The broad $E_g$ Raman-active vibration at around 2125 cm$^{-1}$ indicates the same structural properties for the heavier homologue Mo as already shown for the [Cr(CO)$_6$]$^{1+}$ or V(CO)$_6$$^2$ cases. At room temperature, a very low-lying $D_{3d}$ symmetric transition state ($M = Cr, Mo$) or intermediate ($M = W$) probably allows for equilibration of the two different $D_{3d}$ symmetric ground states (see Scheme 4 and S.I. Section 4$^a$ for an in-depth discussion) – even on the fast time scale of vibrational spectroscopy.

This does not affect the all-symmetric $A_{3g}$ CO stretch. A very broad band, spanning over 100 cm$^{-1}$, is the result. $[W(CO)_6]^{1+}$ shows two very broad bands which cover over 300 cm$^{-1}$ in its Raman spectrum, reaching as far down as 1800 cm$^{-1}$, which is in the range of bridging carboxyl ligands. However, all spectra were measured from crystalline complexes $[M(CO)_6]^{1+}$[F- {Al(OR)₃}₂]⁻, so an intermolecular exchange is impossible – whereas in solution a dimerization-equilibrium of $[W(CO)_6]^{1+}$ and $[W_2(CO)_{12}]^{2+}$ with bridging μ-CO entities could be imaginable, but appears unlikely based on orienting DFT calculations.

The calculated force constants imply an increase in the M-C bond strength as well as a decrease in the C-O bond strengths from Cr to W (Table 2). The dicationic group 7 triad $[M'-(CO)_6]^{2+}$

| Table 2 | Analysis of the characteristic vibrations and their force constants (in parenthesis) as well as XRD data of $[M(CO)_6]$ and $[M(CO)_6]^{1+}$ (M: Cr, Mo, W) as [F- {Al(OR)₃}₂]⁻ salts. DFT: BP86-D3BJ/def2-TZVPP. $O_h$ (neutral carboxyls) and $D_{3d}$ (cations) symmetry; force constants were calculated with Gaussian at BP86/def2-TZVPP, calc. CO(g) as reference: 2123 cm$^{-1}$ (35.70 × 10$^3$ N m$^{-1}$)

<table>
<thead>
<tr>
<th>IR r(CO)/cm$^{-1}$ A$<em>{2u}$/E$</em>{u}$</th>
<th>$[Cr(CO)_6]^{1+}$</th>
<th>$[Mo(CO)_6]^{1+}$</th>
<th>$[W(CO)_6]^{1+}$</th>
<th>$Cr(CO)_6$</th>
<th>Mo(CO)$_6$</th>
<th>W(CO)$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$<em>{2u}$/E$</em>{u}$</td>
<td>2096</td>
<td>2089</td>
<td>2075</td>
<td>2110</td>
<td>2115</td>
<td>2115</td>
</tr>
<tr>
<td>DFT r(CO)/cm$^{-1}$ (10$^2$ N m$^{-1}$) A$<em>{2u}$/E$</em>{u}$</td>
<td>2081(33.78)</td>
<td>2072(33.78)</td>
<td>2062(33.46)</td>
<td>2104(34.50)</td>
<td>2105(34.51)</td>
<td>2104(34.41)</td>
</tr>
<tr>
<td>XRD d(M-C)/pm</td>
<td>198.2(2)</td>
<td>210.5(7)</td>
<td>210.5(9)</td>
<td>191.5(1)$^b$</td>
<td>205.9(4)$^b$</td>
<td>204.9(5)$^b$</td>
</tr>
<tr>
<td>XRD d(C-O)/pm</td>
<td>112.2(2)</td>
<td>112.0(8)</td>
<td>110.8(11)</td>
<td>114.2(1)$^b$</td>
<td>113.4(6)$^b$</td>
<td>113.6(9)$^b$</td>
</tr>
<tr>
<td>DFT d(M-C)/pm</td>
<td>197.5</td>
<td>209.9</td>
<td>210.4</td>
<td>190.2</td>
<td>205.5</td>
<td>206.7</td>
</tr>
<tr>
<td>DFT d(C-O)/pm</td>
<td>113.9</td>
<td>113.9</td>
<td>114.1</td>
<td>115.2</td>
<td>115.2</td>
<td>115.3</td>
</tr>
<tr>
<td>FIA/kJ mol$^{-1}$</td>
<td>711</td>
<td>715</td>
<td>741</td>
<td>36</td>
<td>71</td>
<td>37</td>
</tr>
</tbody>
</table>

$^a$ IR: overlap of A$_{2u}$ and E$_{u}$ CO vibration. $^b$ Fluoride ion affinities FIA$^b$ referenced to [Si(CH$_3$)$_3$]$^+$ = 958 kJ mol$^{-1}$. $^c$

The broad $E_g$ Raman-active vibration at around 2125 cm$^{-1}$ indicates the same structural properties for the heavier homologue Mo as already shown for the [Cr(CO)$_6$]$^{1+}$ or V(CO)$_6$$^2$ cases. At room temperature, a very low-lying $D_{3d}$ symmetric transition state ($M = Cr, Mo$) or intermediate ($M = W$) probably allows for equilibration of the two different $D_{3d}$ symmetric ground states (see Scheme 4 and S.I. Section 4$^a$ for an in-depth discussion) – even on the fast time scale of vibrational spectroscopy.

This does not affect the all-symmetric $A_{3g}$ CO stretch. A very broad band, spanning over 100 cm$^{-1}$, is the result. $[W(CO)_6]^{1+}$ shows two very broad bands which cover over 300 cm$^{-1}$ in its Raman spectrum, reaching as far down as 1800 cm$^{-1}$, which is in the range of bridging carboxyl ligands. However, all spectra were measured from crystalline complexes $[M(CO)_6]^{1+}$[F- {Al(OR)₃}₂], so an intermolecular exchange is impossible – whereas in solution a dimerization-equilibrium of $[W(CO)_6]^{1+}$ and $[W_2(CO)_{12}]^{2+}$ with bridging μ-CO entities could be imaginable, but appears unlikely based on orienting DFT calculations.

The calculated force constants imply an increase in the M-C bond strength as well as a decrease in the C-O bond strengths from Cr to W (Table 2). The dicationic group 7 triad $[M'-(CO)_6]^{2+}$

| Table 3 | Analysis of the characteristic vibrations and their force constants (in parenthesis) as well as NMR and XRD data of $[M(CO)_6](NO)^{1+}$ (M: Cr, Mo, W) as [Al(OR)₃]$^-$ salts. DFT: BP86-D3BJ/def2-TZVPP. $C_{4v}$ symmetry

| IR r(CO)/cm$^{-1}$ E | 2108 | 2099 | 2090 |
| DFT r(CO)/cm$^{-1}$ (10$^2$ N m$^{-1}$) E | 2085(34.16) | 2078(33.98) | 2070(33.71) |
| IR r(NO)/cm$^{-1}$ A$_1$ | 1841 | 1820 | 1818 |
| DFT r(NO)/cm$^{-1}$ (10$^2$ N m$^{-1}$) A$_1$ | 1899(31.22) | 1877(30.42) | 1868(30.09) |
| DFT r(M-N)/cm$^{-1}$ (10$^2$ N m$^{-1}$) A$_1$ | 667(5.55) | 570(3.48) | 537(2.73) |
| NMR (14N) δ/ppm | 17 | 3 | 15 |
| DFT (14N) δ/ppm | 35 | 43 | 30 |
| XRD d(M-C)/pm | 195.6(4) | 208.4(3) | 207.0(6) |
| XRD d(C-O)/pm | 112.6(5) | 112.5(3) | 113.0(8) |
| DFT d(M-C)/pm | 193.0 | 208.3 | 207.5 |
| DFT d(C-O)/pm | 113.9 | 114.1 | 114.2 |

$^a$ Only the most intense CO vibration [E] is shown, force constants (in brackets) were calculated with Gaussian. $^b$ In dFB solution, 298 K, CH$_3$NO$_2$ as reference. $^c$ Average of all M–C/N and C/N–O bonds due to the indistinguishable NO position in the experimental data.
\[ 8 \text{M(CO)}_6 + [\text{Agl}_2] \rightarrow 7 \text{M(CO)}_6 + [\text{NO}] + \text{FSi(CH}_3)_3 \]

an acyl \[ [\text{Si(CH}_3)_3] \] (gas-phase FIA salts (left) and heteroleptic carbonyl/nitrosyl cation \[ [\text{Al(OH)}_3] \] – salts (right).

Fig. 8 Comparison of IR (CO and NO region respectively) and \(^{14}\text{N} \) NMR (298 K, oDFB, ref. \( \text{CH}_2\text{Cl}_2 \)/EPR (4 K, oDFB/TFB solution) spectra of the group 6 triad as homoleptic carbonyl cation \[ [\text{F}-(\text{Al}^{1}\text{OR})_3] \] – cations, although we tend to interpret this with caution: more recent studies show no direct relation between NMR chemical shifts and carbon charges for selected transition metal alkylidene complexes – further analysis is needed here.

\(|\text{M} = \text{Fe, Ru, Os}|\) features the same trend in their CO force constants.\(^{33}\) For the all-symmetric \( \text{A}_{1g} \) stretching vibration, the force constants are in contrast to the observed Raman values for the group 6 triad, be it the neutral or cationic carbonyls. This might indicate a trend in the ability for \( \pi \)-back donation that does not reflect in the CO vibration. Yet, more data points are required to allow for a proper interpretation of these observations.

For the heteroleptic nitrosyl complexes, the two different coupled \( \text{M} - \text{N}/\text{M} - \text{C} \) \( \text{A}_1 \) vibrations do not follow a clear trend (Table 3). The CO/NO vibrations, however, decrease just as the shifts in \(^{13}\text{C} \) NMR (202/187; 193/180; 186/180 ppm) and \(^{14}\text{N} \) NMR (17; 3; –15 ppm) do (Fig. 8, Table 3 and S1†). The same trend in \(^{13}\text{C} \) NMR shifts is seen for the \( \text{M(CO)}_6 \) ‘parent’ compounds (212; 204; 192 ppm).\(^{46}\) According to a previous DFT study on homoleptic hexacarbonyls,\(^{46}\) within a triad, the chemical shift is decreasing as \( \sigma \)-donation becomes more important for the 5d homologues. This might also be the case for the \( \text{M(CO)}_6\text{[NO]}_\text{c}^+ \) cations.

\( ^a \) The \( \text{F}^- \) is weakly bound to the metal (\( \text{Cr} - \text{F} \) distance: 260 pm) – in the actual minimum structure \( \Delta = –30 \text{ kJ mol}^{-1} \), the \( \text{F}^- \) is bound to the CO as an acyl fluoride.\(^{34}\) COSMO solution thermodynamics in \( \text{CH}_2\text{Cl}_2 \) \( \Delta = 8.93 \) and oDFB \( \Delta = 13.8 \) with the BP86 functional.\(^3 \) FIA referenced to \( [\text{Si(CH}_3)_3] - \) (gas-phase FIA = 958 kJ mol\(^{-1} \), solution FIA = 404 (\( \text{CH}_2\text{Cl}_2 \)/370 (oDFB) \text{ kJ mol}^{-1} \).

Table 4 Reaction enthalpies of selected model reactions in gas-phase and solution. All calculations were carried out using dispersion correction D3BJ and the def2-TZVPP basis set.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \Delta_H^\circ \text{(kJ mol}^{-1} )</th>
<th>( \Delta_G^\circ \text{(kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>( \text{M(CO)}_6 + [\text{NO}] \rightarrow [\text{M(CO)}_6] + \text{NO} )</td>
<td>Cr: –71 Mo: –82 W: –84</td>
</tr>
<tr>
<td>7</td>
<td>( \text{M(CO)}_6 + [\text{NO}] \rightarrow [\text{M(CO)}_6(\text{NO})] + \text{CO} )</td>
<td>Cr: –240 Mo: –252 W: –254</td>
</tr>
<tr>
<td>8</td>
<td>( \text{M(CO)}_6 + [\text{Agl}_2] \rightarrow [\text{M(CO)}_6] + \text{AgI} )</td>
<td>Cr: 58 Mo: 8 W: –8</td>
</tr>
</tbody>
</table>

Table 5 NBO and AIM charge analyses of the \( \text{M(CO)}_6\text{[NO]}_\text{c}^+ \) triad (\( \text{at}\)BP86-D3BJ/def2-TZVPP, \( D_{3d} \) symmetry)

<table>
<thead>
<tr>
<th>Charge (NBO)</th>
<th>Charge (AIM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [\text{Cr(CO)}_6] )</td>
<td>Cr: –0.95</td>
</tr>
<tr>
<td></td>
<td>O: +0.67</td>
</tr>
<tr>
<td></td>
<td>Mo: –0.35</td>
</tr>
<tr>
<td>( [\text{Mo(CO)}_6] )</td>
<td>C: +0.60</td>
</tr>
<tr>
<td></td>
<td>O: –0.34</td>
</tr>
<tr>
<td>( [\text{W(CO)}_6] )</td>
<td>W: –0.34</td>
</tr>
<tr>
<td></td>
<td>C: +0.56</td>
</tr>
<tr>
<td></td>
<td>O: –0.34</td>
</tr>
</tbody>
</table>
Thermodynamics. To evaluate our synthetic observations, we carried out DFT calculations for the gas phase thermodynamics of some model reactions (Table 4). Reaction (6) and (7) show that the ternary nitrosyl/carbonyl complexes are energetically highly favored over the homoleptic radical cations but without significant difference in between the metal triad. This supports our claim that the observed immediate reaction of Mo(CO)\textsubscript{6} and W(CO)\textsubscript{6} with N\textsubscript{2}O[WCA] is solely due to the different kinetics.\textsuperscript{**}

In reaction (8), the formal transfer of an iodine cation (I\textsuperscript{+}) in a possible explanation for the observed carbonyl/iodide cations was examined: the reaction of the heavier congeners is about 50–60 kJ mol\textsuperscript{-1} more exothermic. Gas-phase and solution thermodynamics (calculated with the COSMO\textsuperscript{**} model using respective dielectric constants of the solvents CH\textsubscript{2}Cl\textsubscript{2} (\varepsilon = 8.93) and oDFB (\varepsilon = 13.8)) are here in accordance. For Cr(CO)\textsubscript{6}, the equilibrium is far to the left so that the effective concentration for AgI would be much less than its solubility constant. In contrast, for Mo(CO)\textsubscript{6} and W(CO)\textsubscript{6}, the equilibrium constants ranges around 1, so if any [AgI\textsubscript{2}]+ is present, molecular AgI is initially formed, which then precipitates and further promotes the reaction. This means experimentally that the availability of [AgI\textsubscript{2}]+ needs to be sufficiently suppressed in order to prevent the availability of the formal “I\textsuperscript{+}” species. Keeping the [AgI\textsubscript{2}] [WCA]\textsubscript{2} complex intact underlines the importance of non-coordinating solvents.

Interestingly, the difference in the actual iodide affinity of for the homoleptic hexacarbonyl cations is nonexistent (BP86) or only about 30 kJ mol\textsuperscript{-1} (B3-LYP). The gas-phase reaction of [M(CO)\textsubscript{6}]\textsuperscript{+} with AgI to Ag\textsuperscript{+} and M(CO)\textsubscript{6} is equally disfavored (ca. 480 kJ mol\textsuperscript{-1}) for all three metals [these and additional reaction enthalpies are deposited in the S.I]. This both indicates that the reaction to the iodide containing side-products probably happens before and (not after) [M(CO)\textsubscript{6}]\textsuperscript{+} is formed.

The fluoride ion affinities (FIA) of the [M(CO)\textsubscript{6}]\textsuperscript{+} species were calculated in reaction (9). If referenced to [Si(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{+} (gas-phase FIA = 958 kJ mol\textsuperscript{-1}),\textsuperscript{5} the values increase from 711 for [Cr(CO)\textsubscript{6}]\textsuperscript{+}, over 715 for [Mo(CO)\textsubscript{6}]\textsuperscript{+} to 741 kJ mol\textsuperscript{-1} for [W(CO)\textsubscript{6}]\textsuperscript{+}. To put this into a general perspective, these species are 120 to 150 kJ mol\textsuperscript{-1} more Lewis acidic than gaseous SbF\textsubscript{5} and are in the range of phosphenium cations.\textsuperscript{44} In solution, the FIA values with respect to [Si(CH\textsubscript{3})\textsubscript{3}]\textsuperscript{+} are generally lower, yet also in solution the expected trend of an increasing Lewis acidity from Cr to W is visible.

It shall be noted here that the calculated seven-coordinate Cr(CO)\textsubscript{6}F complex features an imaginary vibration, if the fluoride ion is bound to Cr. In the actual minimum structure, the fluoride is bound to a CO ligand as an acyl-fluoride. This underlines the incapability of Cr to adopt coordination numbers >6 and shows that the CO ligand is the actual Lewis-acidic center, not the metal – similarly seen in the Hieber base reaction.\textsuperscript{45} For consistency reasons, the Cr–F bound structure was used in the calculations to compare only the ‘metal-centered’ Lewis acidity.

In regard to the Lewis acidity of our complexes, we carried out a natural bond orbital (NBO) and atoms in molecules (AIM) charge analysis (Table 5). Although the absolute values of both methods differ greatly, the charge on the metal centers increases from Cr to W in both cases – in agreement with experiment and theory. Furthermore, for [Cr(CO)\textsubscript{6}]\textsuperscript{+} the charge on the carbon atom of the CO group is the highest of the triad, with only a small charge difference between Cr and CO in AIM. For [W(CO)\textsubscript{6}]\textsuperscript{+}, the high reactivity and Lewis acidity also reveals in NBO and AIM charges. It is not only the highest amongst the [M(CO)\textsubscript{6}]\textsuperscript{+} triad, but also the AIM charge is very high for the W atom – a truly sharp and reactive metal center. We note that the absolute values of the partial charges differ enormously between AIM and NBO. This reiterates our notion that partial charges are no physical observables and their magnitude has to be used with caution.\textsuperscript{46}

In a final analysis, we compared the experimental CO stretch vibrations of all homoleptic hexacarbonyl complexes known to date (Fig. 9), ranging from 1748 cm\textsuperscript{-1} for [Ti(CO)\textsubscript{6}]\textsuperscript{2–} to 2254 cm\textsuperscript{-1} for [Ir(CO)\textsubscript{6}]\textsuperscript{3–}. The electron deficient 17 VE species V(CO)\textsubscript{6} and the [M(CO)\textsubscript{6}]\textsuperscript{+} triad all showcase (slightly) higher CO vibrational frequencies than the general trend for the 18 VE (truly octahedral) complexes.

Conclusion

By oxidation of the neutral group VI hexacarbonyl precursors M(CO)\textsubscript{6} (M = Cr, Mo, W) with NO[Al(OR\textsubscript{3})\textsubscript{3}], the CO/NO
exchange gives the novel heteroleptic carbonyl nitrosyl cations \([\text{MO}(\text{CO})_5(\text{NO})]^-\) as \([\text{Al}(\text{ORF})_4]^-\) salts. They can be accessed selectively and (near) quantitatively and were fully characterized by single-crystal and powder XRD, as well as NMR and vibrational spectroscopy. The synergistic oxidant system Ag\([\text{F}-\text{[Al(ORF)]}_3]\)/ 0.5 I\(_2\) leads to the formation of the homoleptic radical cations \([\text{MO}(\text{CO})_5]^{+}\) as \([\text{F}-\text{[Al(ORF)]}_3]^{2+}\) salts. However, for Mo/W and due to the accessibility of coordination number 7, the formation of side-products such as heteroleptic carbonyl/iodides proved difficult to suppress. Especially for the more reactive \([\text{W}(\text{CO})_6]^{+}\), partial abstraction of an alkoxide moiety from the anion leads to \([\text{W}(\text{CO})_6(\text{ORF})][\text{F}-\text{[Al(ORF)]}_3]^{2+}\) which can only be separated by careful manual sorting of both crystalline species. Although unprovable, the synthesis in TFB described here is the best compromise between feasibility and yield to date.

The study of an isostructural and isoelectronic triad of complexes allows for new insights on the bonding situation for homologous carbonyl complexes, which are in agreement with the \([\text{Re}]/\text{Ru}/\text{Os}(\text{CO})_6]^{\pm}\) sequence. The paramagnetic nature of \([\text{MO}(\text{CO})_5]^{+}\) leads to \(D_{4h}\) symmetric ground state (instead of \(O_h\) for the diamagnetic ‘true’ octahedra), which readily fluctuate to give broad Raman vibrations and a pseudo-octahedral crystal structure. EPR studies support these findings and prove the identity of \(d^7\) metal-centered radical cations described in this work.

Overall, our results show the capabilities as well as the limitations of the \(\text{Ag}[\text{WCA}]/0.5\ I_2\) oxidant system for the formation of reactive cations. Innocence and non-innocence is an inherent problem (or feature!) of all strong oxidants that are formation of reactive cations. Innocence and non-innocence is an inherent problem (or feature!) of all strong oxidants that are

**Notes and references**

§ Those type of complexes are therefore also called ‘\(\sigma\)-carbonyls’ or ‘\(\sigma\)-only-bonded’.
¶ Exemplarily, both seven-coordinate complexes \(\text{W}(\text{CO})_6(\text{NO})\) and \([\text{W}(\text{CO})_6(\text{NO})]^+\) are not stable in our gas phase DFT (BP86def2-TZVPP/D3BJ) calculations and loose a NO/CO ligand respectively without an energy barrier. || CCDC search (ConQuest 2.0.4), as of 12/2019.
** E.g. the scale of a typical reaction (~250–300 mg silver salt) requires an exact stoichiometric amount in the range of 6 mg of Cl\(_2\).
†† The combined system potentials \(E_{1/2}^0\) of the 2 Ag+/Hal\(_2\) systems are +1.49 V (I\(_2\)), +1.82 V (Br\(_2\)) and +1.93 V (Cl\(_2\)) in aqueous solution.
¶¶ Only \(\text{Ag}[\text{WCA}]/I_2\) is somewhat soluble in \(\text{CeF}_4\) and moderately soluble in \(\text{CeF}_6\). The neutral carbonyls as well as all products of the reaction are insoluble in these media and the reaction is effectively carried out as a suspension.
§§ Typically, \([\text{F}-\text{[Al(ORF)]}_3]^{2+}\) is obtained, when \([\text{Al}(\text{ORF})_4]^-\) is decomposed in the presence of extreme electrophiles, which either abstract a fluoride (e.g. small silylum ions like \([\text{Me}_3\text{Si}]^+\) or a perfluorinated alkoxide group (e.g. \([\text{PCl}_3]^-\)).
¶¶¶ \([\text{F}-\text{[Al(ORF)]}_3]^{2+}\) can be crystallized “naked” (without solvent molecules) from TFB solutions. By contrast, a salt \(\text{Ag}[\text{DFB}]^+/\text{[F}-\text{[Al(ORF)]}_3]^{2+}\) including three coordinated DFB molecules crystallizes from DFB solution.
|| It shall be noted here that the calculations in literature are done with the Cotton–Kraihanzel method,\(^{24}\) which is based on the experimental values of the CO stretch.

**** The different kinetics also reflect in the surprisingly high stability of \([\text{Cr}(\text{CO})_5]^-\); unlike the heavier homologues, it only very slowly decomposes on air or in NO atmosphere.


