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Ligand properties of Cp*Ga: new examples of Mo–Ga and W–Ga complexes

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Abstract

The compounds [*fac*-(Cp*Ga)₃M(CO)₃] (**1a**, M = Mo; **1b**, M = W) were synthesized by reaction of [*fac*-(RCN)₃M(CO)₃] (R = Me, Et) with Cp*Ga. The treatment of **1a** with one equivalent of [*fac*-(MeCN)₃Mo(CO)₃] gives the dimeric cluster compound [Mo₂(CO)₆(μ²-(GaCp*))₃] (**2**). Addition of Cp*Ga to the Lewis-acidic unsaturated metal centres of [CpM(CO)₂]₂ (M = Mo, W) yields the dimeric complexes [(OC)₂(Cp)M(μ²-(η¹-GaCp*))]₂ (**3a**: M = Mo, **3b**: M = W). The new compounds **1–3** were characterized fully including single crystal X-ray diffraction studies.

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Keywords: Gallium; Molybdenum; Tungsten; Group 13 transition metal bonds; X-ray single crystal structure analysis

1. Introduction

The discovery of the first transition metal–carbene complex [(OC)₅W=C(OMe)(Ph)] by Fischer and Maasböl in 1964 [1] raised the general interest in transition metal main group element multiple bonding and in particular initiated the quest for related examples of the higher homologues of carbon and the adjacent elements of the periodic table. Today tailored ruthenium carbene complexes serve as highly sophisticated, innovative tools for olefin metathesis in organic synthesis for unusual and most selective ring opening and closing reactions [2]. Ever since Fischer's discovery, the heuristic concept of multiple bonding between heavier elements has never been exhausted and still attracts unbroken fascination. Among the innumerable wealth of examples the phospho- and sila-alkenes such as [(Mes*)P=P(Mes*)] by Yoshifuji et al. [3] and [(Mes)₂Si=Si(Mes)₂] by West et al. (Mes*: 1,3,5-tritertbutylphenyl) [4] certainly repre-

sent landmarks in main group chemistry. Namely Huttner and Herrmann established the chemistry of cumulene-like transition metal-main group metal complexes featuring so-called 'naked' main group elements surrounded solely by transition metal fragments, such as [(OC)₂(Cp)Mn=Pb=Mn(Cp)(CO)₂] [5]. More recently, the coordination chemistry of heteroatom-stabilized Arduengo carbene-transition metal complexes emerged and immediately the heavier analogues with Group 14 and 15 elements (Si, Sn, P, As) have been in the focus of interest, such as [Ni(silylene)₃] by West and coworkers [6] or the [RP=W(CO)₂(Cp)] complex synthesized by Gudat et al. [7].

Much early work on the coordination chemistry of transition metals with the Group 13 elements dates back to the days of Fischer's pioneering carbene and carbyne chemistry and was certainly stimulated by this. However, being much constrained to the main group elements in the oxidation state +3 many compounds reveal more or less trivial structures without unusual bonding situations. In the early 1970s, Hsieh and Hays reported on insertions of Indium(I) halides to metal–metal and metal–halogen bonds [8]. An outstanding development in the chemistry of transition metal bor-

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ylenes $L_xM=B-R$ has been set up by Braunschweig et al. [9].

The variety of different reaction types leading to complexes containing a d-block metal and an earth metal is immense; suitable compounds may serve as precursors for acquiring intermetallic phases and alloys by MOCVD or as precursors for mixed-metal-nanoparticles [10].

Only quite recently Schnöckel and Uhl opened the door to novel low valent and thus low coordinated group 13 metal species of the type E^1R ($E = Al, Ga, In$; $R = Cp^*, C(SiMe_3)_3$) as starting compounds for further syntheses. As being formally isolobal to carbon monoxide and as well to the carbyne cation $[H-C:]^+$, the chemical behaviour of the E^1R species exhibits a certain amount of a carbenoid character [11]. For example Schnöckel et al. have shown that aluminium(I) halides and arduengo-like aluminium(I) heterocycles add to carbynes giving cyclopropene derivatives [12]. Consequently the ligand properties of the E^1R compounds were studied emphasizing the coordination to metal carbonyl fragments. In contrast to CO, the E^1R ligands behave as very strong σ -donors and the π -acceptor capability depends very much on the choice of E and R [13]. Numerous examples reveal the E^1R ligands in a bridging position between transition metal centres [14]. A common synthetic route to these E^1R bridged complexes is the substitution of ligands such as CO or olefins. Hence, the complexes $[Mn_2(CO)_8\{\mu^2-(In-C(SiMe_3)_3)\}_2]$ [15], $[Co_2(CO)_6\{\mu^2-AlCp^*\}_2]$ [16] or $[Ni_4(\mu^2-GaCp^*)_4(CO)_6]$ [17] were obtained by reaction of the parent carbonyl cluster compounds with E^1R . Related complexes exhibiting E^1R in a terminal position are still not very widespread. $[Cp^*Al-Fe(CO)_4]$ was the first example of a terminally coordinated Cp^*Al ligand and confirmed the isolobal analogy between CO and E^1R [18]. Other examples include $[Cp^*Al-Cr(CO)_5]$ [19] or $[Cp^*Ga-Fe(CO)_4]$ [17]. Recently, the complex $[Cp^*Ga-W(CO)_5]$ has been synthesized by Leiner and Scheer [20]. Obviously, compounds with more than one terminal E^1R unit are also in the focus of research, such as $[cis-(Cp^*Ga)_2Mo(CO)_4]$ [21]. In addition, a series of homoleptic complexes of the type $M(ER)_4$ has been derived for the nickel group elements (Ni, Pd, Pt) with $E = Ga$ and In and $R = Cp^*$ and $C(SiMe_3)_3$, nicely demonstrating the relation to $Ni(CO)_4$ as well to $M(PR_3)_4$, i.e. Uhl's $[M\{E(C(SiMe_3)_3)\}_4]$ ($M = Ni, E = Ga$ [22a]; $M = Pt, E = In$ [22b]), $[Ni(GaCp^*)_4]$ by Jutzi [21] and our $[M(GaCp^*)_4]$ complexes ($M = Pd, Pt$) [23]. The capability to form multinuclear homoleptic cluster compounds which have no direct carbonyl or phosphine analogue has been shown for $[Pt_2(GaCp^*)_5]$ [24] and $[Pd_3(InCp^*)_8]$ [25] with tetra-coordinated metal centres.

Contrasting this, in mononuclear heteroleptic carbonyl containing complexes of the type $M(CO)_a(E^1R)_b$ the strong σ -donor ligand E^1Cp^* is strengthening the M–

CO bonds and so inhibiting further substitution of CO. In addition, the steric bulk of the Cp^* residue has to be taken into account. As a consequence of this situation Jutzi stated that ‘...From molecular models it can be concluded that it is difficult to prepare compounds with three terminal Cp^*Ga ligands at an octahedrally coordinated metal centre.’ [21]. We thus got interested to further investigate the ligand properties of E^1R and looked in some detail into the chemistry of Cp^*Ga with the substitution labile complexes $[fac-(RCN)_3M(CO)_3]$ ($R = Me, Et$) and the coordinatively unsaturated, multiple bonded dimers $[Cp(CO)_2M]_2$ ($M = Mo, W$).

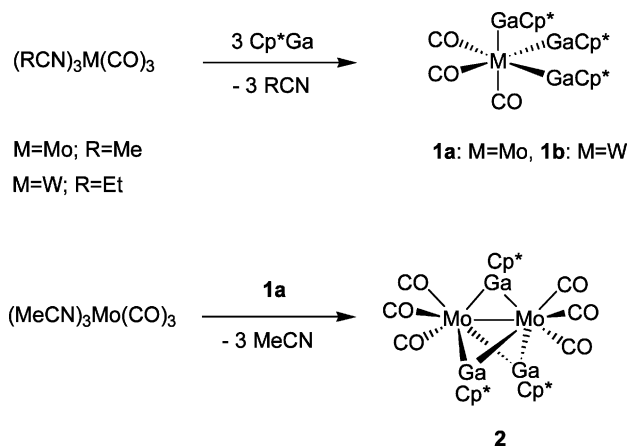
2. Results and discussion

The substitution of labile ligands (e.g. nitriles, olefins) in transition metal carbonyls by strong σ -donors like phosphines is a basic reaction in the organometallic chemistry. Virtually all Cp^*Ga containing complexes result from ligand substitution reactions, i.e. the complexes $[Cp^*Ga-Cr(CO)_5]$ [17] and $[(Cp^*Ga)_2Mo(CO)_4]$ [21] were obtained by substitution of cyclooctene and norbornadiene, respectively. In contrast, the addition of Cp^*Ga to coordinatively unsaturated centres is only known for the in situ formed $[(dcpe)_2Pt]$ complex leading to $[(dcpe)_2Pt(GaCp^*)_2]$ ($dcpe = bis(dicyclohexylphosphino)ethane$) [26]. Metal–metal multiple bonded systems typically represent a coordinatively unsaturated situation. It is well known that a variety of soft nucleophiles (e.g. phosphines, phosphites, acetylenes or dialkyl disulfides) rapidly add to the metal–metal triple bonds at room temperature, giving products with both terminal and bridging ligands [27]. We selected the compounds of the type $[CpM(CO)_2]_2$ ($M = Mo, W$) as prototypical examples to probe that reactivity.

2.1. Syntheses and properties of 1–3

The treatment of green $[fac-(MeCN)_3Mo(CO)_3]$ with three equivalents of Cp^*Ga in refluxing toluene (3 h) led to the substitution of all three MeCN ligands by Cp^*Ga forming the complex $[fac-(Cp^*Ga)_3Mo(CO)_3]$ (**1a**) as shown in Scheme 1. The reaction was quantitative as judged by IR-spectroscopy. After slowly cooling the solution to room temperature, a first crop of yellow crystals of **1a** was isolated in 48% yield. The new compound dissolves moderately in various non-polar organic solvents such as *n*-hexane or toluene; it is not soluble in rather polar organic solvents like diethylether and THF. Complex **1a** is not stable to the ambient moist air and decomposes at 150 °C in the solid state.

The 1H -NMR of **1a** in C_6D_6 displays only one singlet for the Cp^* methyl protons at 1.90 ppm, the ^{13}C -NMR gives rise to two resonances at 9.7 and 114.2 ppm indicating the methyl groups of the Cp^* ligand and the

Scheme 1. Syntheses of compounds **1a**, **1b** and **2**.

ring carbon atoms, respectively. In addition, one resonance assignable to CO is observed (δ 221.4). The IR spectrum of **1a** reveals two sharp absorptions at 1927 and 1846 cm^{-1} in the wavenumber region typical for terminal CO ligands, indicating the facial coordination of the three Cp*Ga ligands (point group C_{3v}). In comparison to the IR absorption of the CO ligands in $Mo(CO)_6$ (2004 cm^{-1}), the absorptions in complex **1a** are significantly shifted to much lower wavenumbers, indicating an increased Mo–C backbonding caused by the strong σ -donor Cp*Ga [13]. Compound **1b** was derived in a quite similar manner and closely reveals related spectroscopic features (Scheme 1). In the 1H -NMR spectrum (in C_6D_6) one singlet at 1.87 ppm for the Cp* protons is visible. As expected, the ^{13}C -NMR spectrum of **1b** reveals three signals of the CO carbon (221.8 ppm), the Cp* ring carbons (114.4 ppm) and the Cp* methyl groups (10.0 ppm). The IR absorptions of the CO ligands of 1921 and 1836 cm^{-1} are quite comparable with compound **1a**.

Compound **1a** serves as building block for further synthesis; the combination of **1a** with one equivalent of $[fac-(MeCN)_3Mo(CO)_3]$ in refluxing toluene leads quantitatively to the formation of the dark red dinuclear complex $[Mo_2(CO)_6\{\mu^2-(GaCp^*)\}_3]$ (**2**) (Scheme 1). The air sensitive Mo_2Ga_3 complex **2** was purified by crystallization from toluene in yields of 70–80%. It is readily soluble in non-polar organic solvents and decomposes at 224 °C in the solid state. The 1H -NMR spectrum in C_6D_6 exhibits only one resonance at 2.12 ppm indicating highly symmetric η^5 -Cp* units. Accordingly, the ^{13}C -NMR spectrum reveals one type of Cp* groups (δ 10.1 and 116.6), thus confirming the equivalence of all three GaCp* ligands. In addition, one resonance assignable to CO is observed (δ 219.7). In the ν_{CO} region of the IR spectrum two absorptions for terminal CO ligands are detected (1921 and 1857 cm^{-1}).

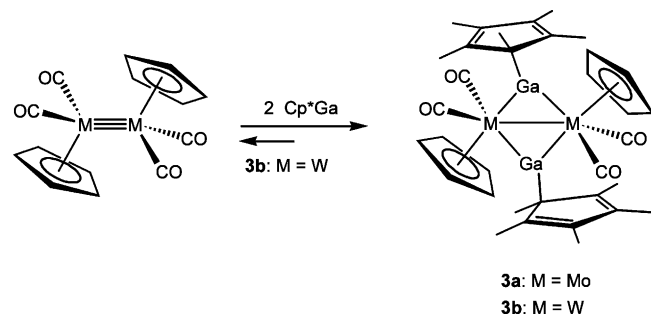
The starting compound $[fac-(MeCN)_3Mo(CO)_3]$ does not react with Cp*In. However, 1H -NMR experiments

gave evidence that the related reaction of $[fac-(MeCN)_3Mo(CO)_3]$ with Cp*Al leads to a mixture of two compounds, presumably consisting of $[fac-(Cp^*Al)_3Mo(CO)_3]$ and $[Mo_2(CO)_6\{\mu^2-(AlCp^*)\}_3]$. This observation is currently subject of further investigations.

Treating a suspension of $[CpMo(CO)_2]_2$ in hexane (M = Mo, W) with two equivalents Cp*Ga at room temperature gave the yellow Mo_2Ga_2 compound **3a**. The orange W_2Ga_2 compound **3b** was obtained by refluxing a mixture of $[CpW(CO)_2]_2$ and 2 eq Cp*Ga in hexane (Scheme 2). In both cases the solvent was removed in vacuo and the crude products were washed with hexane.

Complex **3a** is sparingly soluble in non-polar organic solvents but could be recrystallized by slow cooling of a saturated diglyme solution from 150 °C to ambient temperature (yield: 50%). Complex **3a** is stable at room temperature and decomposes above 190 °C in the solid state. Complex **3b** shows a better solubility in non-polar organic solvents and was purified by crystallization from a mixture of toluene and hexane in yields of 40–50%. The IR spectra of **3a** and **3b** reveal the $\nu(CO)$ absorptions at 1888 and 1832 cm^{-1} for complex **3a** and 1874 and 1826 cm^{-1} for complex **3b**, respectively. These shift almost into the range of bridging CO ligands and give an indication for a rather electron-rich transition metal centre. The 1H -NMR spectrum reveals only one signal and the ^{13}C -NMR shows two resonances for the Cp* moieties pointing to the typical fast sigmatropic rearrangement of the Cp* rings on the NMR timescale.

Furthermore, the NMR spectrum of **3b** revealed an interesting temperature dependence above 40 °C in C_6D_6 solution. At room temperature, **3b** exhibits two resonances at δ 4.58 (s, 10 H, Cp) and 2.12 (s, 30 H, Cp*), respectively. Warming up this solution to 40 °C, new signals at δ 4.77 and δ 1.92 were observed, clearly assignable to the starting materials $[CpW(CO)_2]_2$ and Cp*Ga. With rising temperature the intensities of these signals increase to a ratio free Cp*Ga: coordinated Cp*Ga of 17% at 70 °C. After cooling the sample back to room temperature, the original spectrum of **3b** is obtained. These observations are consistent with an equilibrium between the starting materials and complex

Scheme 2. Syntheses of compounds **3a** and **3b**.

3b. Due to entropy this equilibrium is shifted to the dissociated products with increasing temperature. Interestingly, complex **3a** (Scheme 2) appears to be stable against dissociation of Cp*Ga.

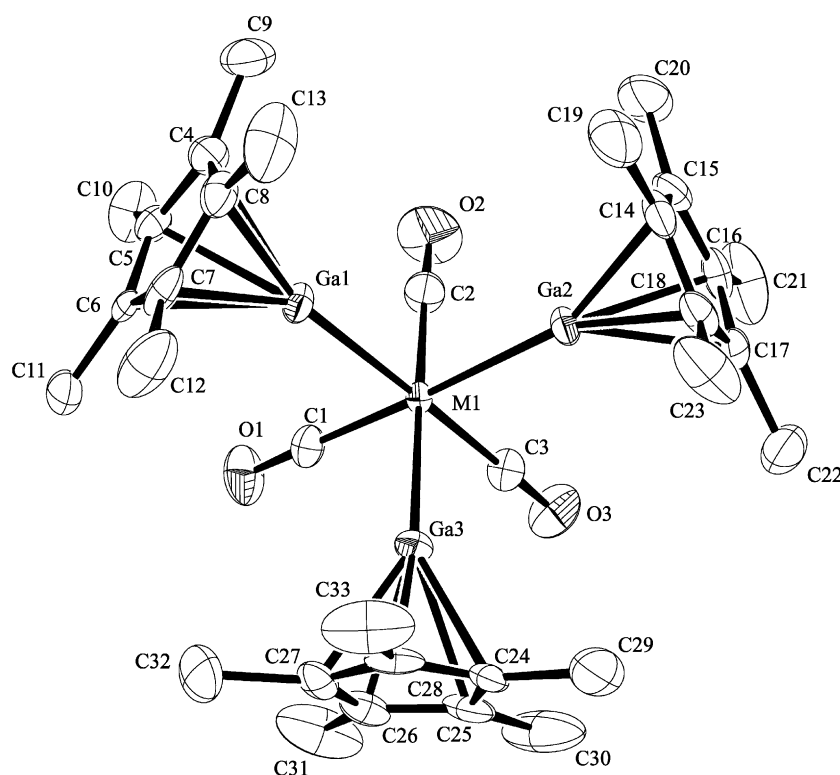
It should be noted here, that the related other low valent Group 13 metal ligands, Cp*Al, Cp*In and CpIn, did not add to the M≡M triple bonds, as checked by in-situ NMR measurements (sealed NMR tubes).

2.2. Structural characterization of complexes 1–3

2.2.1. Molecular structures of 1a and 1b

The molecular structure of **1a** is presented in Fig. 1. Important crystallographic data are summarized in Table 1. Complex **1a** crystallizes in the triclinic space group $P\bar{1}$ and exhibits an octahedrally coordinated molybdenum centre with a facial arrangement of three Cp*Ga and three CO ligands, as expected from the spectroscopic data.

All angles between *cis*-ligands are quite close to 90° and the *trans*-ligand angles are all nearly 180° [Ga(1)–Mo(1)–Ga(2) 91.10(3)°, Ga(1)–Mo(1)–C(2) 89.6(2)° and Ga(3)–Mo(1)–C(3) 178.4(2)°]. The Mo–Ga distances lie around 2.52 Å (2.5228(8) and 2.5188(8) Å, respectively) and are quite similar to the Mo–Ga distances in the closely related complex [*cis*-Mo(Cp*Ga)₂(CO)₄] with Mo–Ga 2.554(1) and 2.537(1) Å [21]. The Cp*_{centroid}–Ga distance (1.947(3) Å) is slightly shortened compared to the free ligand (2.081 Å) (gas phase, monomer) [28]. This is a well established indirect measure for the polarity of the Mo–Ga bond and an indication for the σ-donor capacity of the Cp*Ga fragment in the given complex. In agreement with the results of Jutzi et al. [21] the Cp*_{centroid}–Ga distances in complexes of the type [M(Cp*Ga)_x(CO)_{6-x}] ($x \leq 3$) depend on the metal M and the number x and are generally elongated with increasing x . The shortest distances are observed in [Cr(Cp*Ga)(CO)₅] (1.910(4)



1a: M = Mo, **1b:** M = W

Fig. 1. View of the molecular structures of **1a** and **1b** (ORTEP drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 30% probability). Selected bond lengths (Å) and angles (°) for **1a**: Mo(1)–Ga(1) 2.519(8), Mo(1)–Ga(2) 2.520(9), Mo(1)–Ga(3) 2.523(8), Ga(1)··Ga(2) 3.604, Mo(1)–C(1) 1.958(7), Mo(1)–C(2) 1.970(7), Mo(1)–C(3) 1.951(7), Ga(1)–Cp*(1)_{centroid} 1.948(3), Ga(2)–Cp*(2)_{centroid} 1.941(3), Ga(3)–Cp*(3)_{centroid} 1.947(3), C(1)–O(1) 1.168(8), C(2)–O(2) 1.154(8), C(3)–O(3) 1.168(8), Mo(1)–C(1)–O(1) 179.3(7), Ga(3)–Mo(1)–C(3) 178.4(2), Ga(1)–Mo(1)–C(2) 89.6(2), Ga(1)–Mo(1)–Ga(2) 91.1(3), C(1)–Mo(1)–C(2) 90.3(3), Mo(1)–Ga(1)–Cp*(1)_{centroid} 166.2. Selected bond lengths (Å) and angles (°) for **1b**: W(1)–Ga(1) 2.5198(13), W(1)–Ga(2) 2.5211(11), W(1)–Ga(3) 2.5221(12), Ga(1)··Ga(2) 3.601, W(1)–C(1) 1.946(10), W(1)–C(2) 1.981(10), W(1)–C(3) 1.980(10), Ga(1)–Cp*(1)_{centroid} 1.936(5), Ga(2)–Cp*(2)_{centroid} 1.952(5), Ga(3)–Cp*(3)_{centroid} 1.944(4), C(1)–O(1) 1.170(12), C(2)–O(2) 1.159(11), C(3)–O(3) 1.162(12), W(1)–C(1)–O(1) 178.0(10), Ga(3)–W(1)–C(3) 177.8(3), Ga(1)–W(1)–C(2) 87.5(3), Ga(1)–W(1)–Ga(2) 91.14(4), C(1)–W(1)–C(2) 90.7(4), W(1)–Ga(1)–Cp*(1)_{centroid} 166.3.

Table 1
Crystallographic and data correction parameters for compounds 1–3

	1a	1b	2	3a	3b
Empirical formula	C ₃₃ H ₄₅ O ₃ MoGa ₃	C ₃₃ H ₄₅ O ₃ WGa ₃	C ₃₆ H ₄₅ O ₆ Mo ₂ Ga ₃	C ₃₄ H ₄₀ O ₄ Mo ₂ Ga ₂	C ₃₄ H ₄₀ O ₄ W ₂ Ga ₂
Molecular weight	794.82	882.70	974.79	844.01	1019.81
Temperature (K)	213(2)	213(2)	213(2)	213(2)	213(2)
Wavelength Mo–K _α (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal size (mm ³)	0.44 × 0.30 × 0.28	0.30 × 0.20 × 0.20	0.12 × 0.18 × 0.25	0.32 × 0.25 × 0.20	0.24 × 0.20 × 0.16
Crystal system	Triclinic	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>Pbca</i>
Unit cell dimensions					
<i>a</i> (Å)	8.5243(15)	8.4993(3)	22.227(5)	14.528(3)	14.444(3)
<i>b</i> (Å)	11.569(2)	11.553(2)	12.603(3)	12.080(2)	12.094(3)
<i>c</i> (Å)	18.712(3)	18.713(8)	17.519(4)	18.694(4)	18.669(4)
α (°)	89.21(2)	89.215(7)	90	90	90
β (°)	89.82(2)	89.850(7)	111.735(4)	90	90
γ (°)	79.09(2)	79.041(7)	90	90	90
<i>V</i> (Å ³)	1811.8(5)	1803.8(13)	4558.8(17)	3280.9(11)	3261.2(12)
<i>Z</i>	2	2	4	4	4
<i>D</i> _{calc} (g cm ⁻³)	1.457	1.625	1.420	1.709	2.077
μ (mm ⁻¹)	2573	5.423	2.320	2.407	8.702
<i>F</i> (000)	804	868	1944	1688	1944
θ Range for data collection (°)	1.79–25.00	2.44–25.18	2.06–25.10	2.45–27.50	2.45–27.50
Index ranges	–9 ≤ <i>h</i> ≤ 10, –10 ≤ <i>k</i> ≤ 13, –22 ≤ <i>l</i> ≤ 20	–9 ≤ <i>h</i> ≤ 10, –9 ≤ <i>k</i> ≤ 13, –22 ≤ <i>l</i> ≤ 22	–24 ≤ <i>h</i> ≤ 26, –15 ≤ <i>k</i> ≤ 12, –20 ≤ <i>l</i> ≤ 20	–18 ≤ <i>h</i> ≤ 6, –10 ≤ <i>k</i> ≤ 10, –22 ≤ <i>l</i> ≤ 24	–18 ≤ <i>h</i> ≤ 18, –3 ≤ <i>k</i> ≤ 15, –18 ≤ <i>l</i> ≤ 17
Reflections collected	10230	10112	22905	8672	8742
Reflections unique	6227 [<i>R</i> _{int} = 0.0413]	6273 [<i>R</i> _{int} = 0.0565]	8018 [<i>R</i> _{int} = 0.0478]	2995 [<i>R</i> _{int} = 0.0272]	3225 [<i>R</i> _{int} = 0.0296]
Reflections observed	4702 <i>F</i> _o > 4σ(<i>F</i> _o)	4982 <i>F</i> _o > 4σ(<i>F</i> _o)	5781 <i>F</i> _o > 4σ(<i>F</i> _o)	2386 <i>F</i> _o > 4σ(<i>F</i> _o)	2482 <i>F</i> _o > 4σ(<i>F</i> _o)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6227/0/376	6273/0/361	8018/0/424	2995/0/226	3225/60/225
Absorption correction	Empirical	Empirical	Empirical	Empirical	Empirical
Max. and min. transmission	1.000 and 0.802	1.000 and 0.321	0.560 and 0.665	1.000 and 0.867	1.000 and 0.746
Goodness-of-fit on <i>F</i> ²	1.097	0.984	0.953	1.034	1.120
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0439, <i>wR</i> ₂ = 0.1100	<i>R</i> ₁ = 0.0522, <i>wR</i> ₂ = 0.1240	<i>R</i> ₁ = 0.0384, <i>wR</i> ₂ = 0.0824	<i>R</i> ₁ = 0.0379, <i>wR</i> ₂ = 0.0964	<i>R</i> ₁ = 0.0305, <i>wR</i> ₂ = 0.0602
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0656, <i>wR</i> ₂ = 0.1351	<i>R</i> ₁ = 0.0675, <i>wR</i> ₂ = 0.1332	<i>R</i> ₁ = 0.0609, <i>wR</i> ₂ = 0.0882	<i>R</i> ₁ = 0.0502, <i>wR</i> ₂ = 0.1035	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.0658
Largest difference peak and hole (e Å ⁻³)	0.792 and –0.666	2.381 and –3.420	0.464 and –0.412	2.070 and –0.468	1.078 and –1.175

$$R_1 = \Sigma(|F_o| - |F_c|) / \Sigma|F_o|^{1/2}. \quad wR_2 = [\Sigma_w(F_o^2 - F_c^2)^2 / \Sigma_w(F_o^2)]^{1/2}. \quad \text{GOF} = [\Sigma_w(F_o^2 - F_c^2)^2 / (N_o - N_p)]^{1/2}.$$

Å) and [Fe(Cp*Ga)(CO)₄] (1.863(4) Å) [17]. A comparison of that value for [*cis*-Mo(Cp*Ga)₂(CO)₄] of 1.930(6) Å with the value for [*fac*-Mo(Cp*Ga)₃(CO)₃] (**1a**) of 1.947(3) Å clearly proves the trend to less polarized Mo^{δ-}–Ga^{δ+} bonds in higher substituted complexes as fewer carbonyl ligands act as competing acceptors for electron density at the transition metal. The strong σ-donor ability of Cp*Ga in **1a** also results in shortened Mo–CO bond lengths (1.959 Å average) and slightly elongated C–O bond lengths (1.163 Å

average) compared to [*cis*-(Cp*Ga)₂Mo(CO)₄] (Mo–C_{axial} 2.042(6) Å and Mo–C_{equatorial} 1.975(5) Å and C–O between 1.144(6) and 1.158(5) Å) [21]. The Cp* moieties in **1a** are almost symmetrically coordinated to the gallium centres and a small deviation from linearity is observed for the Cp*_{centroid}–Ga–Mo angles (163° average).

Complex **1b** is isostructural to complex **1a** (Fig. 1). All bond lengths and angles correspond to the lengths and angles in complex **1a** and show just slight deviations.

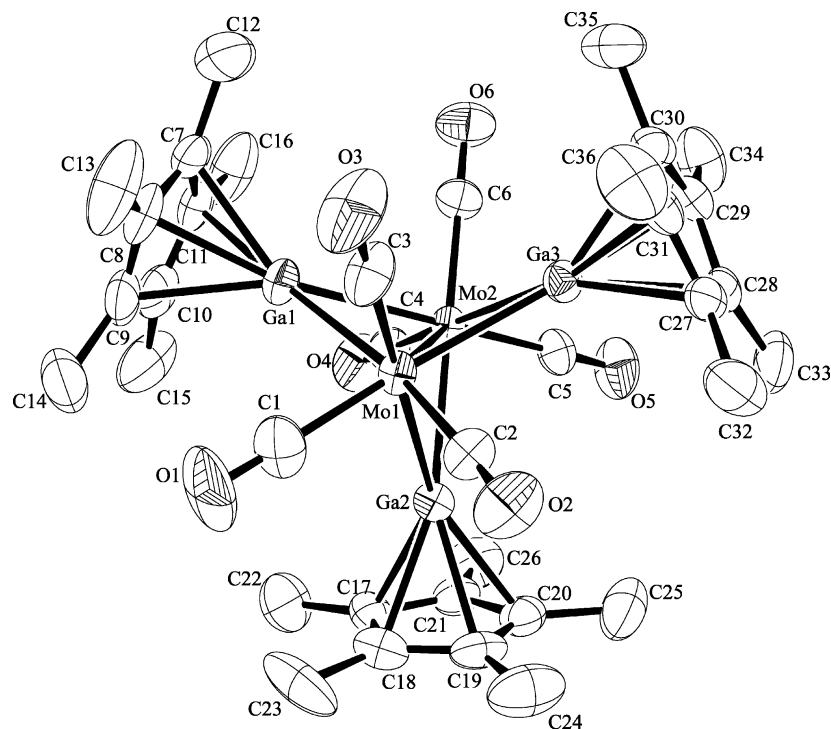


Fig. 2. View of the molecular structure of **2** (ORTEP drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°): Mo(1)–Mo(2) 2.7661(6), Ga(1)···Ga(2) 3.864(3), Mo(1)–Ga(1) 2.6796(8), Mo(1)–Ga(3) 2.6567(8), Mo(2)–Ga(1) 2.6616(8), Mo(1)–C(1) 1.948(5), Mo(1)–C(2) 1.964(5), Mo(1)–C(3) 1.968(5), Mo(2)–C(4) 1.945(5), Mo(2)–C(5) 1.952(5), Mo(2)–C(6) 1.955(5), Ga(1)–Cp*(1)_{centroid} 1.911(4), Ga(1)–Mo(1)–Ga(2) 101.38(2), Ga(1)–Mo(1)–Ga(3) 92.66(2), Ga(1)–Mo(2)–Ga(2) 101.51(2), Ga(1)–Mo(2)–Ga(3) 92.60(2), Mo(1)–Ga(1)–Mo(2) 62.571(16), Mo(1)–Mo(2)–Ga(1) 58.484(18), Mo(1)–C(1)–O(1) 179.8(6), Ga(1)–Mo(1)–C(1) 89.00(16), Ga(1)–Mo(1)–Mo(2)–Ga(2) 115.4(2), Ga(1)–Mo(1)–Mo(2)–Ga(3) 114.9(2), Ga(2)–Mo(1)–Mo(2)–Ga(3) 129.7(2).

2.2.2. Molecular structure of **2**

The molecular structure of compound **2** in the solid state is depicted in Fig. 2. Crystal structure parameters are given in Table 1. Complex **2** crystallizes in the monoclinic space group $P2_1/c$. The structure consists of a central unit of two molybdenum atoms Mo(1) and Mo(2) with a Mo–Mo distance of 2.7661(6) Å. This value is much shorter than in the single bonded complex $[\text{CpMo}(\text{CO})_3]_2$, i.e. 3.235(1) Å [30], but longer than in the triple bonded complex $[\text{CpMo}(\text{CO})_2]_2$, i.e. 2.448(1) Å [31]. For example, the Mo–Mo distance in **2** is comparable to the vinylidene bridged double bonded complexes $[(\text{CpMe})_2(\text{CO})_4\text{Mo}_2(\mu^2\text{-CC}_{12}\text{H}_8)]$, i.e. 2.798(1) Å [32] and $[(\text{Cp}^*)_2(\text{NCO})(\text{CO})_3\text{Mo}_2(\mu^2\text{-NCMe}_2)]$, i.e. 2.745(2) Å [33]. Here, it should be stated that complex **2** is the very first dimeric Mo(0) complex with two MoL_3 units bridged by three ligands L' . The Mo_2 unit of **2** is surrounded by three bridging Cp^*Ga ligands and six terminal carbonyl ligands oriented in an almost eclipsed conformation with a deviation less than 2°. All Mo–C and C–O distances are almost equal with average values of 1.955 Å (Mo–C) and 1.169 Å (C–O), respectively. The core of the molecule can be formally described as a Mo_2Ga_3 ‘cluster’ of trigonal-bipyramidal symmetry with the molybdenum atoms in axial and the gallium atoms in equatorial positions. The torsion

angles Ga–Mo–Mo–Ga differ from the ideal 120° by less than 10°. The similarity of all Mo–Ga distances from 2.6567(7) to 2.6851(7) Å certifies the high symmetry of the μ^2 -coordination of the Cp^*Ga units. The Mo–Ga bond lengths are only slightly elongated by 5% as compared with the terminal Cp^*Ga ligands in **1a** and **1b**. The molecular structure of **2** corresponds to a slightly distorted D_{3h} symmetry for the $(\text{CO})_6\text{Mo}_2\text{Ga}_3$ framework, which is comparable to the Fe_2Ga_3 complex $[(\text{OC})_3\text{Fe}\{\mu^2\text{-}(\eta^5\text{-Cp}^*\text{Ga})_2\mu^2\text{-}(\eta^3\text{-Cp}^*\text{Ga})\}\text{Fe}(\text{CO})_3]$ [17] with two η^5 - and one η^3 -bonded Cp^* ligand also featuring a hexacoordinated transition metal centre. For **2**, all Cp^* moieties are bound to the Ga centres in an almost ideally symmetric η^5 -mode with average values of 1.910 Å for the $\text{Cp}^*_{\text{centroid}}\text{-Ga}$ distances. This distance is shorter than the average $\text{Cp}^*_{\text{centroid}}\text{-Ga}$ distance in complex **1a** (1.947 Å) reflecting slightly increased electron donation of the bridging Ga-units over the terminal ones. The related distances of typical bridging Cp^*Ga moieties range from 2.241 to 2.338 Å, i.e. $[\text{Ni}_4(\mu^2\text{-GaCp}^*)_4(\text{CO})_6]$ (2.322(6) Å), $[(\text{OC})_3\text{Co}(\mu^2\text{-}(\eta^5\text{-GaCp}^*)_2)\text{Co}(\text{CO})_3]$ (2.241(3) and 2.338(4) Å) [17].

The Ga···Ga distances in complex **2** lie in the range of 3.860–4.129 Å, in complex **1** these distances are 3.606 Å in average. These values are a bit shorter but still comparable to the situation in $(\text{Cp}^*\text{Ga})_6$ with Ga···Ga

distances in the range of 4.073(2) to 4.173(3) Å. This hexameric structure was reported to be primarily a result of van der Waals interactions of the organic moieties [14a,28]. In sharp contrast, the Ga–Ga bonding interactions in $[\text{Ga}\{\text{C}(\text{SiMe}_3)_3\}]_4$ are distinctly shorter with values between 2.678(4) and 2.702(3) Å [34]. We thus conclude that there is certainly no indication for a Ga–Ga bond in our complexes **1a**, **1b** and **2**.

At a first glance the short Mo–Mo distance in complex **2** suggests relatively strong bonding interactions between the two molybdenum centres. However, the Mo_2Ga_3 core can be viewed as being composed of three 3 centre-2 electron bonds involving the unoccupied frontier orbitals of the two C_{3v} - $\text{Mo}(\text{CO})_3$ fragments and the three lone pairs of the Cp^*Ga ligands which have predominantly s-character. Complex **2** can simply be described as two face sharing octahedral MoL_3 units, allowing an 18 electron count for both molybdenum centres without any direct Mo–Mo interaction. The short Mo–Mo distance of **2** is basically a consequence of the rather short Mo–Ga bonds and the small Mo–Ga–Mo bridging angle of 60° , both being connected with the high σ -contribution to the lone pair of the Cp^*Ga ligand. In face sharing octahedral structures the two metal centres need to come close even without metal–metal interaction. From the point of view of the HSAB principle the Cp^*Ga ligand can be regarded as a rather soft base with a comparably extended lone electron pair giving rise to a bridging capability which goes beyond CO ligands and typical other soft two electron donors such as phosphines. Hence, we suggest that the analogy of Cp^*Ga ligands with other very soft 2e-donors, such as the hydride ligand may have some conceptual or heuristic value for further syntheses.

2.2.3. Molecular structure of **3a** and **3b**

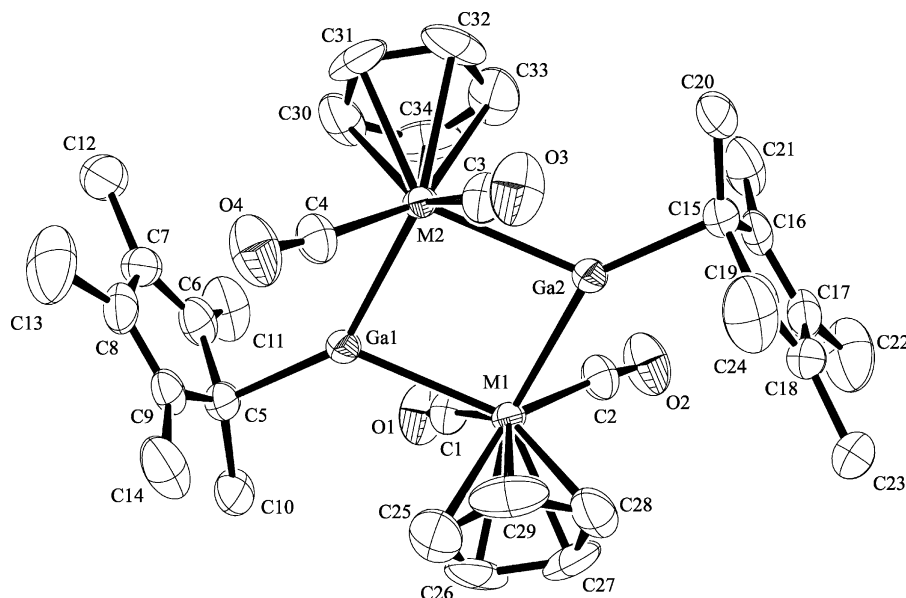
Compounds **3a** and **3b** are isostructural and crystallize in the orthorhombic space group *Pbca* (Schönflies symbol D_{2h}). The molecular structures of **3a** and **3b** (Fig. 3) consist of a central unit of two gallium atoms and two molybdenum or tungsten atoms, respectively. The Ga_2M_2 rings are planar with an inversion centre. Small deviations from 90° of the Ga–Mo–Ga ($93.6(2)^\circ$) (Ga–W–Ga $94.3(2)^\circ$) and Mo–Ga–Mo angles ($86.39(2)^\circ$) (W–Ga–W $85.7(2)^\circ$) as well as slightly different Mo–Ga (W–Ga) distances of 2.5374(7) Å (W–Ga 2.5356(8) Å) and 2.6063(7) Å (W–Ga 2.6081(8) Å) result in a faintly distorted square geometry. The distances between the transition metal centres are remarkably long, being 3.521 Å in **3a** and 3.498 Å in **3b**, respectively. These M–M distances appear too long to postulate a metal–metal bonding interaction. A comparison of the M–M distance in **3a** and **3b** with metal–metal single bonds in the selected complexes $[\text{CpMo}(\text{CO})_3]_2$ (3.235(1) Å) [30], $[\{(\text{CO})_2\text{CpM}\}_2\text{As}_2]$ (M = Mo: 3.038(2) Å, M = W: 3.027(2) Å) [35a],

$[(\text{Cp})_2\text{Mo}_2(\text{CO})_4(\mu^2\text{-I})(\mu^2\text{-H})]$ (3.310(2) Å) [35b] and $[(\text{Cp}^*)(\text{S})\text{W}-\text{W}(\text{CO})_2(\text{Cp}^*)(\mu^2\text{-S})]$ (3.045(2) Å) [35c] demonstrates that the M–M distances in **3a** and **3b** are considerably longer. To our knowledge only few dimeric Mo- and W-complexes with longer metal–metal distances are known. The complex $[\text{HMo}_2(\text{CO})_9(\text{NO})]$ shows a Mo–Mo distance of 3.540(1) Å [35d]. This uniquely long distance was reported to be the result of interatomic repulsions between the mutually eclipsed equatorial ligands. In $[\text{HW}_2(\text{CO})_7(\text{P}(p\text{-C}_6\text{H}_4\text{F})_3)_2(\text{NO})]$ [35e] the W–W distance equals 3.5345(5) Å, hence the authors did not discuss any metal–metal interaction except the 3 centres-2 electrons W–H–W unit. Nevertheless, complexes **3a** and **3b** contain the $[\text{Cp}(\text{CO})_2\text{M}]$ fragment with an odd electron count of 15. Because of the diamagnetic nature of the Cp^*Ga bridged complexes some M–M interaction is certainly present.

The Ga···Ga distances in **3a** and **3b** are 3.750(7) and 3.772(8) Å, respectively, and lie in the range of the Ga···Ga distances in complexes **1–2**. Therefore, we conclude that there is no evidence for a Ga–Ga bond in **3a** and **3b**.

Most interestingly, the Cp^* ligands in **3a** and **3b** are η^1 -bonded to the Ga atoms. Hence, the C–C bond lengths of the C_5 ring alternate, with C=C double bond distances around 1.36 Å and C–C single bond distances around 1.45 Å. The C atom attached to the gallium is sp^3 -hybridized, which results in a non planar Cp^* ring with torsion angles of $31.8(7)^\circ$ in **3a** and $36.2(9)^\circ$ in **3b**, respectively. The Cp rings η^5 -bonded to the molybdenum and tungsten atoms, respectively, show C–C distances of 1.382(10) Å and 1.413(9) Å, respectively. The η^1 -coordination of the Cp^* rings in complex **3a** and **3b** as well as in the formal related new dimeric rhodium complex $[\{\text{CpRh}(\text{C}_2\text{H}_4)(\mu^2\text{-}(\eta^1\text{-GaCp}^*))_2\}]$ [36] are to our knowledge the first examples for transition metal compounds with bridging η^1 - Cp^*Ga ligands.

It is likely that this special bonding behaviour is a consequence of the increased steric demand of the Cp^* ligand. But a η^1 -coordination should also facilitate π -backbonding from the molybdenum to the gallium atoms. However, the stretching frequencies of CO in **3a** and **3b** are shifted towards even lower wavenumbers, indicating a high electron density at the transition metal centre. Looking on this feature, a more ionic interaction between W and Ga, e.g. $\text{W}^{2-}/\text{Ga}^{3+}$ as an extreme formulation may be postulated. The Mo–Ga bond lengths in **3a** are significantly shorter than the expected values for bridging Cp^*Ga ligands with a $\eta^5\text{-Cp}^*$. Thus, complex **2** exhibits a Mo–Ga bond length of 2.666 Å in average, whereas this distance in **3a** equals 2.5374(7) and 2.6063(7) Å, respectively. These values are similar to $[(\eta^5\text{-C}_5\text{H}_4\text{Me})(\text{CO})_3\text{MoGaI}_2\cdot\text{Et}_2\text{O}]$ (2.5882(2) Å) [37] but shorter than in $[(\text{CpMo}(\text{CO})_3\text{Ga}(\text{tBu})_2)]$ (2.7376(5) Å) [38] both with Ga in the oxidation state +3. Complexes **3a** and **3b** exhibit a Ga–C bond length of



3a: M = Mo, 3b = M = W

Fig. 3. View of the molecular structure of **3a** (ORTEP drawing; hydrogen atoms are omitted for clarity; non-hydrogen atoms are shown as thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (°) for **3a**: Mo(1)–Ga(1) 2.5374(7), Mo(1)–Ga(2) 2.6063(7), Mo(1)–Mo(2) 3.521(7), Ga(1)···Ga(2) 3.750(7), Mo(1)–C(1) 1.971(4), Mo(1)–C_{pcentroid} 1.999(4), Ga(1)–C(5) 2.055(4), C(5)–C(10) 1.515(7), C(5)–C(6) 1.462(6), C(6)–C(7) 1.365(7), Mo(1)–Ga(1)–Mo(2) 86.39(2), Ga(1)–Mo(1)–Ga(2) 93.6(2), Mo(1)–C(1)–O(1) 173.5(4), C(1)–Mo(1)–C(2) 74.52(19), Mo(1)–Ga(1)–C(1) 144.63(14), Mo(2)–Ga(1)–C(1) 128.96(14), C(10)–C(5)–C(6)–C(11) 31.8(7). Selected bond lengths (Å) and angles (°) for **3b**: W(1)–Ga(1) 2.5356(8), W(1)–Ga(2) 2.6081(8), W(1)–W(2) 3.498(8), Ga(1)···Ga(2) 3.772(8), W(1)–C(1) 1.972(7), W(1)–C(2) 1.946(6), W(1)–C_{pcentroid} 1.996(4), Ga(1)–C(5) 2.039(6), C(5)–C(10) 1.519(9), C(5)–C(9) 1.484(9), C(9)–C(8) 1.366(9), W(1)–Ga(1)–W(2) 85.7(2), Ga(1)–W(1)–Ga(2) 94.3(2), C(1)–W(1)–C(2) 74.6(3), W(1)–C(1)–O(1) 171.4(6), W(1)–C(2)–O(2) 174.1(5), W(1)–Ga(1)–C(3) 144.74(17), W(2)–Ga(1)–C(3) 129.67(17), C(10)–C(5)–C(6)–C(11) 36.2(9).

2.055(4) and 2.039(6) Å, respectively. Frenking et al. have pointed out that the characterisation of the bonding properties of E¹R ligands towards transition metal centres does not fit well into the simple σ/π -donor/acceptor picture and more subtle effects have to be taken into account including local effects of the actual electron distribution and electrostatic (dipole) interaction [13]. The reason for the η^1 -coordination mode is not clear and probably warrants a deeper theoretical analysis.

3. Conclusion

Five new Mo–Ga and W–Ga complexes were synthesized and were fully characterized. The synthesis of the monomeric complexes [*fac*-(Cp*Ga)₃Mo(CO)₃] (**1a**) and [*fac*-(Cp*Ga)₃W(CO)₃] (**1b**) was quite straightforward by rapid and quantitative substitution of weakly bounded alkylnitrile ligands against Cp*Ga using [*fac*-(MeCN)₃Mo(CO)₃] and [*fac*-(EtCN)₃W(CO)₃] as starting compounds. Complexes

1a and **1b** are the first examples of mononuclear octahedral transition metal complex bearing three facially coordinated terminal E¹R ligands. The structural data show no unusual distortions and give no indication of steric overcrowding. Additionally, it was shown that **1a** can be used as building blocks for the synthesis of dinuclear transition metal complexes. In the reaction of **1a** with an equimolar amount of [*fac*-(MeCN)₃Mo(CO)₃], the dimeric Cp*Ga bridged complex [Mo₂(CO)₆(μ^2 -(GaCp*))₃] (**2**) is formed. This result nicely demonstrates that the bridging capability of the Cp*Ga ligands goes well beyond the isolobal CO ligand. While the other known E¹R bridged complexes of the type [M₂(μ^2 -E¹R)_n(CO)_m] directly correlate to the iso-electronic carbonyl congeners [M₂(CO)_{m+n}] (e.g. M = Fe, Co), the carbonyl analogue of compound **2**, [(CO)₃Mo(μ^2 -CO)₃Mo(CO)₃] does not exist. Finally, the addition of Cp*Ga to the coordinatively unsaturated M≡M triple bond of [CpM(CO)₂]₂ (M = Mo, W) is described, leading to the dinuclear addition products **3a** and **3b**. The Cp*Ga coordination appears to be surprisingly weak as shown by the existence of a temperature

dependent association/dissociation equilibrium, an effect which appears to be probably due to steric crowding.

4. Experimental

All procedures were carried out under purified argon using standard Schlenk and glove box techniques. All solvents were dried by conventional procedures. The compounds Cp*Ga [39], *fac*-(MeCN)₃Mo(CO)₃ [40], *fac*-(EtCN)₃Mo(CO)₃ [41], [CpMo(CO)₂]₂ [42] and [CpW(CO)₂]₂ [43] were prepared according to the literature. TG measurements were performed on a Seiko 6300S11 instrument (temperature range: 25–500 °C, heating rate: 10 °C min⁻¹). ¹H- and ¹³C-NMR spectra were recorded in C₆D₆ on a Bruker Avance DPX 250 spectrometer (¹H, 250.1 MHz, ¹³C, 62.9 MHz). The chemical shifts are reported in δ (ppm) and are referenced to the solvent resonance as internal standard (C₆D₆ at 7.15 ppm). Infrared spectra of the samples (nujol mulls between NaCl plates) were recorded by using a Perkin–Elmer 1720X Fourier transform spectrometer. Elemental analyses were provided by the Service Centre Department of the Ruhr-University of Bochum (CHNSO Vario EL 1998). X-ray single crystal measurements were performed on a Bruker AXS CCD 1000 diffractometer (Mo–K_α radiation). The structures were solved with direct methods (SHELXS-97) and empirical absorption correction, all non-hydrogen atoms were refined using anisotropic thermal parameters with the SHELXL-97 program suite. All refinements were made by full-matrix least-squares on *F*². The contribution of the disordered solvent molecule within the elementary cell of complex **2** to the structure factors was taken into account by back-Fourier transformation using PLATON/SQUEEZE [29].

4.1. Synthesis of [*fac*-(Cp*Ga)₃Mo(CO)₃] (**1a**)

A mixture of *fac*-(MeCN)₃Mo(CO)₃ (200 mg, 0.66 mmol) and Cp*Ga (470 mg, 2.30 mmol) in toluene (5 ml) was refluxed for 1 h, while the green suspension turned to a dark red solution. After cooling the solution slowly to room temperature (r.t.) over a period of 1 day, yellow crystals of **1a** were isolated. Yield: 250 mg (48%). M.p. 150 °C (decomp.). ¹H-NMR (C₆D₆, 300 K): δ 1.90 (s, 15 H, C₅Me₅). ¹³C {¹H}-NMR (C₆D₆, 300 K): δ 221.4 (CO), 114.2 (C₅Me₅), 9.7 (C₅Me₅). IR (Nujol, cm⁻¹): ν = 1927, 1846 (vs, CO). Anal. Calc. for C₃₃H₄₅O₃MoGa₃ (M = 794.82 g mol⁻¹): C, 49.87; H, 5.71. Found: C, 49.38; H, 5.66%.

4.2. Synthesis of [*fac*-(Cp*Ga)₃W(CO)₃] (**1b**)

Cp*Ga (270 mg, 1.32 mmol) was added to a suspension of 165 mg [*fac*-(EtCN)₃W(CO)₃] (0.38 mmol) in toluene (5 ml) and refluxed for 3 h, while the mixture turned to a dark red solution. After cooling to r.t. over a period of 3 h yellow crystals of **1b** were formed. The crystals were washed with hexane and dried. Yield: 455 mg (74%). ¹H-NMR (C₆D₆, 300 K): δ 1.87 (s, 15 H, C₅Me₅). ¹³C {¹H}-NMR (C₆D₆, 300 K): δ 221.8 (CO), 114.4 (C₅Me₅), 10.0 (C₅Me₅). IR (Nujol, cm⁻¹): ν = 1921, 1836 (vs, CO). Anal. Calc. for C₃₃H₄₅O₃WGa₃ (M = 882.70 g mol⁻¹): C, 44.90; H, 5.14. Found: C, 44.69; H, 4.68%.

4.3. Synthesis of [Mo₂(CO)₆(μ²-(GaCp*))₃] (**2**)

A mixture of **1a** (500 mg, 0.63 mmol) and *fac*-(MeCN)₃Mo(CO)₃ (191 mg, 0.63 mmol) in toluene (20 ml) was refluxed for 2 h, while the orange solution turned dark red. After cooling to r.t., the solvent was removed in vacuo. The residue was washed twice with hexane and dried in vacuo. The product was purified by recrystallization from toluene. Yield: 455 mg (74%). M.p. 224 °C (decomp.). ¹H-NMR (C₆D₆, 300 K): δ 2.12 (s, 15 H, C₅Me₅). ¹³C {¹H}-NMR (C₆D₆, 300 K): δ 219.7 (CO), 116.6 (C₅Me₅), 10.1 (C₅Me₅). IR (Nujol, cm⁻¹): ν = 1921, 1857 (vs, CO). Anal. Calc. for C₃₆H₄₅O₆Mo₂Ga₃ (M = 974.79 g mol⁻¹): C, 44.36; H, 4.65. Found: C, 44.34; H, 4.67%.

4.4. Synthesis of [(OC)₂(Cp)Mo(μ²-(η¹-GaCp*))₂] (**3a**)

Cp*Ga (354 mg, 1.73 mmol) was added to a suspension of [CpMo(CO)₂]₂ (250 mg, 0.58 mmol) in hexane (5 ml). After stirring the mixture for 1 h at r.t., the solvent was removed in vacuo. The yellow residue was washed with hexane and dried in vacuo. The product was purified by crystallization from a saturated solution in diglyme (170 °C) and slow cooling. Yield: 245 mg (50%). M.p. 196 °C (decomp.). ¹H-NMR (C₆D₆, 300 K): δ 4.61 (s, 10 H, C₅H₅), 2.08 (s, 30 H, C₅Me₅). ¹³C {¹H}-NMR (C₆D₆, 300 K): δ 219.8 (CO), 120.6 (C₅Me₅), 82.1 (C₅H₅), 12.9 (C₅Me₅). IR (Nujol, cm⁻¹): ν = 1888, 1832 (vs, CO). Anal. Calc. for C₃₄H₄₀O₄Mo₂Ga₂ (M = 844.01 g mol⁻¹): C, 48.38; H, 4.78. Found: C, 48.62; H, 4.80%.

4.5. Synthesis of [(OC)₂(Cp)W(μ²-(η¹-GaCp*))₂] (**3b**)

Cp*Ga (90 mg, 0.44 mmol) was added to a solution of [CpW(CO)₂]₂ (90 mg, 0.15 mmol) in hexane (5 ml) and refluxed for 1 h, while the dark red solution turned light red. The solvent was removed in vacuo, the orange

residue was washed twice with hexane and dried in vacuo. The product **3b** was recrystallized from a toluene–hexane mixture. Yield: 62 mg (41%). M.p. 183 °C (decomp.). ¹H-NMR (C₆D₆, 300 K): δ 2.12 (s, 30 H, C₅H₅), 4.58 ppm (s, 10 H, C₅Me₅). ¹³C {¹H}-NMR (C₆D₆, 300 K): δ 220.9 (CO), 122.2 (C₅Me₅), 82.4 (C₅H₅), 12.3 (C₅Me₅). IR (Nujol, cm⁻¹): ν = 1874, 1826 (vs, CO). Anal. Calc. for C₃₄H₄₀O₄W₂Ga₂ (M = 1019.81 g mol⁻¹): C, 40.04; H, 3.95. Found: C, 39.73; H, 4.09%.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 204455, 204457, 204456, 204899 and 204900 for compounds **1a**, **1b**, **2**, **3a** and **3b**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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