Theoretical Studies of Inorganic Compounds, Part 6[≠]

The Nature of the Gallium–Iron Bond in [Ar*GaFe(CO)$_4$]

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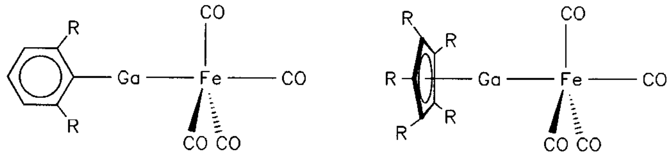
Abstract: The question of whether the gallium–iron bond in [Ar*GaFe(CO)$_4$] (Ar* = 2,6-(2,4,6-triisopropylphenyl)-phenyl) (**1**) should be considered as a single or a triple bond has been addressed by means of quantum chemical methods. Gradient-corrected density functional theory (BP86) calculations are reported for the gallium model complexes [(C$_6$H$_5$)GaFe(CO)$_4$] (**1a**) and [CpGaFe(CO)$_4$] (**2a**). Analysis of the bonding using the CDA partitioning schemes shows that there is a substantially higher degree of Ga ← Fe π backbonding in **1a** than that of **2a**. The Ga–Fe bond dissociation energy (D_e) of **1a** (54.9 kcal mol^{-1}) is also clearly higher than in **2a** (32.8 kcal mol^{-1}). This result lends some credence to the formulation of **1** with a Ga–Fe triple bond. However, the concepts applied in the discussion of the largely ionic Ga–Fe bonding situation in terms of single or multiple bonds are not appropriate. Neither the formula with a Ga–Fe single bond nor the Lewis form with a Ga–Fe triple bond is a proper representation of the bonding interactions. The discussion for and against the triple-bond character of **1** is a pseudo-conflict caused by application of an ill-defined bonding model that is inappropriate.

Keywords: backbonding · bonding analysis · density functional calculations · gallium · iron

Introduction

Experimental attempts to synthesize molecules with multiple bonds between atoms heavier than second-row elements have been remarkably successful in the last two decades.[1,2] A recent highlight was the first isolation of a compound with a triple bond between group 13 metals, the gallyne Na$_2$[Ar*-Ga≡GaAr*] (Ar* = 2,6-(2,4,6-triisopropylphenyl)phenyl) reported by Robinson et al.[3] The formal assignment of a Ga–Ga triple bond has been questioned,[4] but a careful theoretical analysis showed that the bond order of the *trans*-bent R–Ga–Ga–R moiety is between double and triple, which justifies the term gallyne for the new compound.[5]

The same group reported recently the synthesis of another spectacular molecule, [Ar*GaFe(CO)$_4$] (**1**), which was written with an iron–gallium triple bond (Figure 1).[6] Compound **1** was regarded as the first ferrogallyne because of: 1) the short Ga–Fe bond, which is approximately 0.2 Å shorter than typical Ga–Fe bonds, and 2) the two-coordinate linear arrangement about the gallium atom.[6] The interpretation of the Ga–Fe bond as a triple bond has been criticized by Cotton and Feng,[7] who presented qualitative arguments and quantum chemical calculations using density functional theory (DFT) as evidence against the multiple-bond character of Ga–Fe. By comparing **1** with [R$_3$PFe(CO)$_4$] they concluded that all experimental data as well as theory support the formulation of this bond as a single Ga→Fe bond.[7] It is hardly possible to formulate more antipodal positions than those taken by the two groups of workers! The nature of the Ga–Fe bond in **1** and the Ga–Ga bond in Na$_2$[Ar*-Ga≡GaAr*] has been very controversial.[8] The opposing opinions of prominent scientists on whether these bonds have a multiple character show clearly that fundamental aspects of chemical bonding need to be addressed by a careful analysis of the electronic structure of **1**.



R = 2,4,6-iPr$_3$C$_6$H$_2$ **1**   R = Me **2**

R = H **1a**   R = H **2a**

Figure 1. Experimentally observed molecules **1** and **2** and model compounds **1a** and **2a**.

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We became interested in the bonding situation of **1** because recently we studied the electronic structure of the related compound [CpAlFe(CO)$_4$], which served as a model for the experimentally observed complex [Cp*AlFe(CO)$_4$].[9] This work was part of our ongoing investigations of the nature of metal–ligand donor–acceptor interactions in transition metal[10] and main-group compounds.[11] In order to analyze quantitatively the donor–acceptor interactions in Lewis acid–base complexes in terms of synergetic donation/backdonation as suggested by Dewar,[12a] and Chatt and Duncanson,[12b] we developed the CDA (charge decomposition analysis) partitioning scheme, which was very helpful for gaining insight into chemical bonding of complexes.[13] Since the central issue concerns the degree of Ga ← Fe π backdonation in the Ga–Fe bond in **1**, a CDA investigation of the bonding situation should be particularly helpful for addressing whether **1** should be regarded as a ferrogallyne. Details of the method are outlined below. The CDA results for [CpAlFe(CO)$_4$] showed that the Fe–Al bonding is dominated by Coulomb attraction between the positively charged Al and the negatively charged Fe and by Al → Fe σ donation, while the Al ← Fe π backdonation is negligible.[8] It follows that the Fe–Al bond should be considered as a single bond. The formally empty 3p$_\pi$ orbitals at Al are partly filled by Al ← Cp π donation; this is why [Cp*AlFe(CO)$_4$] is stable enough to be isolated. The gallium analogue [Cp*GaFe(CO)$_4$] (**2**) has also been synthesized and its X-ray structure analysis reported.[14] Before Robinson's work, compounds of general formula [RMFe(CO)$_4$] (M = Al, Ga), where R was *not* capable of stabilizing M electronically by M ← R backdonation, had been isolated only when additional donor ligands such as amines were coordinated at M.[15]

The reported synthesis of **1** was therefore surprising, because the aryl ligand should have little Ga ← Ar π backdonation; even then, only one 4p$_\pi$ orbital of Ga might be stabilized by π donation from the aryl ring. Steric protection of the Ga atom against nucleophilic attack by the bulky aryl group is certainly one reason for the stability of **1**, but the short Ga–Fe distance suggests that, unlike the situation in **2**, there is considerable Ga ← Fe π backdonation. The degree of donation and backdonation can be quantified with the CDA method, so we carried out a theoretical analysis of the bonding situation in the model compounds [(C$_6$H$_5$)GaFe(CO)$_4$] (**1a**) and [CpGaFe(CO)$_4$] (**2a**) (Figure 1). The crucial questions addressed in this study are: Has **1a** substantially higher Ga ← Fe π backdonation than **2a**? Is the Ga–Fe π-bonding contribution large enough to consider **1** as a ferrogallyne?

Computational Methods

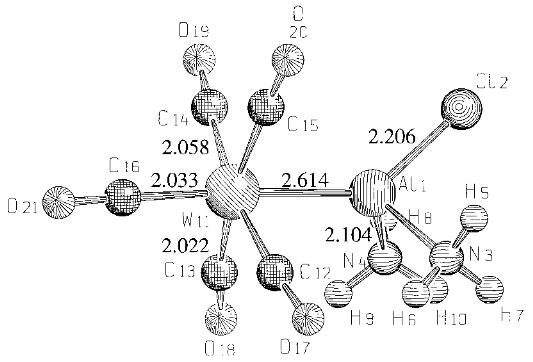
The geometries of the molecules have been optimized by means of gradient-corrected density functional theory (DFT) with the functionals BP86[16] as given in the Gaussian 94 program.[17] The BP86 calculations were performed with a quasi-relativistic small-core effective core potential (ECP)[18] at Fe with a (311111/22111/411) basis set for the 3s^{2}3p^{6}4s^{2}3d^6 outer-core and valence electrons; 6-31G(d) all-electron basis sets were used for C, O, and H.[29] An ECP has also been employed for Ga with a (31/31/1) valence basis set.[20] The d-type polarization function of Ga has an exponent $\zeta = 0.207$.[21] This is called basis set I. Vibrational frequencies of the stationary points were calculated at BP86/I with numerical second derivatives of the energy with respect to the coordinates. All structures reported here are minima on the potential-energy surface.

The metal–ligand donor–acceptor interactions were inspected by means of the CDA method,[13] in which the (canonical, natural, or Kohn–Sham) molecular orbitals of the complex are expressed in terms of the MOs of appropriately chosen fragments. In the present case, the Kohn–Sham (KS) orbitals of the complexes [LFe(CO)$_4$] are formed in the CDA calculations as a linear combination of the orbitals of Fe(CO)$_4$ fragment and of the ligand L being investigated, in the geometry of the complex. The orbital contributions are divided into three parts: i) mixing of the occupied σ-type MOs of L and the unoccupied σ-type MOs of Fe(CO)$_4$ {σ-donation, [L → Fe(CO)$_4$] }; ii) mixing of the unoccupied π-type MOs of L and the occupied π MOs of Fe(CO)$_4$ {π backdonation, [L ← Fe(CO)$_4$]}; and iii) mixing of the occupied MOs of L and the occupied MOs of Fe(CO)$_4$ {repulsive polarization, [L ↔ Fe(CO)$_4$]}. A similar breakdown of the orbital contributions was made for the Fe–CO interactions. The method and the interpretation of the results are presented in more detail in ref. [13]. Further examples in which the CDA method was helpful in elucidating the bonding in donor–acceptor complexes of transition metals and main-group elements have been published elsewhere.[10,11b,c] The CDA calculations were performed with the CDA 2.1 program.[22] The charge distribution in the compounds and the electronic configuration at Fe were calculated with the NBO partitioning scheme.[23]

Results and Discussion

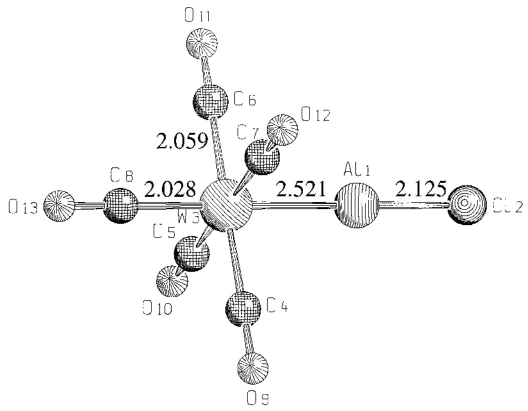
Before presenting and discussing the results of our calculations, we shall examine the arguments of Robinson et al.[6] in favor of, and of Cotton and Feng[7] against, the interpretation of **1** as having an iron–gallium triple bond.

The reasons for calling **1** a ferrogallyne were i) the two-coordinate linear arrangement about the gallium atom and ii) the very short Ga–Fe bond length.[6] We do not think that these arguments give any evidence for a triple-bond character: we calculated recently the structure and bonding situation of the related aluminum complexes [(NH$_3$)$_2$ClAlW(CO)$_5$] (**3a**) and [ClAlW(CO)$_5$] (**3b**) (Figure 2).[15,24] Compound **3a** is a model for the experimentally known complex **3**, which has an *N*,*N*,*N*′,*N*′-tetramethylpropylenediamine (tmpda) ligand at Al instead of two NH$_3$ groups. The X-ray structure analysis of **3** is in good agreement with the calculated geometry of **3a**.[15] Calculations for the base-free model compound **3b** and a comparison with **3a** gave interesting insights into the nature of the metal–ligand interactions. Although the Al–W bond in **3a** (2.614 Å; for **3**, experimental Al–W = 2.645 Å) is clearly longer than that in **3b** (2.521 Å), the Al–W bond dissociation energy (BDE) of **3a** (69.2 kcal mol^{-1}) is substantially higher than that of **3b** (40.5 kcal mol^{-1}). Analysis of the Al–W interactions using the CDA method showed that Al → W σ-donation is higher and the Al ← W π backdonation is lower in **3b** than in **3a** (Table 1). Thus, the *d*/*b* ratios of Al → W σ donation and Al ← W π backdonation in **3a** (1.64) and **3b** (1.96) suggest that Al ← W π backdonation in **3a** is even more important than in **3b**, although **3a** has a longer Al–W bond than **3b**. It follows that the Al–W bond shortening in **3b** is *not* caused by stronger Al ← W π backdonation. The shorter, yet weaker, Al–W bond in **3b** than in **3a** can be explained when the aluminum lone-pair donor orbitals of the two compounds are examined. The σ-donor orbital is sp$^{4.00}$ hybridized in **3a**, and sp$^{2.61}$ hybridized in **3b**.[24] A higher p character of the lone-



3a

D_e(Al-W) = 69.2 kcal/mol



3b

D_e(Al-W) = 40.5 kcal/mol

Figure 2. Calculated geometries (BP86/I) of the aluminum complexes **3a** and **3b** (bond lengths in Å; 2ref. [24]).

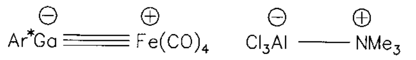
Table 1. Calculated NBO charge distribution at BP86/I.[a]

		$q(\mathrm{Fe(CO)_4})$	q(Fe)	q(Ga)	q(Ga, p_x)	q(Ga, p_z)
[PhGa–Fe(CO)$_4$]	**1a**	−0.67	−0.58	+1.16	0.20	0.17
[CpGa–Fe(CO)$_4$]	**2a**	−0.51	−0.53	+1.01	0.26	0.26

[a] Charges of the Fe(CO)$_4$ fragment: $q(\mathrm{Fe(CO)_4})$, the iron atom: q(Fe), and the gallium atom: q(Ga); p_π populations: q(Ga,p) at the gallium atom. The y axis is parallel to the Ga–Fe bond, the x axis is perpendicular to the phenyl group.

pair orbital makes the donor orbital more diffuse; this leads to a longer donor–acceptor bond in **3a**. The increase in energy of the lone-pair orbital in **3a** because of the higher p character leads to stronger donor–acceptor interactions with the W(CO)$_5$ fragment. It follows that the shorter, yet weaker, Al–W bond in **3b** is an effect of sp hybridization of the Al lone-pair orbital, which has nothing to do with Al ← W π backdonation. Since the hybridization of the Ga lone-pair orbitals in **1** and **2** was not studied, it is possible that the Ga–Fe bond shortening have similar causes. Different Coulomb interactions in **1** and **2** might also be partly responsible for the observed bond shortening.

The following arguments against a Ga–Fe triple-bond character in **1** were given by Cotton and Feng.[7] First, the charge separation entailed by assigning a triple bond to **1** (**A** in Figure 3) was said to be unbelievable. This is not a serious argument! In [Cl$_3$Al–NMe$_3$], for example, the most strongly bonded donor–acceptor complex of main-group elements (experimental bond energy D_o(Al–N) = 47.5 ± 2.0 kcal mol^{-1}),[25] there is no doubt that aluminum is four-coordinate. A formal assignment of the charge separation gives a negative charge at Al (**B** in Figure 3), but a high-level quantum chemical calculation gave a positive partial charge of +1.51 at Al.[11a] This is because all four bonds to Al are strongly polarized with the positive end at Al. It is common knowledge that the formal charge assignment of a molecule written as a Lewis structure has nothing to do with the true charge distribution.



$$\overset{\ominus}{\mathrm{Ar^*Ga}} \equiv \overset{\oplus}{\mathrm{Fe}}\mathrm{(CO)_4} \qquad \mathrm{Cl_3}\overset{\ominus}{\mathrm{Al}} - \overset{\oplus}{\mathrm{N}}\mathrm{Me_3}$$

A **B**

Figure 3. Possible Lewis forms for the donor–acceptor complexes **1** (**A**) and [Cl$_3$AlNMe$_3$] (**B**).

In their second argument, Cotton and Feng refer to the C–O stretching frequencies in **1**. It is said that strong Ga ← Fe π backdonation should lead to weaker OC ← Fe π backdonation; this should then yield higher C–O stretching frequencies. Since the measured C–O stretching frequencies of **1** are even lower than those of [(Ph$_3$P)Fe(CO)$_4$], it is concluded that there is less Ga ← Fe than P ← Fe π backbonding. As the P–Fe bond in [(Ph$_3$P)Fe(CO)$_4$] is clearly a single bond, the Ga–Fe bond would have negligible π-bonding character. We think that this argument also is unconvincing. It has been shown recently[26,27] that not only are the changes in the C–O bond length and stretching frequency in a molecule [L$_n$M(CO)$_n$] influenced by the OC ← M π backdonation, but also that the Coulomb interactions between M and CO play an important role. A positive charge at M in M–CO leads to charge attraction from the carbon side of CO. This makes the C–O bond less polarized and more like the bond in N$_2$, which in turn leads to a shorter and stronger C–O bond and a higher C–O stretching frequency.[26,27] Accordingly, a negative charge at the metal will lead to longer C–O bonds and a lower C–O stretching frequency (Figure 4).[36] Since the Ga and Fe atoms in **1** carry large positive and negative partial charges, respectively (see the results below), the C–O stretching frequencies in **1** should be shifted by the Coulomb interactions towards lower wavenumbers. This could compensate for the weaker OC ← M π backdonation. It follows that the C–O stretching frequencies in **1** may not be used as a probe for the Fe–Ga bonding situation.

Cotton and Feng's third argument[7] against a Ga–Fe triple bond in **1** involves a comparison of the Ga–Fe bond in **1** with the only marginally longer Fe–P bond in [(Ph$_3$P)Fe(CO)$_4$]. In our opinion, a comparison of bond lengths such as Ga–Fe and P–Fe is not very meaningful. Finally, as Kutzelnigg shows clearly in an important review of the chemical bonding of heavier main-group elements,[28] bonding concepts that are derived from the elements of the first full row of the periodic system cannot automatically be extended to the heavier elements.[29] Since most classical models of chemical bonding have been deduced from knowledge of structure and bonding

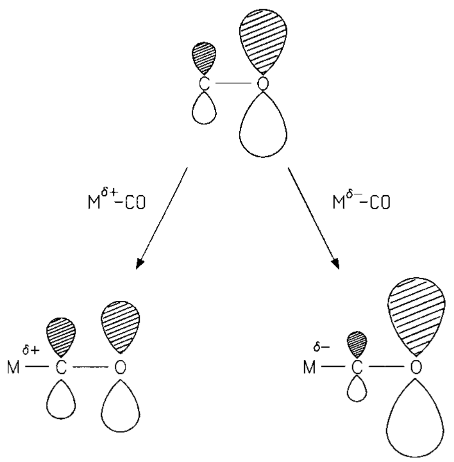
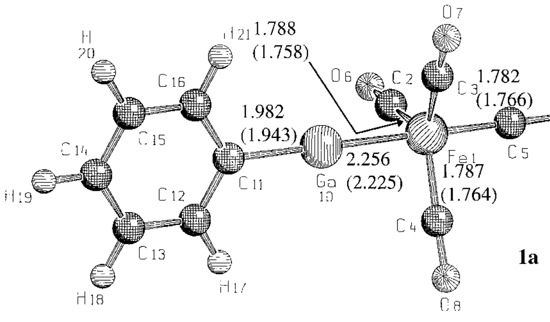


Figure 4. Effect of a positively or negatively charged metal M at the carbon site of CO on the polarization of the C–O π bond. The same polarizing effect is found for the σ-orbitals (ref. [26]).

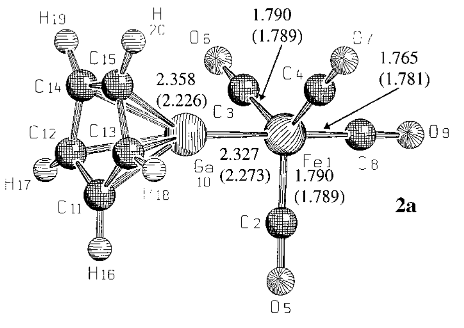
of the lighter elements, one should be cautious when heavier elements are involved, particularly for the transition metals, since the sd-hybridized bonding of these elements is even less well understood than the sp-hybridized bonding of the heavier main-group elements. The Ga–Fe bonding character can only be addressed by a careful analysis of the electronic structure of the molecule; this must be based on a calculation that is in agreement with experimental data.

Figure 5 shows the optimized geometries of **1a** and **2a** at the BP86/I level of theory and the most important experimentally observed bond lengths for **1** and **2**. The calculated Ga–Fe bond in **1a** (2.256 Å) is slightly longer than the experimental value reported for the parent compound **1** (2.225 Å).[6] Therefore analysis of the Ga–Fe bond in **1a** should not lead to an overemphasis of the π-bonding contribution in **1**.[37] The calculated Ga–Fe interatomic distance (2.327 Å) is also slightly longer than the experimental value reported for **2** (2.273 Å).[14] The larger difference between the theoretically predicted Ga–C distance in **2a** (2.358 Å) and the average value given for **2** (2.226 Å) is probably due to the Cp*–Ga bonding in **2** being stronger than the Cp–Ga bonding in **2a**.



1a

D_e(Ga-Fe) = 54.9 kcal/mol



2a

D_e(Ga-Fe) = 32.8 kcal/mol

Figure 5. Optimized geometries (BP86/I) of **1a** and **2a** (bond lengths in Å).

Figure 5 also gives the theoretically predicted Ga–Fe bond dissociation energies at BP86/I. The calculations show that the bond energy of **1a** ($D_e = 54.9$ kcal mol^{-1}) is clearly higher than that of **2a** ($D_e = 32.9$ kcal mol^{-1}). Since the calculated first BDE of [Fe(CO)$_5$] at BP86/I (52.7 kcal mol^{-1}) is approximately 7 kcal mol^{-1} higher than the experimental value (41 ± 2 kcal mol^{-1}),[30] it can be assumed that the theoretical Ga–Fe bond energies may also be slightly too high. The most important result, however, is the trend of the bond energies: **1a** has a much stronger Ga–Fe bond than **2a**. The stronger bond is partly caused by enhanced Coulomb attraction between the gallium and iron atoms. Table 1 gives the relevant partial charges. The gallium atom carries a strong positive charge (+1.16 e) in **1a** and a slightly less positive one in **2a** (+1.01 e). The iron atom in **1a** has a significant negative charge (−0.58 e) and a less negative one (−0.53 e) in **2a**. The calculated charge distribution shows that the gallium–iron bonds in **1a** and **2a** have substantial ionic contributions.

The core of our analysis of the Ga–Fe bond is given by the CDA results (Table 2). We discuss first the data for [CpGa-Fe(CO)$_4$] (**2a**), which by analogy with [CpAlFe(CO)$_4$] can be expected to have a Ga–Fe bond that is dominated by Ga →Fe σ donation with little Ga ← Fe π backdonation.[9] Indeed, the ratio of the Ga →Fe donation in **2a** (0.480 e) to the Ga ← Fe backdonation (0.163 e; Table 2) is clearly in favor of the former ($d/b = 2.94$). The relative contribution of the Ga ← Fe backdonation in **2a** is slightly higher than in the case of the aluminum analogue [CpAlFe(CO)$_4$] ($d/b = 3.21$).[9] This may be due to gallium having a higher electronegativity than aluminum.[31] The Ga →Fe donation is slightly larger in **1a** (0.507 e) than in **2a**. More important is the increase in the Ga ← Fe π backdonation from 0.183 e in **2a** to 0.335 e in **1a**. This leads to a substantial change for the Ga–Fe interaction

Table 2. CDA results at BP86/I for the metal–ligand donor–acceptor bonds.[a]

		Bond	Donation (d)	Back-donation (b)	Re-pulsion	d/b
[PhGa–Fe(CO)$_4$]	**1a**	Ga–Fe	0.507	0.335	−0.326	1.51
[PhGa–Fe(CO)$_4$]	**1a**	Fe–CO$_{trans}$	0.612	0.376	−0.251	1.63
[CpGa–Fe(CO)$_4$]	**2a**	Ga–Fe	0.480	0.163	−0.285	2.94
[CpGa–Fe(CO)$_4$]	**2a**	Fe–CO$_{trans}$	0.600	0.398	−0.243	1.51
[Fe(CO)$_5$]		Fe–CO$_{ax}$	0.568	0.325	−0.305	1.75
[(NH$_3$)$_2$ClAl–W(CO)$_5$]	**3a**	Al–W	0.503	0.308	−0.217	1.64
[ClAl–W(CO)$_5$]	**3b**	Al–W	0.586	0.297	−0.195	1.96

[a] Ligand-to-metal donation L →M, backdonation L ← M, repulsive polarization L ↔ M and donation/backdonation ratio d/b.

from $d/b = 2.94$ in **2a** to $d/b = 1.51$ in **1a**. The contribution of the Ga ← Fe π backdonation to the gallium–iron bond in **1a** is nearly twice as great as in **2a**! This cannot be attributed to the Ga–Fe bond length being slightly shorter in **1a** than in **2a**. As shown above, the d/b ratio for the Al–W donor–acceptor bond suggests that Al ← W π backdonation in **3a** is more important than in **3b**, although **3b** has a significantly shorter bond than **3a**.

The CDA results indicate that the $4p_\pi$ valence orbitals in **1a** become partially occupied by Ga ← Fe π backdonation. At the same time there is less OC ← Fe π backdonation for the *trans*-CO ligand in **1a** than in **2a**. The d/b ratio for the Fe–CO_{trans} bond in **1a** ($d/b = 1.63$) is higher than in **2a** ($d/b = 1.51$; Table 2). It should be noted that the changes in the OC ← Fe π backdonation and the Fe partial charges in **1a** and **2a** have opposite effects on the C–O stretching frequency. The higher negative partial charge at Fe in **1a** should induce lower C–O wavenumbers (Figure 4), while the lower OC ← Fe π backdonation should yield higher C–O stretching frequencies. The calculated C–O stretching modes of **1a** and **2a** are nearly the same (Table 3). Thus, the changes in the vibrational spectra from **1** to **2** are not very helpful for an analysis of the Ga–Fe bonding situation.

Table 3. Calculated stretching frequencies at BP86/I.

		$\tilde{\nu}_1$ [cm^{-1}]	$\tilde{\nu}_2$ [cm^{-1}]	$\tilde{\nu}_3$ [cm^{-1}]	$\tilde{\nu}_4$ [cm^{-1}]
[PhGa–Fe(CO)$_4$]	**1a**	1958	1960	1985	2038
[CpGa–Fe(CO)$_4$]	**2a**	1959	1959	1983	2040

The occupation of the $4p_\pi$ valence AOs of Ga in **1a** and **2a** gives further information about the Ga–Fe and Ga–C interaction. The orbital charges in **2a** for each of the $4p_\pi$ Ga orbitals are 0.26 *e* (Table 1). The numbers indicate the degree of Cp → Ga donation, since this is the main component of the π interactions at Ga in **2a** rather than Ga ← Fe π backdonation. The $4p_\pi$ orbitals of Ga in **1a** are no longer degenerate. The $4p_\pi$ orbital of Ga, which is in the plane of the phenyl ring, is occupied by 0.17 *e* (Table 1). This can be taken as a measure of the pure Ga → Fe π backdonation, because the hyperconjugative donation from the C_α–C_β bond of the phenyl ring should be negligible. A small additional donation may be expected from the p_π orbital of C_α to the Ga $4p_\pi$ orbital which is perpendicular to the phenyl ring (Figure 1). Indeed, the occupation of the out-of-plane Ga $4p_\pi$ orbital is slightly higher (0.20 *e*) than that of the in-plane orbitals.[37] The difference of 0.03 *e* indicates the negligible Ph → Ga π-donation in **1a**. It is noteworthy that the total occupation of the Ga $4p_\pi$ orbitals given by the NBO method (0.37 *e*) is quite similar to the Ga ← Fe π backdonation calculated by the CDA method (0.34 *e*). It is gratifying that two different theoretical methods give similar values for the extent of Ga ← Fe π backdonation.

Cotton and Feng[37] reported that the overlap of π type orbitals between Fe and Ga is practically nil, and that the Ga $4p_\pi$ orbitals are unoccupied. Unfortunately, they do not say which method they used to calculate orbital occupancies. Since the calculations were carried out with Gaussian 94,[17] we assume that the Mulliken population analysis was employed. This assumption is supported by our finding that the π overlap population of the Ga–Fe bond of **1a** given by the Mulliken procedure is nearly zero. However, the shortcomings of the Mulliken procedure in the assignment of charge distributions are well known and it has been concluded that Mulliken population in general performs rather poorly in highly ionic species.[34] Since the bond between Ga [q (charge density) $= +1.16$] and Fe ($q = -0.58$) in **1a** is highly ionic, we think that the Mulliken population analysis gives unreliable results in this case. This would explain the difference between our results and those of Cotton and Feng.

There is another argument against the formulation of the Fe–Ga bond as a pure σ-bond without a π contribution as suggested by Cotton and Feng.[37] This would imply that **1** is a stable molecule in which gallium has only four electrons in the valence shell. It is well known that compounds of the group 13 elements B–In with an electron sextet in the valence shell are difficult to isolate. Stable compounds of group 13 elements have either π-donor substituents at the electron-deficient atom, or they are dimers or oligomers. Also, a bonding analysis of the recently synthesized binary indium complex [Ni{InC(SiMe$_3$)$_3$}$_4$][40] and gallium complex [Ni{GaC(SiMe$_3$)$_3$}$_4$] showed significant In ← Ni and Ga ← Ni π backdonation.[41]

The results of the CDA method and the NBO partitioning scheme show clearly that there is a substantially higher π-bonding character in the Ga–Fe bond of **1a** than in **2a**. Does this justify writing **1** with a Ga–Fe triple bond? It could be argued that while the d/b ratio for the Ga–Fe bond in **1a** (1.51) indicates a much higher π-bonding character than in **2a** ($d/b = 2.94$), it is only slightly lower than that for the Fe–CO_{trans} bond in **1a** (1.63). Since the iron–carbonyl bond in [LFe(CO)$_4$] is generally considered to be single rather than triple, the analogy would lead to the conclusion that the Ga–Fe bond is also single. We do not think that such a comparison is valid, because valence bond (VB) structures for a donor–acceptor complex are usually written in terms of traditional concepts and not as the result of a theoretical analysis of the bonding interactions. For example, Davidson has shown that the dominant part of the Cr–CO bond energy in [Cr(CO)$_6$] comes from the OC ← Cr π backdonation, while the OC → Cr σ-donation contributes little to the bonding energy because it is nearly cancelled by Cr ↔ CO repulsive interactions.[35] It follows that the best VB structure for [Cr(CO)$_6$] has Cr–CO (π) double bonds, which would probably not be accepted by traditional chemists. The following points must be considered in a discussion of the Ga–Fe bonding character of **1**.

1) The formulation of a donor–acceptor bond in terms of single or multiple bonds is not well defined. In particular, there is no reference to a Ga–Fe single, double, or triple bond.

2) The Lewis formula for a transition metal complex usually follows the octet rule for the main-group element that is bonded to the transition metal. For example, the bonding in transition metal oxides [L$_n$M=O] is usually written with a double bond between M and O, although in compounds like [Cl$_4$WO] the π bond between tungsten and oxygen involves both p_π orbitals at oxygen; that is, a triple bond would be more appropriate.[32] The CDA result for the donor–ac-

ceptor bonding between $W(CO)_5$ and NO^+ gives $d/b = 0.31$ for $[(CO)_5W{-}NO]^+$, which indicates predominantly $ON^+ \leftarrow W(CO)_5$ backbonding,[10f] but the most common Lewis form has a W–N single bond. Compare this with Fischer-type carbyne complexes, which are usually written with a metal–carbon triple bond. The CDA for $[Br(CO)_4W{\equiv}CMe]$ gives $d/b = 0.62$; that is, the relative contribution of the π-bonding is less than in $[(CO)_5W{-}NO]^+$.[10h] If **1** were written with a Ga–Fe single bond, the gallium atom would have a valence shell with an electron quartet rather than an octet. It would be difficult to understand why **1** is a stable compound when the Ga atom is electronically highly unsaturated. Since the occupation of the $4p_\pi$ orbital of Ga in **1a** comes mainly from the Ga ← Fe π backdonation, writing **1** with a Ga–Fe triple bond can be justified. The calculated occupation of the $4p_\pi$ orbitals of Ga in **1a** [0.37 *e* (NBO) and 0.34 *e* (CDA)] may appear to be too low to formulate a genuine triple bond. However, the charge donation in $Cl_3Al \leftarrow NMe_3$ is only 0.18 *e*[11a] and yet the complex is usually written with a single bond between Al and N. Writing arrows (→) rather than bonds (–) might be appropriate, but this would become clumsy for two Ga–Fe π bonds.

Points 1 and 2 summarize the difficulty of assigning a formal bond order to the gallium–iron bond in **1**. The Ga–Fe bond also has a strong ionic character, which has not been considered in refs. [6] and [7]. The most important conclusion from our study is the following one.

3) The discussion in terms of single, double, and triple bonds describes the situation in molecules by using a simple valence bond model, which is not suitable for describing the bonding between heavier atoms,[28] and particularly not for donor–acceptor bonds in transition metal complexes. There are clearly more sophisticated models available to describe the bonding interactions in these compounds. The Dewar–Chatt–Duncanson (CDC) model[12] is much more appropriate for describing donor–acceptor bonds. Since modern quantum chemical partitioning schemes have been developed to quantify the energies[33] and the charge distributions[13] associated with the DCD model, it is advisable to use these models for a description of the bonding situation in **1**. The insight into the electronic structure that is available from the analysis of accurate quantum chemical calculations shows clearly that the discussion of whether **1** has a Ga–Fe single or triple bond is outdated.

Summary and Conclusion

The analysis of the bonding situation in the model compounds $[(C_6H_5)GaFe(CO)_4]$ (**1a**) and $[CpGaFe(CO)_4]$ (**2a**) using the CDA partitioning scheme shows that there is a substantially higher degree of Ga ← Fe π backbonding in **1a** than in **2a**. The Ga–Fe bond dissociation energy of **1a** ($D_e = 54.9\ \text{kcal mol}^{-1}$) is also clearly higher than in **2a** ($D_e = 32.8\ \text{kcal mol}^{-1}$). This result lends some credence to the formulation of **1** with a Ga–Fe triple bond. However, the discussion of the Ga–Fe bonding situation in terms of single or multiple bonds uses concepts that are not suited to its proper description. Neither the formula with a Ga–Fe single bond nor the Lewis form with a Ga–Fe triple bond gives a reasonable representation of it. The discussion for and against the triple-bond character of **1** is a pseudo-conflict caused by the application of an inappropriate bonding model.

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