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Steric Control between Neutral Metal-Only Lewis Pairs and Metal-Stabilized Gallenium and Gallinium Cations

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Supporting Information

ABSTRACT: Reaction of a series of zerovalent Fe Lewis bases with Lewis acid $GaCl_3$ leads to both conventional, neutral metal-only Lewis pairs in the case of small metal complexes and cationic gallenium species in the case of larger metal bases. The results suggest the predominance of steric bulk in controlling the outcome of group 13 trihalide Lewis acid additions to metal bases.



The existence-and utility-of dative bonding between maingroup atoms is well-accepted in contemporary chemistry. In contrast, dative bonding between metal atoms is much less well-understood. The existence of dative bonds between metal atoms dates back at least half a century: to our knowledge the first mention of such an interaction is in a 1964 report from Coffey, Lewis, and Nyholm,¹ while the first structurally authenticated M \rightarrow M dative bond appears to be that in $[(\eta^5 C_{5}H_{5}(OC)_{2}Co \rightarrow HgCl_{2}$, as reported by Nowell and Russell in 1967.² Despite this relatively early beginning, most so-called metal-only Lewis pairs (MOLPs) reported in the intervening years were prepared serendipitously and were often not recognized as such. Our 2012 review on MOLPs was an attempt to formalize the concept of metal-metal dative bonding through the compilation of the scattered reports of structurally characterized examples of these complexes.³ However, there are presumably many more complexes in the literature that escaped our attention due to lack of structural data or uncertain bonding situations. Since that time, work from our group and those of Jones, Stasch, and Krossing have expanded the field markedly,⁴ and the MOLP concept has since been used as a basis for a description of oxidation states and metal-metal dative bonds in a technical report published by the International Union of Pure and Applied Chemistry (IUPAC).⁵

When we began our work in this field, perhaps the most wellstudied subset of MOLPs was that featuring zerovalent group 8 donors (M^0L_n , M = Fe, Ru, Os) and transition metal acceptors, thanks to extensive work by the groups of Pomeroy, Mak, and Dixneuf (and subsequently also Krossing).^{41,6} However, MOLPs featuring zerovalent group 8 donors and simple main-group Lewis acids were at that time unknown. After our discovery that gallium trihalides form stable Lewis adducts with pentacoordinate Fe⁰ complexes, we began a systematic study of MOLPs of the form $[L_nFe^0/L_nRu^0\rightarrow GaX_3]$.^{7,8} Using a range of different donor ligands bound to the group 8 metal centers, we were able to establish trends in the Lewis basicity of Fe⁰ and



Ru⁰ complexes by comparisons of M–Ga bond distances, sums of X–Ga–X angles, and computationally derived bond dissociation energies. Lewis acid transfer experiments between metal–ligand fragments (including strongly Lewis basic PtL₂ complexes) enabled us to draw up experimental hierarchies of Lewis basic precursors, which may be useful fundamental information for future catalytic endeavors.

Recent work in our laboratories involving addition of gallium halides to bulkier Fe^0 complexes has shown new reactivity patterns, leading to rare examples of compounds with tricoordinate, cationic gallium centers and in one case a dinuclear cationic complex wherein a GaCl₂ fragment bridges two iron centers. These results, described herein, suggest that sterically bulky Lewis basic M^0 complexes may induce the disproportionation of GaCl₃.

RESULTS AND DISCUSSION

Synthesis of MOLPs from Tri- and Tetracarbonyl Fe⁰ Complexes. In an attempt to increase the steric bulk at the metal center of pentacoordinate Fe⁰ complexes, we turned to the tetracarbonyl complexes $[Fe(CO)_4(PCy_3)]$ (1a) and $[Fe(CO)_4(IMes)]$ (1b; IMes = 1,3-dimesitylimidazol-2-ylidene).⁹ Treatment of solutions of 1a or 1b with an equimolar amount of the Lewis acid GaCl₂ led to isolation of the Lewis adducts trans-[(Cy₃P)(OC)₄Fe→GaCl₃] (1b; yield 83%) and *trans*-[(IMes)(OC)₄Fe \rightarrow GaCl₃] (**2b**; yield 93%) as white solids in good yields (Figure 1). Both structures show only one carbonyl stretching band in their IR spectra (1b: 2036 cm⁻¹; 2b: 2062 cm⁻¹), suggesting that the GaCl₃ sits trans to the phosphine or carbene ligand. Phosphine MOLP 1b additionally shows a ³¹P NMR signal at δ_P 55.6, significantly upfield from that of precursor 1a ($\delta_{\rm P}$ 80.2). The apparently greater electron density at the phosphorus atom of 1b over that of 1a is somewhat surprising given the presence of a Lewis acidic GaCl₃

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Figure 1. Synthesis of *trans*- $[L(OC)_4Fe \rightarrow GaCl_3]$ with $L = PCy_3$ (1b) or IMes (2b).

unit in *trans* position, even considering the strongly π -acidic CO ligand present *trans* to the phosphine in **1a**.

Single-crystal X-ray diffraction analysis of both adducts confirmed the structures suggested by IR spectroscopy (Figure 2). However, the *trans* geometry of **1b** and **2b** contrasts with the *cis* geometry observed in the less sterically bulky *cis*- $[(Me_3P)(OC)_4Fe \rightarrow GaCl_3]^7$ and *cis*- $[(Me_3P)(OC)_4Ru \rightarrow GaCl_3]$.⁸ The Fe–Ga bond distance of **1b** (2.5072(5) Å) is also slightly longer than that of the previously published complex *cis*- $[(Me_3P)(OC)_4Fe \rightarrow GaCl_3]$ (2.4844(3) Å), with the alternative geometry.

In order to increase the steric bulk of the Lewis base slightly, 2a was photolyzed in the presence of one equivalent of PMe₂ to form the tricarbonyl complex $[Fe(CO)_3(IMes)(PMe_3)]$ (3a; see Supporting Information for more details). Adding the Lewis acid GaCl₃ to this complex led to spontaneous precipitation of a white solid over 1 h. The ³¹P NMR spectrum of this solid suggested the presence of two isomers of the MOLP mer- $[(IMes)(Me_3P)(OC)_3Fe \rightarrow GaCl_3]$ (3b,c) (Figure 3), with signals at $\delta_{\rm P}$ 8.5 and 13.5, as well as two sets of signals in the ¹H NMR spectrum in a ratio of 1:0.7, respectively. Singlecrystal X-ray diffraction of the two different crystal forms confirmed the presence of isomers in which the Ga atom (3b)and the P atom (3c) are situated *trans* to the carbene ligand (Figure 2). Variable-temperature NMR across the range -80 to +70 °C showed no change in the relative intensities of the signals, indicating no interconversion between the two formed complexes. The Fe-Ga bond distances of 3b (2.4683(7) Å) and 3c (2.4836(11) Å) are both shorter than that of 1b (2.5072(5) Å) but closer to that of $cis_{4}Fe \rightarrow$ GaCl₃] (2.4844(3) Å).

Synthesis of Gallenium and Gallinium Salts Using Sterically Bulky Fe⁰ Bases. In order to increase the steric bulk of the iron Lewis bases further still, we turned to tricarbonyl complexes with bulky donor ligands, namely, the tricarbonyl complexes $[Fe(CO)_3(PCy_3)_2]$ (4a) and [Fe- $(CO)_3(IMes)_2$ [5a).⁹ Treatment of a solution of 4a with one equivalent of GaCl₃ led to the observation of approximately 50% conversion to a new product (4b, Figure 4) by ³¹P NMR $(\delta_{\rm P} \sim 63)$, in addition to unreacted starting material. Doubling the amount of GaCl₃ used led to complete conversion to 4b and spontaneous precipitation of a white crystalline solid. Infrared spectral data on a solution of 4b showed three CO stretching bands (2065, 2009, 1971 cm⁻¹), in accordance with a mer tricarbonyl structure. Based on the need for two equivalents of GaCl₃ for complete conversion to 4b, and our recent observation of halide abstraction from the MOLP trans,mer-[(Me₃P)₂(OC)₃Ru \rightarrow GaCl₃] by GaCl₃⁸ it was assumed that the complex was a halide-bridged dimer of cation trans,mer-[(Cy_3P)₂(OC)₃Fe \rightarrow GaCl₂]⁺. However, a single-crystal X-ray diffraction study showed the structure of 4b to be the nondimeric salt trans, mer-[(Cy_3P)₂(OC)₃Fe \rightarrow GaCl₂][GaCl₄] shown in Figure 5, with an effectively planar Fe-bound Ga



Figure 2. Crystallographically derived structures of MOLPs 1b, 2b, 3b, and 3c. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, solvent molecules, and some ellipsoids have been omitted for clarity. Selected bond lengths [Å] and angles [deg] for 1b: Fe1–P1 2.3343(8), Fe1–Ga1 2.5072(5); P1–Fe1–Ga1 174.57(3). For 2b: Fe1–C5 2.026(2), Fe1–Ga1 2.5009(5); C5–Fe1–Ga1 175.09(6). For 3b: Fe1–P1 2.2858(6), Fe1–C4 2.056(2), Fe1–Ga1 2.4683(7); C4–Fe1–Ga1 176.59(5). For 3c: Fe1–P1 2.306(1), Fe1–C4 2.038(4), Fe1–Ga1 2.484(1); C4–Fe1–Ga1 177.4(1).



Figure 3. Synthesis of the two geometrical isomers of mer-[(IMes)(Me₃P)(OC)₃Fe \rightarrow GaCl₃] (3b,c).



Figure 4. Synthesis of the salts $trans,mer-[L_2(OC)_3Fe \rightarrow GaCl_2]-[GaCl_4]$ with $L = PCy_3$ (4b) or IMes (5b).



Figure 5. Crystallographically derived structures of salts 4b, 5b, and 6b. Thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms, the counterions $[GaCl_4]^-$, solvent molecules, a second cation (for 5b), and some ellipsoids of the ligands are omitted for clarity. Selected bond length [Å] and angles [deg] for 4b: Fe1–Ga1 2.3694(5); C1–Fe1–Ga1 179.08(7), P1–Fe1–P2 173.51(2). For 5b: Fe1–Ga1 2.3590(8); C1–Fe1–C2 173.4(2), C3–Fe1–Ga1 166.1(1). For 6b: Fe1–Fe2 2.8692(7), Fe1–Ga1 2.4718(6), Fe2–Ga1 2.4858(6), Fe1–C3 2.043(3), Fe2–C3 2.012(3), C1–Ga1 2.499(3), C5–Ga1 2.481(3); Fe1–Ga1–Fe2 70.72(2), Fe1–C3–Fe2 90.1(1), C3–Fe1–Ga1 99.39(8), C3–Fe2–Ga1 99.81(8).

atom, indicating the absence of cation-cation interactions. The inability of the cation of 4b to dimerize is presumably due to

hindrance from the steric bulk of the PCy₃ ligands. Unsurprisingly, given the reduced coordination number at Ga and the positive charge on the complex, the Fe–Ga distance in **4b** (2.3694(5) Å) is significantly shorter than that of the analogous PMe₃ MOLP *trans,mer*-[(Me₃P)₂(OC)₃Fe→GaCl₃] (2.4612(6) Å).⁷

Similarly to the case of 4b, addition of one equivalent of GaCl₃ to 5a led to spontaneous precipitation of a low yield of a [GaCl₄]⁻ salt that showed three CO bands in its IR spectrum (2025, 2006, 1974 cm^{-1}) and one set of NHC signals in its ¹H NMR spectrum (5b, Figure 4); doubling the amount of added GaCl₃ increased the yield to 65%. A single-crystal X-ray diffraction study confirmed the structure of 5b to be the analogous nondimeric salt trans, mer-[(IMes)₂(OC)₃Fe \rightarrow GaCl₂][GaCl₄] with an effectively planar Fe-bound Ga atom and orthogonally oriented IMes units. Salt 5b shows both a completely different metal-center geometry and a significantly shorter Fe-Ga distance (2.3590(8) Å) than its neutral bis(carbene) MOLP analogue cis,mer-[(IMe)₂(OC)₃Fe \rightarrow $GaCl_3$ (2.4443(4) Å), presumably a result of the larger NHC ligands in the former. It should be noted that very few examples of cationic, tricoordinate gallium compounds have been reported,¹⁰ and of these only a handful exhibit planar, rather than pyramidal, Ga atoms.

The cations of **4b** and **5b** can be depicted in two resonance forms as shown in Figure 4. The two resonance structures represent (formal) extremes of the Fe–Ga bonding situation, one a dative gallenium $Fe(o) \rightarrow Ga^+$ MOLP, the other a covalent gallyl Fe(II)⁺–GaCl₂ cation where the positive charge resides on the iron center. However, in reality the bonding situation presumably lies somewhere between these two extremes. Readers are directed to a related discussion about the notation and formalisms in metallaboratrane (M \rightarrow B) complexes in two letters to this journal by Hill and Parkin from 2006,¹¹ as well as discussions of metal–metal dative bonds in our *Chemical Reviews* article from 2012.³

A similar reactivity pattern was noticed when the diiron complex $[Fe_2(\mu-CO)(CO)_4(\mu-dcpm)_2]$ was treated with two equivalents of GaCl₃. This reaction was envisaged as a possible route to dinuclear bis(MOLP) complexes in which two connected metal centers each donate to one Lewis acid unit. Instead, this reaction led to the isolation of a good yield of the $[GaCl_4]^-$ salt **6b** (92%, Figure 6) after recrystallization. The ³¹P



Figure 6. Synthesis of the salt $[(dcpm)_2(OC)_5Fe \rightarrow (\mu-GaCl_2)]$ -[GaCl₄] (6b).

NMR spectrum of **6b** shows one signal (δ 57.7) that is shifted to higher field compared to that of **6a** (δ 76.5, Table 1). The IR

Table 1. Fe–Ga Distances and ³¹P NMR Data of Published Complexes and Those Prepared in This Work

complex	d(Fe-B) (Å)	$\delta(^{31}\text{P})(\text{ppm})$
Pentacarbonyl MOLP		
$[(OC)_5 Fe \rightarrow GaCl_3]^7$	2.547(1)	n.a.
Tetracarbonyl MOLPs		
[(Me₃P) (OC)₄Fe→GaCl₃] ⁷	2.4844(3)	9.75
1b	2.5072(5)	55.6
2b	2.5009(5)	n.a.
Tricarbonyl MOLPs		
3b	2.4683(7)	8.5, 13.5 ^a
3c	2.484(1)	
Cationic Fe–Ga Complexes		
4b	2.3694(5)	62.5
5b	2.3590(8)	n.a.
6b	2.4718(6), 2.4858(6)	57.7
^a The ³¹ P NMR resonances of 3a,b could not be differentiated.		

spectrum showed three carbonyl stretching bands (1980, 1947, 1785 cm⁻¹), the lowest energy band of which presumably corresponds to the bridging CO ligand. The crystallographically determined molecular structure of 6b indicated the presence of the dinuclear gallinium salt $[Fe_2(\mu-CO)(CO)_4(\mu-dcpm)_2(\mu-dcpm)$ $GaCl_2$ [GaCl₄]. The complex showed a longer Fe–Fe distance (2.8692(7) Å) than that of the dppm analogue of precursor **6a** (2.711(1) Å),¹² reflective of a reduced Fe–Fe interaction upon addition of the GaCl₂ ligand. The Fe-Ga distances in 6b (2.4718(6), 2.4858(6) Å) were also found to be significantly longer than those of mononuclear cations 4b and 5b, approaching those of the neutral MOLPs described above, presumably a consequence of the increased coordination at gallium. Weak interactions between the carbonyl carbon atoms and the Fe-bound gallium atom are evident from the relatively short Ga-C1/C5 distances (2.499(3), 2.481(3) Å). In contrast to the above syntheses of gallenium salts 4b and 5b, the selective formation of gallinium salt 6b cannot be solely attributed to steric effects, since the presence of two Lewis-basic metal centers in 6a leads to two (presumably stabilizing) $Fe \rightarrow$ Ga interactions in the product 6b.

Similar to cations **4b** and **5b**, **6b** can be depicted in a number of different resonance forms, from the double-dative gallenium $Fe(0)/Fe(0)/Ga^+$ MOLP form depicted in Figure 6 to the double-covalent gallate $Fe(II)/Fe(II)/Ga^-$. The true bonding situation lies presumably somewhere between these extremes.

Herein we have presented the outcomes of reactions of gallium trichloride with a series of zerovalent iron complexes with increasing steric bulk. When the electron density of the metal complex is kept relatively constant but the steric bulk is increased markedly, disproportionation of the GaCl₃ occurs (even when one equivalent is used), resulting in metal-stabilized gallenium salts. A similar disproportionation reaction is observed with a dinuclear iron(0) complex, in this case providing a cationic complex with a bridging GaCl₂ ligand.

EXPERIMENTAL SECTION

General Information. All syntheses were performed under an inert atmosphere of dry argon using standard Schlenk techniques or in a glovebox (MBraun). Solvents were dried by distillation over potassium (benzene, toluene), Na/K alloy (hexane, THF), or

phosphorus pentoxide (fluorobenzene, CH₂Cl₂) under argon and stored over molecular sieves (4 Å). C6D6 and CD2Cl2 were degassed by several freeze-pump-thaw cycles and stored over molecular sieves. The NMR spectra were recorded on a Bruker AMX 400 (¹H: 400.1 MHz, ¹³C: 100.6 MHz, ¹¹B: 128.4 MHz, ³¹P: 162.0 MHz) and/or a Bruker Avance 500 FT-NMR spectrometer (¹H: 500.1 MHz, ¹³C: 125.8 MHz, ¹¹B: 160.5 MHz, ³¹P: 202.5 MHz). Chemical shifts are given in ppm and were referenced to external TMS (¹H, ¹³C{¹H}), $[BF_3 \cdot OEt_2]$ (¹¹B{¹H}) and 85% H₃PO₄ (³¹P{¹H}), and coupling constants are given in Hz. Elemental analyses were obtained from an Elementar Vario MICRO cube instrument. Infrared spectra were measured on a JASCO FT/IR-6200 type A spectrometer. The light source for photochemical experiments was a Hg/Xe arc lamp (400-550 W) equipped with IR filters, irradiating at 210-600 nm. Trimethylphosphine,¹³ 1,3-dimesitylimidazol-2-ylidene,¹⁴ tricyclohexylphosphine,¹⁵ bis(dicyclohexylphosphino)methane (dcpm),¹⁶ [Fe- $(CO)_4(PCy_3)$] $(1a)_{,9a}^{,9a}$ [Fe $(CO)_4(IMes)$] $(2a)_{,9b}^{,9b}$ and [Fe $(CO)_3(IMes)_2$] $(5a)_{,9b}^{,9b}$ were prepared according to literature procedures. [Fe(CO)₅] was purchased from Strem Chemicals, and GaCl₃ from Sigma-Aldrich; both were used without further purification.

Synthesis of [Fe(CO)₃(IMes)(PMe₃)] (3a). A solution of [Fe(CO)₄(IMes)] (2a) (465 mg, 0.98 mmol) in 50 mL of benzene was treated with an excess of PMe₃ (0.31 mL, 224 mg, 2.95 mmol). The solution was irradiated in front of a mercury lamp for 16 h. The solvent was subsequently removed under vacuum, and the residue was recrystallized in toluene at -30 °C to yield **3a** (418 mg, 0.80 mmol, 81%) as a yellow crystalline solid. IR (CH₂Cl₂): 1852 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, C₆D₆, 297 K): $\delta = 1.08$ (d, ²J_{HP} = 10 Hz, 9H, CH₃), 2.14 (s, 12H, CH₃), 2.28 (s, 6H, CH₃), 6.28 (s, 2H, CH), 6.88 (s, 4H, CH). ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 297 K): $\delta = 18.6$ (s, 4C, CH₃), 19.1 (d, ¹J_{CP} = 32 Hz, 9C, CH₃), 21.2 (s, 2C, CH₃), 123.4 (d, ⁴J_{CP} = 3 Hz, 2C, CH_{Imid}), 129.5 (s, 4C, CH), 136.7 (s, 4C, C_q), 138.5 (s, 2C, C_q), 138.6 (s, 2C, C_q), 196.2 (d, ²J_{CP} = 12 Hz, C, C_{Imid}), 218.3 (d, ²J_{CP} = 32 Hz, 3C, CO). ³¹P{¹H} NMR (202.5 MHz, C₆D₆, 297 K): $\delta = 45.9$ (s). Anal. (%) Calcd for C₂₇H₃₃FeN₂O₃P: C 62.32; H 6.39; N 5.38. Found: C 62.48; H 6.26; N 5.38.

Synthesis of [Fe(CO)₃(PCy₃)₂] (4a). The literature synthesis of **4a**^{9a} was altered slightly. A procedure similar to that used for the preparation of **3a** was applied by using [Fe(CO)₅] (0.24 mL, 350 mg, 1.79 mmol) and PCy₃ (1.10 g, 3.93 mmol) to provide **4a** (970 mg, 1.43 mmol, 80%) as a white solid. IR (CH₂Cl₂): 1855 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, C₆D₆, 297 K): δ = 1.12–1.31 (m, 18H, Cy), 1.55–1.62 (m, 6H, Cy), 1.71–1.84 (m, 24H, Cy), 2.26–2.35 (m, 18H, Cy). ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 297 K): δ = 27.0 (s, 6C, Cy), 28.4 (vt, $N = |^2J_{CP} + ^4J_{CP}| = 10$ Hz, 12C, Cy), 30.6 (s, 12C, Cy), 39.4 (vt, $N = |^1J_{CP} + ^3J_{CP}| = 20$ Hz, 6C, Cy), 218.0 (t, ² $_{ZP} = 27$ Hz, 3C, CO). ³¹P{¹H} NMR (202.5 MHz, C₆D₆, 297 K): δ = 86.1 (s). Anal. (%) Calcd for C₃₉H₆₆FeO₃P₂: C 66.85; H 9.49. Found: C 67.00; H 9.38.

Synthesis of [Fe₂(CO)₅(dcpm)₂] (6a). A solution of [Fe(CO)₅] (0.5 mL, 725 mg, 3.70 mmol) in 70 mL of benzene was treated with dcpm (1.51 g, 3.70 mmol). The solution was irradiated in front of a mercury lamp for 8 d, and the resulting precipitate was filtered off. The residue was dried under vacuum and recrystallized from toluene at -30 °C to yield 6a (1.44 g, 1.31 mmol, 71%) as a light brown solid. IR (CH₂Cl₂): 1687, 1853, 1930 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, C₆D₆, 297 K): δ = 1.25–1.35 (m, 8H, Cy), 1.38–1.52 (m, 16H, Cy), 1.66–1.79 (m, 24H, Cy), 1.90–1.99 (m, 16H, Cy), 2.03–2.09 (m, 4H, CH₂), 2.26–2.35 (m, 8H, Cy), 2.42–2.54 (m, 16H, Cy). ¹³C{¹H} NMR (125.8 MHz, C₆D₆, 297 K): δ = 22.4 (s, 2C, CH₂), 26.7 (s, 8C, Cy), 28.1 (s, 16C, Cy), 30.0 (m, 16C, Cy), 40.6 (m, 8C, Cy), 237.7–238.3 (m, 5C, CO). ³¹P{¹H} NMR (202.5 MHz, C₆D₆, 297 K): δ = 76.5 (s). Anal. (%) Calcd for C₅₅H₉₂Fe₂O₅P₄: C 61.80; H 8.67. Found: C 61.44; H 8.43.

Synthesis of $[(Cy_3P)(OC)_4Fe \rightarrow GaCl_3]$ (1b). To a solution of $[Fe(CO)_4(PCy_3)]$ (1a) (50.0 mg, 0.12 mmol) in benzene (7 mL) was added GaCl₃ (19.6 mg, 0.12 mmol). The mixture was shaken and allowed to stand for 1 h. The resulting precipitate was filtered off, and the residue washed with benzene (3 × 5 mL) and pentane (3 × 5 mL). The white solid was recrystallized from C_6H_5F at -30 °C to yield 1b

(57.2 mg, 0.09 mmol, 83%) as a white crystalline solid. IR (CH₂Cl₂): 2036 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): δ = 1.30– 1.40 (m, 12H, Cy), 1.49–1.56 (m, 6H, Cy), 1.80–1.97 (m, 12H, Cy), 2.21–2.23 (m, 3H, Cy). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 26.1 (d, ⁴J_{CP} = 2 Hz, 3C, Cy), 27.7 (d, ²J_{CP} = 11 Hz, 6C, Cy), 29.9 (d, ³J_{CP} = 3 Hz, 6C, Cy), 37.9 (d, ¹J_{CP} = 20 Hz, 3C, Cy), 205.7 (d, ²J_{CP} = 10 Hz, 4C, CO). ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 297 K): δ = 55.6 (s). Anal. (%) Calcd for C₂₂H₃₃Cl₃FeGaO₄P: C 42.32; H 5.33. Found: C 42.03; H 5.34.

Synthesis of [(IMes)(OC)₄**F**e→**GaCl**₃] **(2b).** A procedure similar to that used for the preparation of **1b** was applied by using [Fe(CO)₄(IMes)] **(2a)** (30.0 mg, 0.06 mmol) and 1 equiv of GaCl₃ (11.2 mg, 0.06 mmol) to provide **2b** (38.4 mg, 0.059 mmol, 93%) after recrystallization in CH₂Cl₂ at −30 °C as a white solid. IR (CH₂Cl₂): 2062 (ν_{CO}) cm^{-1.} ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): δ = 2.09 (s, 12H, CH₃), 2.39 (s, 6H, CH₃), 7.13 (s, 4H, CH), 7.41 (s, 2H, CH_{1mid}). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 17.2 (s, 3C, CH₃), 20.9 (s, 2C, CH₃), 127.3 (s, 2C, CH_{1mid}), 128.3 (s, 4C, C_{Ar}), 130.2 (s, 4C, CH_{Ar}), 135.4 (s, 2C, C_{Ar}), 141.9 (s, 2C, C_{Ar}), 173.1 (s, 1C, C_{Imid}), 202.9 (s, 4C, CO). Anal. (%) Calcd for C₂₅H₂₄Cl₃FeGaN₂O₄. (CH₂Cl₂)_{0.75}: C 43.43; H 3.61; N 3.93. Found: C 43.27; H 3.68; N 3.90. One molecule of dichloromethane is observed in the crystal, some of which presumably was removed when these crystals were placed under high vacuum for elemental analysis measurement.

Synthesis of [(IMes)(Me₃P)(OC)₃Fe→GaCl₃] (3b,c). A procedure similar to that used for the preparation of 1b was applied by using $[Fe(CO)_3(PMe_3)(IMes)]$ (3a) (20.0 mg, 38.4 μ mol) and 1 equiv of $GaCl_3$ (6.8 mg, 38.4 μ mol) to provide **3b**, c (18.3 mg, 26.3 μ mol, 68%) as a colorless crystalline solid. IR (CH₂Cl₂): 2073, 2012, 1985 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): $\delta = 1.50$ (d, ²J_{HP} = 11 Hz, 9H, CH₃), 1.55 (d, ${}^{2}J_{HP} = 11$ Hz, 9H, CH₃), [2.01 (s, 12H, CH_{Ar}), 2.35 (s, 6H, CH_{Ar})], [2.34 (s, 12H, CH_{Ar}), 2.53 (s, 6H, CH_{Ar})], 6.98 (br, 2H, CH_{Ar}), 7.04 (br, 4H, CH_{Ar}), 7.14 (s, 4H, CH_{Ar}), 7.27 (2H, CH_{Ar}) (spectrum contained signals for both isomers). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 18.55 (d, ¹J = 34 Hz, 3C, CH₃), 19.00 (s, 2C, CH₃), 20.44 (d, ${}^{1}J$ = 32 Hz, 3C, CH₃), 20.71 (s, 2C, CH₃), 21.16 (s, 4C, CH₃), 21.18 (s, 4C, CH₃), 124.47 (d, ${}^{4}J_{CP}$ = 3 Hz, 2C, CH_{Imid}), 125.73 (s, 2C, CH_{Imid}), 127.23 (s, 4C, CH), 129.55 (s, 2C, CH_{Imid}), 123.73 (s, 2C, CH_{Imid}), 127.23 (s, 4C, CH), 129.33 (s, 4C, CH), 130.67 (s, 4C, C_q), 136.24 (s, 4C, C_q), 136.71 (s, 4C, C_q), 138.60 (s, 4C, C_q), 140.92 (s, 2C, C_q), 141.41 (s, 2C, C_q), 179.29 (d, ${}^{2}J_{CP} = 13$ Hz, C, C_{Imid}), 183.96 (d, ${}^{2}J_{CP} = 16$ Hz, C, C_{Imid}), 207.98 (d, ${}^{2}J_{CP} = 32$ Hz, 2C, CO), 208.07 (d, ${}^{2}J_{CP} = 19$ Hz, 1C, CO), 208.34 (d, ${}^{2}J_{CP} = 25$ Hz, 2C, CO), 209.23 (d, ${}^{2}J_{CP} = 23$ Hz, 1C, CO) (spectrum contained signals for both isomers). ³¹P{¹H} NMR (202.5 MHz, CD_2Cl_2 , 297 K): $\delta = 8.5$ (s), 13.5 (s). Anal. (%) Calcd for C₂₇H₂₂Cl₂FeGaN₂O₂P: C 46.56, H 4.78, N 4.02. Found: C 46.38, H 4.70, N 3.69.

Synthesis of [(Cy₃P)₂(OC)₃Fe→GaCl₂][GaCl₄] (4b). A procedure similar to that used for the preparation of 1b was applied by using [Fe(CO)₃(PCy₃)₂] (4a) (30.0 mg, 44.3 µmol) and 2 equiv of GaCl₃ (15.6 mg, 88.7 µmol) in toluene to provide 4b (35.2 mg, 41.3 µmol, 93%) as a colorless crystalline solid. IR (CH₂Cl₂): 2065, 2009, 1971 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): δ = 1.38–1.44 (m, 18H, Cy), 1.65–1.67 (m, 12H, Cy), 1.83 (s, 6H, Cy), 1.99–2.03 (m, 24H, Cy), 2.35–2.37 (m, 6H, Cy). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 25.8 (s, 6C, Cy), 27.8 (vt, $N = |^{2}J_{CP}+^{4}J_{CP}| = 10$ Hz, 12C, Cy), 31.0 (s, 12C, Cy), 40.3 (vt, $N = |^{1}J_{CP}+^{3}J_{CP}| = 18$ Hz, 12C, Cy), 207.3 (t, ²J_{CP} = 17 Hz, 2C, CO), 208.0 (t, ²J_{CP} = 19 Hz, 2C, CO). ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 297 K): δ = 62.5 (s). Anal. (%) Calcd for C₃₉H₆₆Cl₆FeGa₂O₃P₂: C 44.49, H 6.32. Found: C 43.97, H 6.10.

Synthesis of [(IMes)₂**(OC)**₃**Fe**→**GaCl**₂]**[GaCl**₄] **(5b).** A procedure similar to that used for the preparation of **1b** was applied by using [Fe(CO)₃(IMes)₂] **(5a)** (30.0 mg, 40.1 µmol) and 2 equiv of GaCl₃ (14.1 mg, 80.2 µmol) to provide **5b** (28.8 mg, 26.1 µmol, 65%) as a colorless crystalline solid. IR (CH₂Cl₂): 2025, 2006, 1974 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): δ = 1.97 (s, 24H, CH₃), 2.38 (s, 12H, CH₃), 7.08 (s, 8H, CH), 7.23 (s, 4H, CH). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 18.76 (s, 8C, CH₃), 21.34 (s, 4C,

CH₃), 129.20 (s, 8C, CH_{Mes}), 131.35 (s, 4C, CH_{Imid}), 135.12 (s, 8C, C_q), 137.55 (s, 4C, C_q), 143.22 (s, 4C, C_q), 169.76 (s, 2C, C_{Imid}), 204.50 (s, 1C, CO), 205.39 (s, 2C, CO). Anal. (%) Calcd for C₄₅H₄₈Cl₆FeGa₂N₄O₃: C 49.09, H 4.39, N 5.09. Found: C 49.42, H 4.46, N 5.42.

Synthesis of [(dcpm)₂(OC)₅Fe₂(μ-GaCl₂)][GaCl₄] (6b). A procedure similar to that used for the preparation of 1b was applied by using $[Fe_2(\mu$ -CO)(CO)₅(μ-dcpm)₂] (6a) (50.0 mg, 45.6 μmol) and 2 equiv of GaCl₃ (16.1 mg, 91.2 μmol) to provide 6b (60.5 mg, 42.2 μmol, 92%) as a red crystalline solid. IR (CH₂Cl₂): 1980, 1947, 1785 (ν_{CO}) cm⁻¹. ¹H NMR (500.1 MHz, CD₂Cl₂, 297 K): δ = 1.30– 1.60 (m, 42H, Cy), 1.75–2.17 (m, 38H, Cy), 2.22–2.39 (m, 8H, Cy), 2.41–2.55 (m, 4H, CH₂). ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂, 297 K): δ = 21.2 (s, 1C, CH₂), 22.7 (s, 1C, CH₂), 26.1 (d, ¹J_{CP} = 7 Hz, 8C, Cy), 27.3 (s, 4C, Cy), 28.1 (s, 12C, Cy), 28.7 (m, 4C, Cy), 30.9 (s, 4C, Cy), 31.3 (s, 4C, Cy), 32.2 (s, 4C, Cy), 39.9 (s, 4C, Cy), 44.1 (s, 4C, Cy), 212.5 (br, 2C, CO) 214.5 (t, ²J_{CP} = 7 Hz, 2C, CO), 259.6 (t, ²J_{CP} = 11 Hz, 1C, CO). ³¹P{¹H} NMR (202.5 MHz, CD₂Cl₂, 297 K): δ = 57.7 (s). Anal. (%) Calcd for C₅₅H₉₂Cl₆Fe₂Ga₂O₅P₄: C 46.49, H 6.53. Found: C 46.51, H 6.46.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00045.

Experimental procedures (PDF) Crystallographic data (ZIP)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Coffey, C. E.; Lewis, J.; Nyholm, R. S. J. Chem. Soc. 1964, 1741–1749.

(2) Nowell, I. N.; Russell, D. R. Chem. Commun. 1967, 817-817.

(3) Bauer, J.; Braunschweig, H.; Dewhurst, R. D. Chem. Rev. 2012, 112, 4329-4346.

(4) (a) Bauer, J.; Braunschweig, H.; Damme, A.; Radacki, K. Angew. Chem., Int. Ed. 2012, 51, 10030-10033. (b) Bauer, J.; Braunschweig, H.; Radacki, K. Chem. Commun. 2012, 48, 10407-10409. (c) Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Hupp, F.; Jimenez-Halla, J. O. C.; Radacki, K. Chem. Commun. 2012, 48, 10410-10412. (d) Bauer, J.; Bertermann, R.; Braunschweig, H.; Gruss, K.; Hupp, F.; Kramer, T. Inorg. Chem. 2012, 51, 5617-5626. (e) Bauer, J.; Braunschweig, H.; Dewhurst, R. D.; Radacki, K. Chem. - Eur. J. 2013, 19, 8797-8805. (f) Hupp, F.; Ma, M.; Kroll, F.; Jimenez-Halla, J. O. C.; Dewhurst, R. D.; Radacki, K.; Stasch, A.; Jones, C.; Braunschweig, H. Chem. - Eur. J. 2014, 20, 16888-16898. (g) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Schneider, C. Chem. Commun. 2014, 50, 15685-15688. (h) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Kaufmann, C.; Phukan, A. K.; Schneider, C.; Ye, Q. Chem. Sci. 2014, 5, 4099-4104. (i) Braunschweig, H.; Celik, M. A.; Dewhurst, R. D.; Heid, M.; Hupp, F.; Sen, S. S. Chem. Sci. 2015, 6, 425-435. (j) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Wolf, J. Chem. - Eur. J. 2015, 21, 1860-1862. (k) Ma, M.; Sidiropoulos, A.; Ralte, L.; Stasch, A.; Jones, C. Chem. Commun. 2013, 49, 48-50. (1) Maloinowski, P. J.; Krossing, I. Angew. Chem., Int. Ed. 2014, 53, 13460-13462.

Organometallics

(5) Karen, P.; McArdle, P.; Takats, J. Pure Appl. Chem. 2014, 86, 1017–1081.

(6) (a) Arndt, L. W.; Darensbourg, M. Y.; Delord, T.; Bancroft, B. T. J. Am. Chem. Soc. 1986, 108, 2617-2627. (b) Einstein, F. W. B.; Jones, T.; Pomeroy, R. K.; Rushman, P. J. Am. Chem. Soc. 1984, 106, 2707-2708. (c) Davis, H. B.; Einstein, F. W. B.; Glavina, P. G.; Jones, T.; Pomeroy, R. K.; Rushman, P. Organometallics 1989, 8, 1030-1039. (d) Shipley, J. A.; Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K. Organometallics 1991, 10, 3620-3629. (e) Jiang, F.; Jenkins, H. A.; Biradha, K.; Davis, H. B.; Pomeroy, R. K.; Zaworotko, M. J. Organometallics 2000, 19, 5049-5062. (f) Einstein, F. W. B.; Jennings, M. C.; Krentz, R.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. Inorg. Chem. 1987, 26, 1341-1344. (g) Jiang, F.; Male, J. L.; Biradha, K.; Leong, W. K.; Pomeroy, R. K.; Zaworotko, M. J. Organometallics 1998, 17, 5810-5819. (h) Einstein, F. W. B.; Pomeroy, R. K.; Rushman, P.; Willis, A. C. J. Chem. Soc., Chem. Commun. 1983, 854-855. (i) Funaioli, T.; Marchetti, F.; Fachinetti, G. Chem. Commun. 1999, 2043-2044. (j) Song, L.; Trogler, W. C. Angew. Chem., Int. Ed. Engl. 1992, 31, 770-772. (k) Cathey, C.; Lewis, J.; Raithby, P. R.; Ramírez de Arellano, M. C. J. Chem. Soc., Dalton Trans. 1994, 3331-3332. (1) Song, H.-B.; Wang, Q.-M.; Zhang, Z.-Z.; Mak, T. C. W. J. Organomet. Chem. 2000, 605, 15-21. (m) Song, H.-B.; Zhang, Z.-Z.; Mak, T. C. W. New J. Chem. 2002, 26, 113-119. (n) Chan, W.-H.; Zhang, Z.-Z.; Mak, T. C. W.; Che, C.-M. J. Chem. Soc., Dalton Trans. 1998, 803-810. (o) Coco, S.; Espinet, P.; Mayor, F.; Solans, X. J. Chem. Soc., Dalton Trans. 1991, 2503-2509. (p) Khasnis, D. V.; Le Bozec, H.; Dixneuf, P. H.; Adams, R. D. Organometallics 1986, 5, 1772-1777. (q) Le Bozec, H.; Dixneuf, P. H.; Adams, R. D. Organometallics 1984, 3, 1919-1921. (r) Batchelor, R. J.; Davis, H. B.; Einstein, F. W. B.; Pomeroy, R. K. J. Am. Chem. Soc. 1990, 112, 2036-2037. (s) Batchelor, R. J.; Einstein, F. W. B.; Pomeroy, R. K.; Shipley, J. A. Inorg. Chem. 1992, 31, 3155-3157. (t) Bertsch, S.; Bertermann, R.; Braunschweig, H.; Damme, A.; Dewhurst, R. D.; Phukan, A. K.; Saalfrank, C.; Vargas, A.; Wennemann, B.; Ye, Q. Angew. Chem., Int. Ed. 2014, 53, 4240-4243. (u) Bertsch, S.; Braunschweig, H.; Dewhurst, R. D.; Radacki, K.; Saalfrank, C.; Wennemann, B.; Ye, Q. Organometallics 2014, 33, 3649-3651.

(7) Braunschweig, H.; Dewhurst, R. D.; Hupp, F.; Kaufmann, C.;
Phukan, A. K.; Schneider, C.; Ye, Q. *Chem. Sci.* 2014, *5*, 4099–4104.
(8) Braunschweig, H.; Brunecker, C.; Dewhurst, R. D.; Schneider, C.;
Wennemann, B. *Chem. - Eur. J.* 2015, *21*, 19195–19201.

(9) (a) Whitmire, K. H.; Lee, T. R. J. Organomet. Chem. **1985**, 282, 95–106. (b) Warratz, S.; Postigo, L.; Royo, B. Organometallics **2013**, 32, 893–897.

(10) (a) Korolev, A. V.; Delpech, F.; Dagorne, S.; Guzei, I. A.; Jordan, R. F. Organometallics **2001**, 20, 3367–3369. (b) Bunn, N. R.; Aldridge, S.; Kays, D. L.; Coombs, N. D.; Rossin, A.; Willock, D. J.; Day, J. K.; Jones, C.; Ooi, L.-L. Organometallics **2005**, 24, 5891–5900. (c) Coombs, N. D.; Bunn, N. R.; Kays, D. L.; Day, J. K.; Ooi, L.-L.; Aldridge, S. Inorg. Chim. Acta **2006**, 359, 3693–3698. (d) Slattery, J. M.; Higelin, A.; Bayer, T.; Krossing, I. Angew. Chem., Int. Ed. **2010**, 49, 3228–3231. (e) Lichtenthaler, M. R.; Stahl, F.; Kratzert, D.; Benkmil, B.; Wegner, H. A.; Krossing, I. Eur. J. Inorg. Chem. **2014**, 2014, 4335– 4341.

(11) (a) Hill, A. F. Organometallics **2006**, *25*, 4741–4743. (b) Parkin, G. Organometallics **2006**, *25*, 4744–4747.

(12) Hitchcock, P. B.; Madden, T. J.; Nixon, J. F. J. Organomet. Chem. **1993**, 463, 155–162.

(13) Luetkens, M. L.; Sattelberger, A. P.; Murray, H. H.; Basil, J. D.; Fackler, J. P.; Jones, R. A.; Heation, D. E. *Inorg. Synth.* **1990**, *28*, 305– 310.

(14) Bantreil, X.; Nolan, S. P. Nat. Protoc. 2011, 6, 69-77.

(15) Issleib, K.; Brack, A. Z. Anorg. Allg. Chem. 1954, 277, 258–270.

(16) Wolf, J.; Manger, M.; Schmidt, U.; Fries, G.; Barth, D.; Weberndörfer, B.; Vicic, D. A.; Jones, W. D.; Werner, H. J. Chem. Soc., Dalton Trans. **1999**, 1867–1876.