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Synthesis of *Bis*(trityl)iron(II) and Formation of the Iron(0)-Stabilized *o,o*-isomer of Gomberg's Dimer

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ABSTRACT: Treatment of $Fe(OAc)_2$ in THF with 2 equiv of $Li(CPh_3)$ at –25 °C results in formation of $[Fe(\eta^5\text{-}CPh_3)_2]$ (**1**) in 22% yield. Complex **1** was characterized by X-ray crystallography, NMR spectroscopy, and ^{57}Fe Mössbauer spectroscopy, and features an η^5 binding mode of its trityl ligands. Complex **1** functions as an effective Fe(0) synthon. For example, reaction of **1** with excess CO results in formation of $[Fe(CO)_5]$ and Gomberg's dimer. Additionally, thermolysis of **1** with 5 equiv of $P(OMe)_3$ results in formation of the Fe(0) complex, $[\{(\mu,\eta^4{:}\eta^4\text{-}Ph_2CC_6H_5C_6H_5CPh_2)\{Fe(P(OMe)_3)_3\}_2]$ (**2**), which features the novel *o,o*-isomer of Gomberg's dimer bound by two $[Fe^0(P(OMe)_3)_3]$ fragments via an η^4 interaction.

Since Gomberg's seminal report in 1900,[1] the triphenylmethyl (i.e., trityl) radical has enjoyed enduring interest as the first persistent organic radical. In the solid state, trityl exists as a dimer, which was initially formulated as the hexaphenylethane isomer.[2, 3] However, this α,α-isomer proved controversial, and in 1905 Jacobson suggested that α,p-quinoid isomer was more likley.[2, 4, 5] Lankamp and co-workers subsequently confirmed the α,p-structure of Gomberg's dimer by ^1H NMR spectroscopy in 1968 – an early demonstration of the power of NMR spectroscopy for structure elucidation.[2, 5] Gomberg's dimer has also been crystallographically characterized.[6] More recently, para substitution or aryl ring annulation of the triphenylmethyl fragments has allowed access to the α,α-isomer.[7-10] Aryl ring annulation has also allowed access to the α,o-isomer.[9] Despite these advances, however, the higher energy *o,o*-, *p,p*-, and *o,p*-isomers have remained elusive.[10, 11]

Recently, we completed the characterization of bis(trityl)nickel(II), $[Ni^{II}(\eta^3\text{-}CPh_3)_2]$, which we subsequently employed as an Ni(0) synthon for the synthesis of atomically-precise nanoclusters (APNCs).[12] During the course of this work, we realized that the analogous Fe complex, $[Fe^{II}(CPh_3)_2]$, was unknown. Given the paucity of Fe(0) synthons,[13-17] we pursued its synthesis to evaluate its utility as a APNC precursor. Herein, we report the synthesis and characterization of $[Fe^{II}(\eta^5\text{-}CPh_3)_2)]$. This complex reacts with excess $P(OMe)_3$ to form the $[Fe^0(P(OMe)_3)_3]$-stabilized *o,o*-isomer of Gomberg's dimer.

Reaction of $Fe(OAc)_2$ with 2 equiv of *in situ* generated $[Li][CPh_3]$[12, 18, 19] in THF at −25 °C results in the formation of $[Fe(\eta^5\text{-}CPh_3)_2]$ (**1**), which can be isolated as a deep red crystalline solid in 22% yield after work-up (Scheme 1). We ascribe the low yield of **1** to the unwanted reduction of $Fe(OAc)_2$ by $[Li][CPh_3]$, which results in formation of low valent Fe-containing products. Consistent with this hypothesis, we observe the formation of an insoluble black solid during the reaction. Several attempts were made to improve the yield of **1**. For example, reaction of $FeBr_2$ or $[FeBr_2(THF)_2]$ with 2 equiv of $MCPh_3$ (M = K, Li) also results in formation of **1**, but in comparable yields. In contrast, reaction of FeI_2 or $FeCl_2$ with $MCPh_3$ (M = K, Li) only results in formation of intractable mixtures, whereas treatment of $[Fe(Mes)_2]_2$ with Ph_3CH in C_6D_6 at room temperature did not result in any apparent reaction.
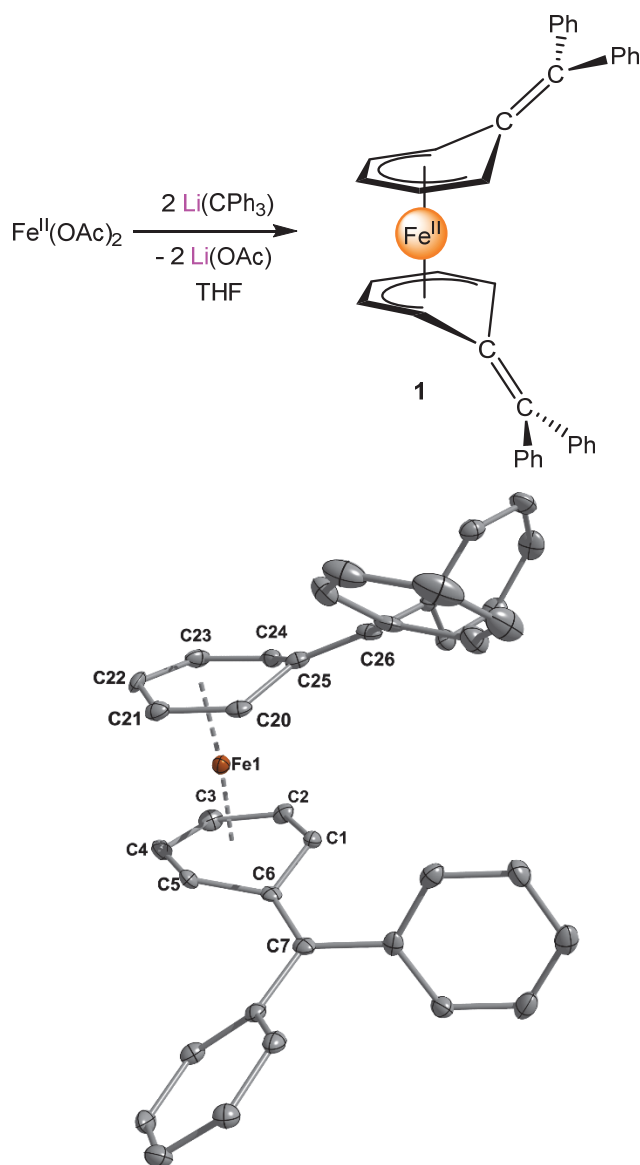
Scheme 1. Synthesis of **1**.

Figure 1. ORTEP drawing of **1**·CH_2Cl_2 shown with 50% probability thermal ellipsoids. All hydrogen atoms and methylene chloride solvate are omitted for clarity. Selected bond lengths (Å): Fe1-C1 = 2.121(3), Fe1-C2 = 2.057(3), Fe1-C3 = 2.066(3), Fe1-C4 = 2.047(3), Fe1-C5 = 2.116(3), Fe1-C20 = 2.141(3), Fe1-C21 = 2.056(3), Fe1-C22 = 2.066(3), Fe1-C23 = 2.046(3), Fe1-C24 = 2.112(3), C6-C7 = 1.366(4), C25-C26 = 1.368(4).

Complex **1** crystallizes in the monoclinic space group $P2_1/n$ as the methylene chloride solvate, **1**·CH_2Cl_2 (Figure 1). Each trityl ligand in **1** adopts an η^5-cyclohexadienyl binding mode, resulting in a ferrocene-like, 18-electron sandwich complex. This binding mode has also been observed in $[Ti(CO)_4(\eta^5\text{-}CPh_3)]$ and the closely-related $[Fe\{\eta^5\text{-}C(SiMe_3)Ph_2\}_2]$,[20, 21] but stands in contrast to the $\eta^1\text{-}CPh_3$ binding mode found in $[L^{Me}Fe(\eta^1\text{-}CPh_3)]$ (L^{Me} = $\{(2,6\text{-}^iPr_2C_6H_3)NC(Me)\}_2CH$).[22] The η^5-bound

rings are folded along the C1-C5 and C20-C24 vectors, with fold angles of 26 and 21°, respectively. For comparison, [Ti(CO)$_4$(η^5-CPh$_3$)]$^-$ features a fold angle of 16°. The average Fe-C distance is 2.083(9) Å (range = 2.046(3) to 2.141(3) Å), whereas the C-C bonds within the Fe-bound portion of cyclohexadienyl unit range from 1.397(4) to 1.414(4) Å. These values are similar to those reported for other edge-bridged, open ferrocene complexes, such as [Fe{η^5-C(SiMe$_3$)Ph$_2$)$_2$}] and [Fe(η^5-6,6'-C$_6$H$_5$Me$_2$)$_2$].[20, 23] The C-C distances within the exocyclic alkene groups (C6-C7 = 1.366(4), C25-C26 = 1.368(4) Å) are consistent with those expected for a double bond. In addition, the sum of angles around C6 (359.24°), C7 (359.99°), C25 (359.54), and C26 (359.82°) are consistent with the expected sp^2 hybridization at those atoms.

As a solid, **1** is stable under an inert atmosphere at −25 °C for several months. However, it quickly decomposes when exposed to air, both in the solid-state and solution. Complex **1** is soluble in THF, toluene, benzene, methylene chloride, and chloroform, but is insoluble in pentane, hexanes, and methanol. It is very sparingly soluble in diethyl ether and acetonitrile. The room temperature ^{1}H NMR spectrum of **1** in C$_6$D$_6$ exhibits resonances at 4.59, 4.24, and 4.17 ppm, in a 4:2:4 ratio, respectively (Figure S2). These resonances are assignable to the C2/C6, C3/C5, and C4 proton environments of η^5-cyclohexadienyl fragment (see SI for atom numbering scheme). A similar pattern of resonances was reported for [Fe(η^5-6,6'-C$_6$H$_5$Me$_2$)$_2$].[24] The ^{13}C{^{1}H} NMR spectrum of **1** features resonances at 143.72 and 112.59 ppm, which are assignable to the *exo* and *endo* alkene environments, respectively. The ESI mass spectrum of **1** in THF, in positive ion mode, displays a single peak at 543.12 *m/z* (calcd 543.17 *m/z*) assignable to [**1** + H]$^+$, consistent with our proposed formulation of **1** (Figures S14-S15). Additionally, the zero-field ^{57}Fe Mössbauer spectrum of **1** at 90 K features a symmetric doublet with δ = 0.38 mm/s and $|\Delta E_Q|$ = 0.49 mm/s (Figure S13). For comparison, Fc has δ = 0.531(3) mm/s and $|\Delta E_Q|$ = 2.419(1) mm/s, whereas [Fe(η^5-6,6'-C$_6$H$_5$Me$_2$)$_2$] has δ = 0.488(1) and $|\Delta E_Q|$ = 1.143(1) mm/s.[25] Finally, the cyclic voltammogram of **1** in CH$_2$Cl$_2$ reveals a reversible oxidation feature at -0.58 V (vs. Fc/Fc$^+$; Figure S20), which we attribute to the Fe(II/III) couple. The more negative potential of this feature vs. that of Fc is consistent with the greater electron density at the Fe center suggested by the ^{57}Fe Mössbauer results. For further comparison, [Fe(η^5-6,6'-C$_6$H$_5$Me$_2$)$_2$] features a reversible Fe(II/III) couple at −0.46 V (vs. Fc/Fc$^+$).[23]

To evaluate the suitability of **1** as an Fe(0) synthon, we monitored the reaction of **1** with CO (1 atm) in CD$_2$Cl$_2$ (Figure S4). The ^{1}H NMR spectrum of the reaction mixture after 4 d at room temperature reveals the complete consumption of **1**, along with formation of Gomberg's dimer and triphenylmethane in 20% and 37% spectroscopic yields, respectively (Scheme 2).[5, 12, 26, 27] The solution-phase IR spectrum of this mixture displays two strong bands at 2023 and 1990 cm^{-1}, which are assignable to the E′ and A$_2$″ stretching modes of [Fe(CO)$_5$] (Figure S12).[28] In addition, the ^{13}C{^{1}H} NMR spectrum of this mixture displays a resonance at 211 ppm, which matches the ^{13}C NMR chemical shift reported for [Fe(CO)$_5$] (Figure S5).[29] Similarly, the reaction of [Ni^{II}(η^3-CPh$_3$)$_2$] with CO forms [Ni(CO)$_4$], although in this case the reaction is essentially instantaneous.[12]

Scheme 2. Reactivity of **1**.
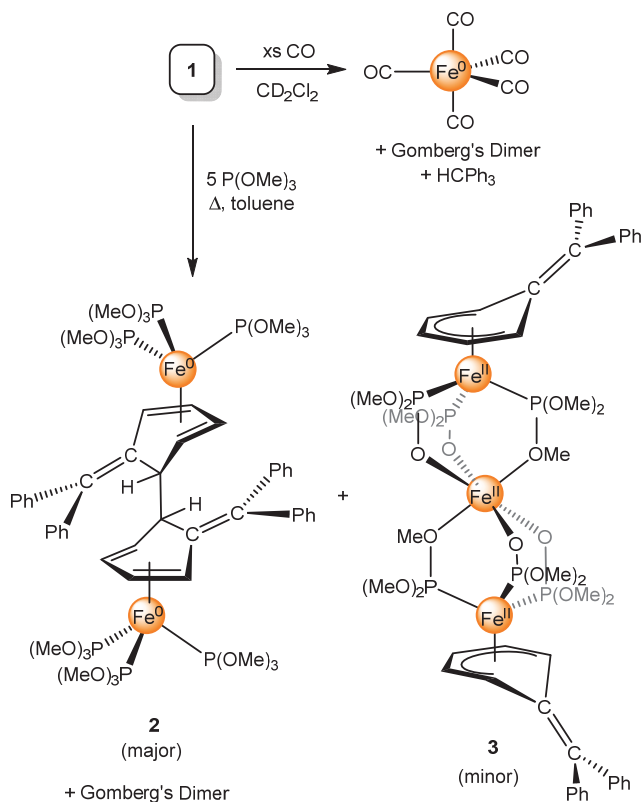
We also screened the reactivity of **1** with excess P(OMe)$_3$. Thus, heating a toluene solution of **1** and P(OMe)$_3$ (5 equiv) for several days resulted in the complete consumption of **1** along with the generation of Gomberg's dimer and two new P(OMe)$_3$-containing complexes, as assayed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy (Figure S8-S9). After work-up, we obtained [(μ,η^4:η^4-Ph$_2$CC$_6$H$_5$C$_6$H$_5$CPh$_2$){Fe(P(OMe)$_3$)$_3$}$_2$] (**2**) and [{(η^5-CPh$_3$)Fe(μ-*P,O*-P(OMe)$_3$(μ-*P,O*-P(O)(OMe)$_2$)$_2$}$_2$Fe] (**3**) as a mixture of crystalline solids in an 19:1 ratio, respectively (Scheme 2). Complexes **2** and **3** are sparingly soluble in pentane and hexanes and are soluble in diethyl ether, benzene, toluene, and tetrahydrofuran. Their similar solubilities precluded their separation by selective crystallization. Because they were isolated as a mixture, we were unable to completely characterize either complex.

Complex **2** crystallizes in the monoclinic space group *P*2$_1$/*n* (Figure 2). It consists of the *o,o*-isomer of Gomberg's Dimer, wherein each cyclohexadiene ring binds an the Fe(P(OMe)$_3$)$_3$ fragment in the η^4 fashion. The C-C bond connecting the two cyclohexadiene rings (C7-C26 = 1.599(7) Å) is somewhat longer than a typical C-C single bond (1.54 Å),[9, 10, 30] as well as the analogous C-C bond in [(μ,η^4:η^4-C$_6$H$_5$C$_6$H$_5$){Fe(CO)$_3$}$_2$] (1.542(7) Å),[31] consistent with higher energy of this isomer. For comparison the α,α C-C distance in [{(4-Ph-3,5-^{t}Bu$_2$C$_6$H$_2$)$_3$C}$_2$] is 1.47(2) Å and the α,*p* C-C distance in Gomberg's dimer is 1.589(6) Å.[6] The Fe-C distances range from 2.031(6) to 2.148(6) Å (avg. 2.09(2) Å). Similar values are observed for [(η^4-C$_6$H$_8$)Fe(CO)$_2$L] (L = CO, PPh$_3$, EtNC, P(*o*-tolyl)$_3$).[32-37] The C-C bond lengths in the Fe-bound portion of the cyclohexadiene ring range from 1.402(8) to 1.435(8) Å. Within this unit, the shortest bonds are observed for C4-C5 (1.402(8) Å) and C23-C24 (1.403(8) Å). This pattern is typical of η^4-cyclohexadiene complexes.[32] The dearomatization of the cyclohexadiene ring is further evidenced by the cyclohexadiene fold angles (38.6° and 37.9°) and by the long C2-C7 and C21-C26 distances (1.525(7) and 1.518(7) Å, respectively). The C-C

distances within the exocyclic alkene groups (C1-C2 = 1.343(8), C20-C21 = 1.363(7) Å) are similar to those observed for **1**. Finally, the average Fe-P distance (2.13(5) Å) is similar to those seen in other Fe(0) phosphite complexes.[38-40] Complex **3** was also characterized by X-ray crystallography (Figure S1), confirming its formulation as a trimetallic complex. Complete crystallographic details can be found in the Supporting Information.
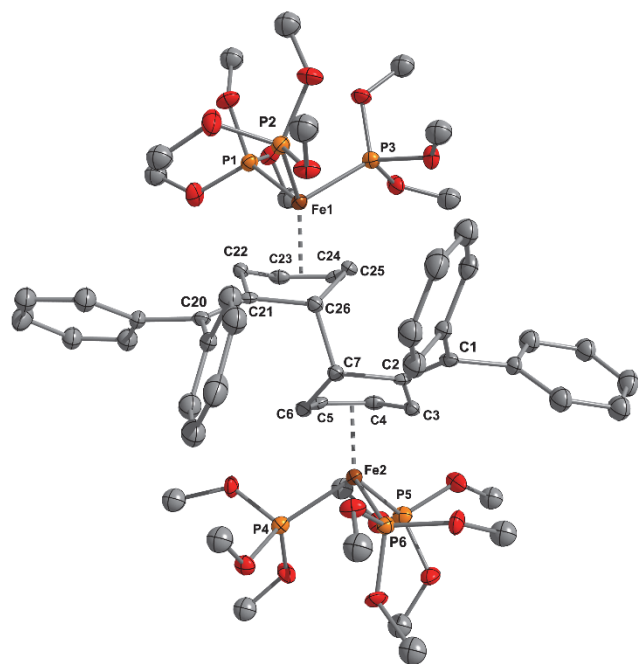

Figure 2. ORTEP drawing of **2** shown with 50% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C7-C26 = 1.599(7), C2-C7 = 1.525(7), C21-C26 = 1.518(7), C1-C2 = 1.343(8), C20-C21 = 1.363(7), C4-C5 = 1.402(8) Å, C23-C24 = 1.403(8), Fe1-C22 = 2.148(6), Fe1-C23 = 2.031(6), Fe1-C24 = 2.040(6), Fe1-C25 = 2.124(5), Fe2-C3 = 2.128(6), Fe2-C4 = 2.037(6), Fe2-C5 = 2.045(5), Fe2-C6 = 2.140(5), Fe1-P1 = 2.1204(18), Fe1-P2 = 2.1353(19), Fe1-P3 = 2.1241(18), Fe2-P4 = 2.1252(19), Fe2-P5 = 2.1429(19), Fe2-P6 = 2.1214(19).

The $^{31}P\{^1H\}$ NMR spectrum of the mixture in C_6D_6 consists of a singlet at 185 ppm (Figure S9), which we have assigned to **2**, along with resonances at 176 (d, 4P, J_{PP} = 143 Hz) and 124 ppm (t, 2P, J_{PP} = 143 Hz), which are assignable to **3**. The ^1H NMR spectrum of this solution features a singlet at 3.47 ppm assignable to the methoxy resonances of the $P(OMe)_3$ ligands of **2** (Figure S8). Additionally, the spectrum features resonances at 2.92, 3.41, 3.60, and 5.36, which are assignable to five unique proton environments of the Fe-bound η^4-cyclohexadienyl fragment of **2**. The most downfield of these consists of two overlapping multiplets, whereas the most upfield of these is assignable to the protons attached to the carbon atoms involved in the C-C bond connecting the two cyclohexadiene rings. This ^1H NMR spectrum also features resonances at 5.69 and 4.37 ppm, which are assignable to the C4 and C2/C6 environments of the Fe-bound η^5-cyclohexadienyl fragment of **3**, respectively (see SI for atom numbering scheme). Finally, the ESI-MS spectrum of the mixture in THF, in positive ion mode, displays a principal peak at 671.14 *m/z*, which is assignable to $[Fe(CPh_3)(P(OMe)_3)_3]^+$ (calcd 671.14 *m/z*) and is in good agreement with the simulated spectrum (Figures S16-S18). No peak

for the parent ion of [**3**]$^+$ was observed in the spectrum, suggesting its gas-phase decomposition.

To account for the formation of **2**, we suggest that thermolysis of **1** in the presence of $P(OMe)_3$ results in loss of trityl radical and formation of the Fe(I) piano-stool complex, $[(\eta^5\text{-}CPh_3)Fe^I(P(OMe)_3)_3]$. This intermediate can then dimerize to form complex **2**, a transformation that is driven by formation of an energetically favorable Fe(0)-η^4-butadiene interaction.[31, 41-45] We propose that this Fe(I) intermediate can also lose Me radical, forming an Fe(II) phosphonate, $[(\eta^5\text{-}CPh_3)Fe^{II}(P(OMe)_3)_2(P(O)(OMe)_2)]$, which serves as a precursor to **3**. Similar reactivity has been reported for $[CpCr(CO)_3]_2$ and $[CpRu(CO)_2]_2$,[46-49] although in our case we do not know the fate of the Me group. Interestingly, the Kläui ligand analog of **3**, $[\{CpCo(P(O)(OEt)_2)_3\}_2Fe]$ features a high spin Fe^{2+} center,[50] whereas the central Fe^{2+} in complex **3** is low spin. We attribute this difference to the tetragonal crystal field imposed by the $\{(\eta^5\text{-}CPh_3)Fe(P(OMe)_3(P(O)(OMe)_2)_2\}$ fragment, which contrast with the octahedral crystal field imposed by the Kläui ligand.

In summary, we have synthesized bis(trityl)iron(II), $[Fe(\eta^5\text{-}CPh_3)_2]$ (**1**). Complex **1** has proven to be a good source of Fe(0), as evidenced by its reactions with CO or $P(OMe)_3$, which result in the formation of $[Fe(CO)_5]$ and $[(\mu,\eta^4:\eta^4\text{-}Ph_2CC_6H_5C_6H_5CPh_2)\{Fe(P(OMe)_3)_3\}_2]$, respectively. The latter complex represents the first example of the *o,o*-isomer of Gomberg's dimer, which differs from the usual α,*p*-isomer observed in solution and the solid-state, and provides further understanding of this historically-important system. Additionally, given our preliminary results, we suggest that **1** could function as a precursor to low-valent Fe APNCs, a class of materials that has resisted isolation thus far.[12, 51, 52]

ASSOCIATED CONTENT

Supporting Information

Experimental, spectroscopic, and crystallographic details for complexes **1**- **3**.

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Notes
The authors declare no competing financial interests.

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REFERENCES

1.	Gomberg, M., AN INSTANCE OF TRIVALENT CARBON: TRIPHENYLMETHYL. *Journal of the American Chemical Society* **1900**, *22*, 757-771.

2.	McBride, J. M., The hexaphenylethane riddle. *Tetrahedron* **1974**, *30*, 2009-2022.

3.	Ullmann, F.; Borsum, W., Zur Kenntniss des Hexaphenyläthans. *Berichte der deutschen chemischen Gesellschaft* **1902**, *35*, 2877-2881.

4.	Jacobson, P., Zur «Triphenylmethyl»-Frage. *Berichte der deutschen chemischen Gesellschaft* **1905**, *38*, 196-199.

5.	Lankamp, H.; Nauta, W. T.; MacLean, C., A new interpretation of the monomer-dimer equilibrium of triphenylmethyl- and alkylsubstituted-diphenyl methyl-radicals in solution. *Tetrahedron Letters* **1968**, *9*, 249-254.

6.	Allemand, J.; Gerdil, R., The crystal structure of the molecular complex between triphenylmethyl dimer and ethyl acetate. *Acta Crystallographica Section B* **1978**, *34*, 2214-2220.

7.	Schreiner, P. R.; Chernish, L. V.; Gunchenko, P. A.; Tikhonchuk, E. Y.; Hausmann, H.; Serafin, M.; Schlecht, S.; Dahl, J. E. P.; Carlson, R. M. K.; Fokin, A. A., Overcoming lability of extremely long alkane carbon–carbon bonds through dispersion forces. *Nature* **2011**, *477*, 308-311.

8.	Grimme, S.; Schreiner, P. R., Steric Crowding Can Stabilize a Labile Molecule: Solving the Hexaphenylethane Riddle. *Angewandte Chemie International Edition* **2011**, *50*, 12639-12642.

9.	Uchimura, Y.; Takeda, T.; Katoono, R.; Fujiwara, K.; Suzuki, T., New Insights into the Hexaphenylethane Riddle: Formation of an α,o-Dimer. *Angewandte Chemie International Edition* **2015**, *54*, 4010-4013.

10.	Takeda, T.; Uchimura, Y.; Kawai, H.; Katoono, R.; Fujiwara, K.; Suzuki, T., Hexaphenylethanes with an Ultralong C–C Bond: Expandability of the C–C Bond in Highly Strained Tetraarylpyracenes. *Chemistry Letters* **2013**, *42*, 954-962.

11.	Clar, E., *The Aromatic Sextet*. Wiley: New York, NY, 1972, p 1-128.

12.	Touchton, A. J.; Wu, G.; Hayton, T. W., Generation of a Ni$_3$ Phosphinidene Cluster from the Ni(0) Synthon, Ni(η^3-CPh$_3$)$_2$. *Organometallics* **2020**, *39*, 1360-1365.

13.	Lavallo, V.; Grubbs, R. H., Carbenes As Catalysts for Transformations of Organometallic Iron Complexes. *Science* **2009**, *326*, 559-562.

14.	Lavallo, V.; El-Batta, A.; Bertrand, G.; Grubbs, R. H., Insights Into the Carbene-Initiated Aggregation of [Fe(cot)2]. *Angewandte Chemie International Edition* **2011**, *50*, 268-271.

15.	Steigerwald, M. L.; Siegrist, T.; Stuczynski, S. M.; Kwon, Y. U., Iron telluride (Et3P)4Fe4Te4: an intermediate between molecular reagents and solid state products. *Journal of the American Chemical Society* **1992**, *114*, 3155-3156.

16.	Gerlach, D. H.; Schunn, R. A.; Bennett, M. A.; Tomkins, I. B.; Turney, T. W., Bis(1,3,5,7-cyclooctatetraene)iron(0). *Inorg. Synth.* **1974**, *15*, 1-4.

17.	Huber, D. L., Synthesis, properties, and applications of iron nanoparticles. *Small* **2005**, *1*, 482-501.

18.	Brook, A. G.; Gilman, H.; Miller, L. S., Analogs of Hexaphenylethane. II.* Triphenylmethyltriphenylsilane. *Journal of the American Chemical Society* **1953**, *75*, 4759-4765.

19.	Tomboulian, P., Chemistry of Trityllithium. Direct Preparation and Some Reactions[1,2]. *The Journal of Organic Chemistry* **1959**, *24*, 229-234.

20.	Tondreau, A. M.; Scott, B. L.; Boncella, J. M., A Tertiary Carbon–Iron Bond as an Fe[I]Cl Synthon and the Reductive Alkylation of Diphosphine-Supported Iron(II) Chloride Complexes to Low-Valent Iron. *Organometallics* **2016**, *35*, 1643-1651.

21.	Fischer, P. J.; Ahrendt, K. A.; Young, V. G.; Ellis, J. E., Trityltitanium Complexes. X-ray Structural Characterization of [Ti(CO)$_4$[η^5-C(4-C$_6$H$_4$R)$_3$]]$^-$ (R = H, OCH$_3$)[1]. *Organometallics* **1998**, *17*, 13-15.

22.	MacLeod, K. C.; DiMucci, I. M.; Zovinka, E. P.; McWilliams, S. F.; Mercado, B. Q.; Lancaster, K. M.; Holland, P. L., Masked Radicals: Iron Complexes of Trityl, Benzophenone, and Phenylacetylene. *Organometallics* **2019**, *38*, 4224-4232.

23.	LeSuer, R.; Basta, R.; Arif, A. M.; Geiger, W. E.; Ernst, R. D., Structural, Spectroscopic, and Electrochemical Studies of Edge-Bridged Open Ferrocenes. *Organometallics* **2003**, *22*, 1487-1493.

24.	DiMauro, P. T.; Wolczanski, P. T., New sandwich complexes containing 6,6-dimethylcyclohexadienyl (dmCh): (dmCh)$_2$M (M = Ti, V, Cr, Fe) and (dmCh)$_2$M-CO (M = Ti, V). *Organometallics* **1987**, *6*, 1947-1954.

25.	Basta, R.; Wilson, D. R.; Ma, H.; Arif, A. M.; Herber, R. H.; Ernst, R. D., Bonding in 'closed,' open, and half-open ferrocenes: new insight from structural and Mössbauer spectroscopic studies. *Journal of Organometallic Chemistry* **2001**, *637-639*, 172-181.

26.	Staab, H. A.; Brettschneider, H.; Brunner, H., Struktur der Triarymethyl-Dimeren. *Chemische Berichte* **1970**, *103*, 1101-1106.

27.	The appearance triphenylmethane in the reaction mixture is likely due the thermal decomposition of Gomberg's dimer, a phenomenon that we have observed previously (See Ref. 12). We can rule out a photochemical route to triphenylmethane formation in this case because we do not observe concomitant formation of 9-phenylfluorene. See: R. L. Letsinger, R. Collat, and M. Magnusson, *J. Am. Chem. Soc.*, **1954**, *76*, 4185–4186 for further details.

28.	Bachler, V.; Grevels, F.-W.; Kerpen, K.; Olbrich, G.; Schaffner, K., A Novel Facet of Carbonyliron-Diene Photochemistry: The η^4-*s-trans* Isomer of the Classical Fe(CO)$_3$(η^4-*s-cis*-1,3-butadiene) Discovered by Time-Resolved IR Spectroscopy and Theoretically Examined by Density Functional Methods. *Organometallics* **2003**, *22*, 1696-1711.

29.	Bramley, R.; Figgis, B. N.; Nyholm, R. S., ^{13}C and ^{17}O n.m.r. spectra of metal carbonyl compounds. *Transactions of the Faraday Society* **1962**, *58*, 1893.

30.	Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R., Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *Journal of the Chemical Society, Perkin Transactions 2* **1987**, S1-S19.

31.	Zou, C.; Ahmed, K. J.; Wrighton, M. S., Thermal and photochemical reactions of (η^5-cyclohexadienyl)$_2$Fe$_2$(CO)$_4$ in the presence of 2e$^-$ donor ligands: isolation and characterization of (η^4-*C,C'*-(cyclohexadiene)$_2$)Fe$_2$(CO)$_4$L$_2$. *Journal of the American Chemical Society* **1989**, *111*, 1133-1135.

32.	Pearson, A. J.; Raithby, P. R., Diene–metal π bonding. Some unexpected effects of Group 5 donor ligands on carbon-13 nuclear magnetic resonance parameters and X-ray crystal structures. *Journal of the Chemical Society, Dalton Transactions* **1981**, 884-891.

33.	Behrens, H.; Thiele, G.; Pürzer, A.; Würstl, P.; Moll, M., Über die kristall- und molekülstruktur von 1,3-cyclohexadien-dicarbonyl-ethylisonitril-eisen(O). *Journal of Organometallic Chemistry* **1978**, *160*, 255-262.

34.	Howell, J. A. S.; Palin, M. G.; Tirvengadum, M.-C.; Cunningham, D.; McArdle, P.; Goldschmidt, Z.; Gottlieb, H. E., Evidence for correlated rotation and diastereoisomer discrimination in (η^4-diene)Fe(CO)$_2$L complexes: the crystal and solution structures of (cyclohexadiene)Fe(CO)$_2$P(o-tolyl)$_3$ and (cycloheptadiene)Fe(CO)$_2$(+)-PPh$_2$(neomenthyl). *Journal of Organometallic Chemistry* **1991**, *413*, 269-286.

35.	Cotton, F. A.; Troup, J. M., Conformations of fused cycloalkanes in organometallic compounds: III. The crystal and molecular structures of tricyclo [6.2.0.02,7] deca-3,5-dienetricarbonyliron, (C$_{10}$H$_{12}$)Fe(CO)$_3$. *Journal of Organometallic Chemistry* **1974**, *77*, 369-379.

36.	Guy, J. J.; Reichert, B. E.; Sheldrick, G. M., (5-exo-Triphenylphosphinocyclohexa-1,3-diene)tricarbonyliron Tetrafluoroborate. *Acta Crystallographica Section B* **1976**, *32*, 2504-2506.

37.	Johnson, B. F. G.; Lewis, J.; Parker, D. G.; Raithby, P. R.; Sheldrick, G. M., The stereochemistry of (5exo-acylcyclohexa-1,3-diene)tricarbonyliron derivatives and the crystal structure of (5-exo-cyanocyclohexa-1,3-diene)tricarbonyliron. *Journal of Organometallic Chemistry* **1978**, *150*, 115-122.

38.	Adams, C. M.; Hafner, A.; Koller, M.; Marcuzzi, A.; Prewo, R.; Solana, I.; Vincent, B.; von Philipsborn, W., Synthesis and Structure of a New Type of Chiral Organoiron and Organoruthenium Complexes. *Helvetica Chimica Acta* **1989**, *72*, 1658-1675.

39.   Berke, H.; Bankhardt, W.; Huttner, G.; v. Seyerl, J.; Zsolnai, L., Eisenkomplexe als Modellverbindungen zur homogenen Hydrierung von Kohlenmonoxid. *Chemische Berichte* **1981**, *114*, 2754-2768.

40.   Valéri, T.; Meier, F.; Weiss, E., Cyclopropene als Komplexliganden: Vinylcarben- und Vinylketen-Komplexe des Eisens und Cobalts: präparative und röntgenographische Ergebnisse. *Chemische Berichte* **1988**, *121*, 1093-1100.

41.   Petrel, T. A.; Stephan, J. M.; McDaniel, K. F.; McMills, M. C.; Rheingold, A. L.; Yap, G. P. A., Preparation and Diazodecomposition Reaction of an α-Diazocarbonyl-Tethered Tricarbonyl(η^4-cyclohexadiene)iron Complex. *The Journal of Organic Chemistry* **1996**, *61*, 4188-4189.

42.   Schaeufele, H.; Hu, D.; Pritzkow, H.; Zenneck, U., Reactive π-complexes of the electron-rich transition metals. 3. (η^4-Methylnaphthalene)iron(0) complexes. X-ray crystal structure of (5-8-η-1,4-dimethylnaphthalene)tris(trimethyl phosphite)iron. *Organometallics* **1989**, *8*, 396-401.

43.   Zhang, L.; Sun, J.; Zhu, H.; Tsumori, N.; Xu, Q.; Chen, J., Thermolytic Products Derived from Thermolysis of Cycloolefin-Coordinated Diiron Bridging Carbene Complexes. *Organometallics* **2007**, *26*, 2630-2636.

44.   Carrondo, M. A. A. F. C. T.; Rogers, D., X-ray comparison of the molecular structures of 4*a*-methyl-1,3,9-triphenyl-4*a*-H-fluorene and its Fe(CO)$_3$ complex. *Journal of Organometallic Chemistry* **1984**, *276*, 219-230.

45.   Mills, O. S.; Robinson, G., Studies of some carbon compounds of the transition metals. IV. The structure of butadiene irontricarbonyl. *Acta Crystallographica* **1963**, *16*, 758-761.

46.   Brill, T. B.; Landon, S. J., Arbuzov-like dealkylation reactions of transition-metal-phosphite complexes. *Chemical Reviews* **1984**, *84*, 577-585.

47.   Goh, L.-Y.; D'Aniello, M. J.; Slater, S.; Muetterties, E. L.; Tavanaiepour, I.; Chang, M. I.; Fredrich, M. F.; Daz, V. W., Metal Clusters in Catalysis. 20. The Chemistry of [η^5-C$_5$H$_5$Cr(CO)$_3$]$_2$. *Inorganic Chemistry* **1979**, *18*, 192-197.

48.   Howell, J. A. S.; Rowan, A. J.; Snell, M. S., Carbon–oxygen and –hydrogen cleavage in the reaction of [Fe$_2$(CO)$_3$(η-C$_5$H$_5$)$_2$L][L = P(OR)$_3$ or PR$_3$] with phosphite and phosphine ligands. *Journal of the Chemical Society, Dalton Transactions* **1981**, 325-327.

49.   Howell, J. A. S.; Rowan, A. J., Carbon–oxygen and carbon–hydrogen bond cleavage in the reaction of [{Ru(CO)$_2$(η^5-C$_5$H$_5$)}$_2$]$^+$ with phosphite and phosphine ligands. *Journal of the Chemical Society, Dalton Transactions* **1980**, 1845-1851.

50.   El Murr, N.; Chaloyard, A.; Klaeui, W., Electrochemistry of half-sandwich and trinuclear sandwich complexes containing phosphonate ligands. *Inorg. Chem.* **1979**, *18*, 2629-2631.

51.   Kang, X.; Li, Y.; Zhu, M.; Jin, R., Atomically precise alloy nanoclusters: syntheses, structures, and properties. *Chemical Society Reviews* **2020**, *49*, 6443-6514.

52.   Jin, R.; Zeng, C.; Zhou, M.; Chen, Y., Atomically Precise Colloidal Metal Nanoclusters and Nanoparticles: Fundamentals and Opportunities. *Chemical Reviews* **2016**, *116*, 10346-10413..

Thermolysis of bis(trityl)iron(II) in the presence of excess $P(OMe)_3$ results in formation of the $[Fe^0(P(OMe)_3)_3]$-stabilized *o,o*-isomer of Gomberg's dimer.