# A Novel Class of Phosphine Enolates Derived from Diarylacetylphosphines: Synthesis of Lithium Diphenylacetylphosphine Enolate and Its Conversion into Mono- and Dimetallic Forms by the Use of Transition Metals

Patrick Veya and Carlo Floriani*

*Section de Chimie, Université de Lausanne, Place du Château 3, CH-1005 Lausanne, Switzerland*

Angiola Chiesi-Villa and Carlo Guastini

*Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy*

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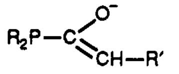
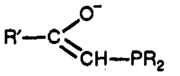
*Summary:* Diphenylacetylphosphine (**1**) was deprotonated with use of LiBu$^n$ to the corresponding lithium enolate $[Ph_2PC(CH_2)OLi(THF)_2]_n$ (**2**). The reaction of **2** with $(cp)_2ZrCl_2$ led to the formation of the oxygen-bonded enolate $[Ph_2PC(CH_2)OZr(cp)_2(Cl)]$ (**3**). Complex **3** showed high reactivity in the normal aldol condensation with benzaldehyde. Its reaction with the 16-ve $Cr(CO)_5$ fragment allowed binding of the chromium through the phosphorus donor atom in $[Ph_2P\{Cr(CO)_5\}]C(CH_2)OZr(cp)_2(Cl)]$ (**5**). The structures of **3** and **5** have been proved by an X-ray analysis.

The introduction of a heteroatom adjacent to the enolate functionality enlarges its use in organic synthesis[1] due to (i) the presence of an alternate functional group in the skeleton (ii) the change in the nucleophilicity of the enolate, and (iii) the introduction of an additional binding site for transition metals besides the enolate functionality itself. Such an operation should be particularly useful for managing the enolate chemistry by the use of transition-metal ions.

Our attention was focused on the phosphorus version (A) of the well-known amide enolates,[2] which are widely used in organic synthesis. Another class of phosphine enolates (B) derived from $\beta$-keto enolates have been successfully used in organometallic chemistry[3] and catalysis.[4]


$R_2P{-}C(O^-){=}CH{-}R'$

A


$R'{-}C(O^-){=}CH{-}PR_2$

B

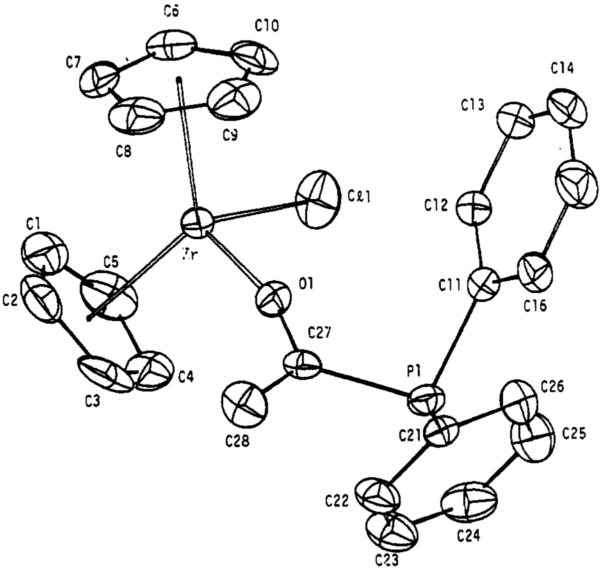
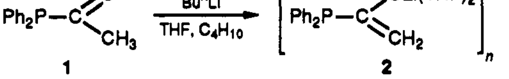


**Figure 1.** ORTEP view of complex **3** (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) are as follows: Zr–cp1 = 2.224 (6), Zr–cp2 = 2.216 (5), Zr–Cl1 = 2.457 (1), Zr–O1 = 1.960 (3), O1–C27 = 1.339 (5), P1–C27 = 1.839 (4), C27–C28 = 1.331 (7); cp1–Zr–cp2 = 128.6 (2), O1–Zr–Cl1 = 98.7 (1), Zr–O1–C27 = 163.6 (3).

A and B are positional isomers. The generation of the A-type phosphine enolate was achieved by deprotonating **1**[5] as shown in eq 1.


$$Ph_2P{-}C({=}O){-}CH_3 \xrightarrow[THF,\ C_4H_{10}]{Bu^nLi} [Ph_2P{-}C(OLi(THF)_2){=}CH_2]_n \qquad (1)$$

**1** **2**

The lithium enolate **2**[6] was isolated in high yield in crystalline form and was fully characterized in the solid

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* To whom correspondence and reprint requests should be addressed.

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[4] Behr, A.; Freudenberg, U.; Keim, W. *J. Mol. Catal.* **1986**, *35*, 9. Agbossou, S.; Bonnet, M. C.; Tkatchenko, I. *Nouv. J. Chim.* **1985**, *5*, 311.

[5] The synthesis of diphenylacetylphosphine was carried out as reported by: Issleib, K.; Priebe, E. *Chem. Ber.* **1959**, *92*, 3183.

[6] Procedure for **2**: To a THF (30 mL) solution of **1** (2.19 g, 9.6 mmol) at −100 °C was added dropwise with a syringe Bu$^n$Li (6.0 mL, 9.6 mmol). After 10 min a white microcrystalline solid precipitated, which was filtered off after adding $Et_2O$ (30 mL) (2.85 g, 78%). The product rapidly loses solvent at room temperature. $^1H$ NMR ($C_6D_6$): $\delta$ 1.41 (m, 8 H, THF), 3.74 (m, 8 H, THF), 3.90 (s, 1 H, $CH_2$, $J_{HP} = 0$), 4.64 (d, 1 H, $CH_2$, $J_{HP} = 13.7$ Hz), 7.05–7.20 (m, 6 H, Ph), 7.6–7.7 (m, 4 H, Ph). $^{13}C$ NMR ($C_6D_6$): $\delta$ 26.0 (s, THF), 68.7 (s, THF), 94.0 (d, $CH_2$, $J_{CP} = 24.5$ Hz), 127.9–140.5 (m, Ph), 169.9 (s, C–O).

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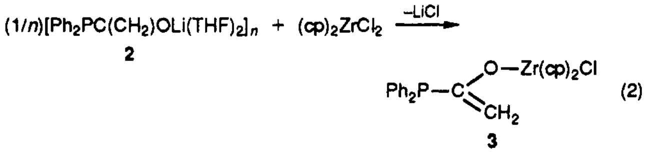
state; however, X-ray analysis has so far been unsuccessful for the very labile solvated form. Complex 2 was transformed into the O-metalated form 3[7] through the use of an oxophilic metal:

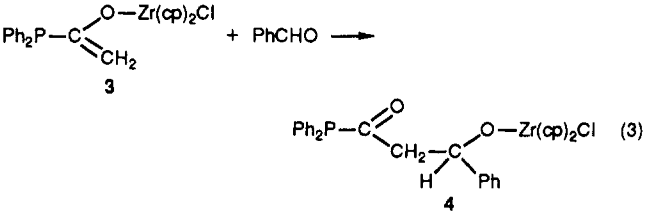


$(1/n)[Ph_2PC(CH_2)OLi(THF)_2]_n + (cp)_2ZrCl_2 \xrightarrow{-LiCl}$ (2)

**2** **3**

An ORTEP diagram of **3**[8] is shown in Figure 1 along with some selected structural parameters. Its structure will be discussed later jointly with that of enolate **5**.

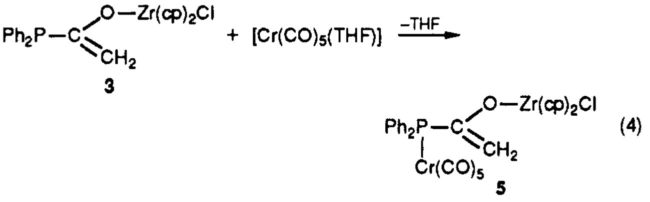
In agreement with the increased nucleophilicity due to the presence of phosphorus, the reaction of **3** with benzaldehyde[9] is much faster than for the analogous zirconium enolates not containing heteroatoms:[10]



(3)

**3** **4**

The enolate **2** or **3** may in principle be bonded to a soft transition metal by the tricovalent phosphorus. According to this idea, we reacted **3** with $[Cr(CO)_5(THF)]$:



(4)

**3** **5**

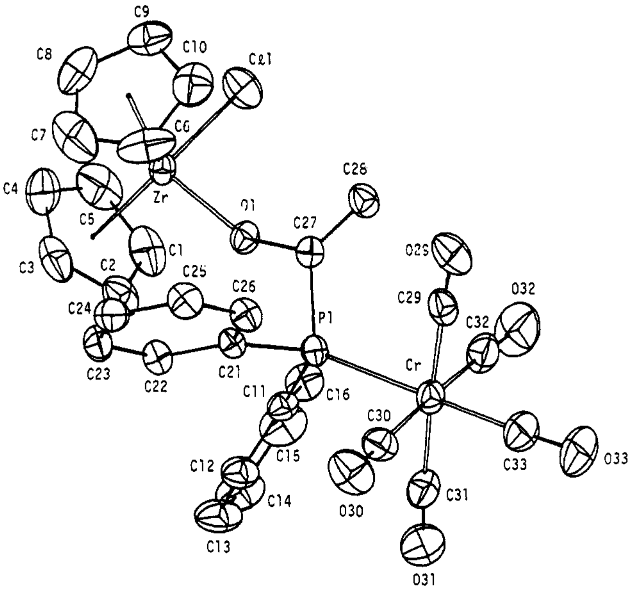


**Figure 2.** ORTEP view of complex **5** (30% probability ellipsoids). Selected bond distances (Å) and angles (deg) are as follows: Zr–cp1 = 2.220 (5), Zr–cp2 = 2.205 (5), Zr–Cl1 = 2.453 (2), Zr–O1 = 1.978 (3), O1–C27 = 1.348 (5), P1–C27 = 1.843 (4), C27–C28 = 1.317 (7), Cr–P1 = 2.387 (1), Cr–C29 = 1.881 (6), Cr–C30 = 1.896 (6), Cr–C31 = 1.897 (7), Cr–C32 = 1.878 (6), Cr–C33 = 1.849 (6); cp1–Zr–cp2 = 130.0 (2), O1–Zr–Cl1 = 96.1 (1), Zr–O1–C27 = 152.5 (3), Cr–P1–C27 = 119.2 (2).

The phosphorus atom replaces the labile THF, and the dimetallic enolate **5** was isolated as a white crystalline solid.[11] Its structure is shown in Figure 2.[12] The comparison between the structural and spectroscopic data of **3** and **5** will allow us to judge the steric and electronic effects due to the introduction of a metal fragment, i.e. $Cr(CO)_5$, at the phosphorus.

The structure of **5** is drawn in Figure 2, along with a list of selected structural parameters. The introduction of the $Cr(CO)_5$ fragment does not affect significantly either the bond distances within the enolate fragment or the nucleophilicity of the "$CH_2$", as can be judged by the $^{13}C$ NMR spectrum,[13] the chemical shift being 105.5 vs 103.0 ppm in **3**. The major influence of the second metalation is on the overall conformation of the molecule, and on the steric hindrance around the nucleophile. The C27–C28 bond is trans in **3**, while it is cis in **5** with respect to the

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(7) Procedure for **3**: $Bu^nLi$ (20 mL, 32.0 mmol) was added to a THF (100 mL) solution of **1** (7.30 g, 32.0 mmol) at −100 °C, avoiding the solution becoming yellow due to the presence of $Ph_2PLi$. The mixture was stirred for 1 h; then $(cp)_2ZrCl_2$ (8.88 g, 32.0 mmol) was added with stirring while the temperature was allowed to rise overnight. The color soon changed to bright orange and then to violet. The solvent was evaporated; the orange oil was dissolved in $Et_2O$ (100 mL), filtered, and extracted with $Et_2O$ (100 mL). After 1 day of extraction, a white-yellow crystalline solid was collected (9.00 g, 62%). Anal. Calcd for $C_{24}H_{22}ClOPZr$: C, 59.55; H, 4.58. Found: C, 59.93; H, 4.55. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 4.43 (d, 1 H, $CH_2$, $J_{HP} = 7.2$ Hz), 4.60 (d, 1 H, $CH_2$, $J_{HP} = 26.45$ Hz), 6.14 (s, 10 H, cp), 7.4–7.5 (m, 10 H, Ph). $^{13}C$ NMR ($CD_2Cl_2$): $\delta$ 103.0 (d, $CH_2$, $J_{CP} = 39.8$ Hz), 114.9 (s, cp), 129.0–136.9 (m, Ph), 169.2 (s, C–O).

(8) Structure of **3**: $C_{24}H_{22}ClOPZr$, $M_r = 484.1$, orthorhombic, space group $P2_12_12_1$, $a = 15.853$ (2) Å, $b = 14.109$ (2) Å, $c = 9.772$ (1) Å, $V = 2185.7$ (5) Å$^3$, $Z = 4$, $\rho_{calcd} = 1.471$ g cm$^{-3}$, $\lambda$(Mo K$\alpha$) = 0.71069 Å, $\mu$(MoK$\alpha$) = 7.01 cm$^{-1}$, crystal dimensions 0.38 × 0.45 × 0.55 mm$^3$; 3213 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Philips PW 1100 diffractomer in the range of $6° < 2\theta < 50°$; $R = 0.030$ (unit weights). The structure was solved with use of SHELX-86 and anisotropically refined. All of the hydrogen atoms were located in a difference map and introduced as fixed contributors in the final stage of refinement. During the refinement the Ph rings were constrained to be regular hexagons (C–C = 1.395 Å).

(9) Reaction 3 was carried out in an NMR tube and was complete in 5 min: **3** (0.048 g) and benzaldehyde (10 µL in 1.0 mL of $C_6D_6$) were mixed; **4** evolved very rapidly, and after 1 day an NMR spectrum showed a mixture of products. Complex **4** has an ABX system which is still coupled with phosphorus. A total of 20 peaks appeared with 5 different coupling constants: $J_{AB}$, $J_{AX}$, $J_{BX}$, $J_{AP}$, $J_{BP}$. $^1H$ NMR for **4** ($C_6D_6$): $\delta$ 2.65 (2 q, 1 H, $CH_2$ (AB)), 3.20 (2 q, 1 H, $CH_2$ (AB)), 5.71 (q, 1 H, CH (X)), 5.90 (s, 5 H, cp), 6.10 (s, 5 H, cp), 6.95–7.20 (m, 10 H, Ph–P), 7.45–7.65 (m, 5 H, Ph). Geminal coupling constant: $J_{AB} - 16.25$ Hz. Vicinal coupling constants: $J_{AX} = 9.00$ Hz, $J_{BX} = 3.45$ Hz. Hydrogen–phosphorus coupling constants: $J_{AP} = 3.15$ Hz, $J_{BP} = 4.40$ Hz.

(10) The reaction of $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4R)]$ (R = $-C(CH_2)OZr(cp)_2Cl$) with benzaldehyde leading to the corresponding aldol condensation product was much slower: Veya, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Manuscript in preparation.

(11) Procedure for **5**: In a 500-mL round bottom flask, a THF (180 mL) solution of $Cr(CO)_5\cdot THF$, prepared *in situ* by starting from $Cr(CO)_6$ (0.77 g, 3.5 mmol), was added dropwise with stirring to a $Et_2O$ (50 mL) solution of **3** (1.58 g, 3.3 mmol). The mixture was stirred for 3–4 h, and the color became deep yellow; then the solvent was evaporated and the oily residue redissolved in anhydrous and oxygen-free $Et_2O$ (50 mL). A solid was obtained, which was extracted with $Et_2O$ (50 mL), giving a white crystalline product (1.15 g, 53%). Anal. Calcd for $C_{29}H_{22}ClCrO_6PZr$: C, 51.52; H, 3.28. Found: C, 51.73; H, 3.33. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 4.59 and 4.76 (2 d, 1 H, $CH_2$, $J_{HH} = 1.3$ Hz, $J_{HP} = 33.8$ Hz), 5.21 and 5.26 (2 d, 1 H, $CH_2$, $J_{HP} = 9.0$ Hz), 5.64 (s, 10 H, cp), 7.0–7.2 (m, 6 H, Ph), 7.55–7.7 (m, 4 H, Ph). $^{13}C$ NMR ($C_6D_6$): $\delta$ 105.5 (d, $J_{CP} = 38.0$ Hz, $CH_2$), 114.6 (s, cp), 127.9–135.3 (mm, Ph), 165.4 (s, C–O), 217.6 (s, Cr–CO), 217.9 (s, Cr–CO), 222.4 (s, Cr–CO). IR (Nujol): $Cr(CO)_5$ 2063 (m), 1991 (w), 1945 (s), 1927 (s) cm$^{-1}$.

(12) Structure of **5**: $C_{29}H_{22}ClCrO_6PZr$, $M_r = 676.21$, monoclinic, space group $P2_1/c$, $a = 10.462$ (2) Å, $b = 14.390$ (1) Å, $c = 19.972$ (1) Å, $\beta = 102.66$ (1)°, $V = 2933.7$ (5) Å$^3$, $Z = 4$, $\rho_{calcd} = 1.531$ g cm$^{-3}$, $\lambda$(MoK$\alpha$) = 0.71069 Å, $\mu$(Mo K$\alpha$) = 8.95 cm$^{-1}$, crystal dimensions 0.28 × 0.35 × 0.58 mm$^3$; 3257 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Siemens AED diffractometer in the range $6° < 2\theta < 50°$; $R = 0.035$ (unit weights). The structure was solved and refined as above with constraints applied to Ph and Cp rings (regular pentagons having C–C = 1.420 Å). All calculations were carried out with use of SHELX-76.

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chlorine atom at zirconium, the torsional angles Cl1–Zr···C27–C28, Cl1–Zr···C27–P1, and Cl1–Zr–O1–C27 being −165.8 (3), 8.5 (2), and −137.6 (9)° in 3 and 38.4 (3), −151.8 (2), and 67.2 (6)° in 5, respectively. The enolato plane is accessible from both axial directions in 3 and 5.

Compounds **2**, **3**, and **5** will allow us to introduce the $Ph_2P$ substituent by use of the enolato methodologies and, in addition, to show how we can control the chemistry of the enolato moiety by the use of different metals.

**Acknowledgment.** We thank the Swiss National Foundation for Scientific Research (Grant No. 20-28470.90) and Ciba-Geigy Co. (Basel, Switzerland) for financial support.

**Supplementary Material Available:** A description of the crystal structure determination and tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters for complexes 3 and 5 (11 pages); tables of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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# Combined Spectroscopic and Molecular Mechanics Investigation of the Flexible Organometallic Compounds $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = $PhCH_2$, Et, MeCO) and $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COMe$

Stephen C. Mackie, Yong-S. Park, Herbert F. Shurvell, and Michael C. Baird*

*Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6*

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*Summary:* Variable-temperature IR spectroscopy is utilized to investigate the conformational preferences of the title compounds; complementary information concerning the conformational energy profiles is successfully obtained by utilizing the molecular modeling program MMX.

Molecular mechanics (MM) calculations have long been utilized to estimate conformational properties of flexible organic molecules[1] and, when used appropriately, are capable of reproducing experimental values of conformational differences as small as a fraction of a kilocalorie per mole.[2] In large part for this reason, the MM approach is often the method of choice for the calculation of conformational energy differences of a variety of organic molecules, more accurately reproducing experimental energy differences than do ab initio and some semiempirical methodologies.[3] In contrast, there have been reported very few attempts to apply MM or any other methodologies to organometallic conformational problems, and only rarely have there been attempts to estimate conformational energy differences as delicate as those mentioned above;[4] as has been pointed out,[3] appropriate computational software has not been available.

In order to explore a possible remedy to this situation, we have been investigating the potential applications of a new molecular modeling package, MMX,[5] to our knowledge the only commercially available MM software which attempts to address the problem of ligand $\pi$ coordination in organometallic compounds. In an attempt to assess the utility of this software, we have carried out calculations to estimate the relative conformational energies and barriers to alkyl and acyl ligand rotation of a series of flexible organometallic compounds, $(\eta^5\text{-}C_5H_5)Fe(CO)L(CH_2R)$ and $(\eta^5\text{-}C_5H_5)Fe(CO)L(COR)$ (R = methyl, phenyl; L = CO, $PPh_3$).[6] We have also obtained relevant experimental spectroscopic information on the conformational energy profiles of these compounds, thus making possible comparison of experimental data with the results of the MMX calculations.

To begin, we have utilized IR spectroscopy to experimentally determine the conformational preferences of compounds of the type $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_2R$; as shown previously,[7] this and related classes of compounds can exist in solution as two staggered rotamers, A and B, of $C_s$ and $C_1$ symmetry, respectively (Chart I). The IR spectra of both rotamers are expected to exhibit pairs of peaks at-

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[1] Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1.

[2] See, for instance: Gundertofte, K.; Palm, J.; Pettersson, I.; Stamvik, A. *J. Comput. Chem.* **1991**, *12*, 200.

[3] A brief summary of the present situation has been recently presented. See: Counts, R. W. *J. Comput.-Aided Mol. Design* **1990**, *4*, 427.

[4] For examples of interesting applications, see: (a) Lauher, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 1521. (b) Slovokhotov, Y. L.; Timofeeva, T. V.; Struchkov, Y. T. *J. Struct. Chem.* (*Engl. Transl.*) **1987**, *28*, 463. (c) Johnston, P.; Denner, L.; Marais, C. F.; Boeyens, J. C. A.; Coville, N. J. *J. Crystallogr. Spectrosc. Res.* **1988**, *18*, 403. (d) Newsam, J. M.; Bradley, J. S. *J. Chem. Soc., Chem. Commun.* **1985**, 759. (e) Bradley, J. S.; Harris, S.; Newsam, J. M.; Hill, E. W.; Leta, S.; Modrick, M. A. *Organometallics* **1987**, *6*, 2060. (f) Bogdan, P. L.; Horowitz, C. P.; Shriver, D. F. *J. Chem. Soc., Chem. Commun.* **1986**, 553. (g) Brown, J. M.; Evans, P. L. *Tetrahedron* **1988**, *44*, 4905. (h) Bogdan, P. L.; Irwin, J. J.; Bosnich, B. *Organometallics* **1989**, *8*, 1450. (i) Casey, C. P.; Whitecker, G. T. *Isr. J. Chem.* **1990**, *30*, 299.

[5] Available as PCMODEL from Serena Software, Bloomington, IN. MMX is based on the MM2 (77) force field, with data for several heteroatoms and transition-metal complexes with $\pi$-bonded ligands added; see: Gajewski, J. J.; Gilbert, K. E.; McKelvey, J. In *Advances in Molecular Modelling*; Liotta, D., Ed.; JAI Press: Greenwich, CT, 1990; Vol. 2, p 65. The calculations were carried out on a Sun SPARCStation 1 utilizing PCMODEL 4.0. Default parameters were found to be appropriate, in general, but it was found best to utilize fixed metal–ligand distances comparable with published crystallographic data. During geometry optimizations, all ligand atoms were free to move, ligand rotation and tilting being only under the influence of van der Waals forces. Barriers to rotation were estimated by varying the $\eta^5\text{-}C_5H_5$ centroid–Fe–$C_\alpha$–$C_\beta$ torsional angle by 5° increments and optimizing each structure while holding only the torsional angle fixed. A similar approach has been utilized to calculate barriers to rotation in medium sized organic molecules; see: Beyer, A.; Wolschann, P.; Becker, A.; Buchbauer, G. *J. Mol. Struct.* **1989**, *196*, 371.

[6] (a) Krüerke, U., Ed. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1983; Part B11. (b) Krüerke, U., Ed. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Springer-Verlag: Berlin, 1984; Part B12.

[7] (a) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 4292. (b) Jetz, W.; Graham, W. A. G. *J. Am. Chem. Soc.* **1967**, *89*, 2773. (c) Dalton, J. *Inorg. Chem.* **1971**, *10*, 1822. (d) Dalton, J. *Inorg. Chem.* **1972**, *11*, 915.

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