Supplementary Information

Mechanochemical and silica gel-mediated formation of highly electron-poor

1-cyanocarbonylferrocene

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1. General Experimental Details

1.1 Equipment. Infrared spectra were recorded on a Perkin Elmer 100 FT-IR spectrometer. A Unicam V-410 spectrophotometer was used to obtain UV-visible measurements. ¹H and ¹³C NMR spectra were recorded on a Brucker-AMX-300 spectrometer. Chemical shifts were reported in parts per million (δ) with reference to CDCl₃ residual solvent resonances for ¹H δ 7.27 ppm, and ¹³C δ 77.0 ppm. EI mass spectra were recorded on a GCT (Waters) spectrometer. Samples were prepared in CH₂Cl₂. Elemental analyses were performed by the Microanalytical Laboratory, SIDI, Universidad Autónoma de Madrid, Spain.

1.2 Electrochemical Measurements. Cyclic voltammetric and square wave voltammetric experiments were recorded on a Bioanalytical Systems BAS-CV-50W potentiostat. CH_2Cl_2 and CH_3CN (spectrograde) for electrochemical measurements were freshly distilled from calcium hydride under argon. The supporting electrolyte used was tetra-*n*-butylammonium hexafluorophosfate (Fluka), which was purified by recrystallization from ethanol and dried in vacuum at 60 °C. The supporting electrolyte concentration was 0.1 M. A conventional three-electrode cell connected to an atmosphere of prepurified nitrogen was used. All cyclic voltammetric experiments were performed using either a platinum-disk working electrode ($A = 0.020 \text{ cm}^2$) or a glassy carbon-disk working electrode ($A = 0.070 \text{ cm}^2$) (both Bioanalytical Systems), each of which were polished on a Buehler polishing cloth with Metadi II diamond paste, rinsed thoroughly with purified water and acetone, and dried. All potentials were referenced to the saturated calomel electrode (SCE). Under our conditions, the ferrocene redox couple $[FeCp_2]^{0/+}$ is +0.462, and decamethylferrocene redox couple $[FeCp*_2]^{0/+}$ is -0.056 V vs SCE in $CH_2Cl_2/0.1 \text{ M}$ n-Bu₄NPF₆. A coiled platinum wire was used as a counter electrode. Solutions were, typically, 10^{-3} M in the redox active species. The solutions for the electrochemical experiments were purged with nitrogen and kept under an inert atmosphere throughout the measurements. Square wave voltammetry (SWV) was performed using frequencies of 10 Hz.

1.3 X-ray Crystal Structure Determination. Compound **2** as well as its cyanomethyl precursor **1** were structurally characterized by single-crystal X-ray diffraction. Orange single crystals of **1** and purple crystals of **2** were obtained by slow evaporation of a mixture of hexane and dichloromethane (2:1) at 4 °C.

Suitable orange crystals of **1** and **2** of dimensions $0.16 \times 0.19 \times 0.21$ mm and $0.04 \times 0.10 \times 0.18$ mm, respectively, were coated with Paratone oil and mounted on a Mitegen MicroLoop. The samples were transferred to a Bruker D8 KAPPA series II with APEX II area-detector system equipped with graphite monochromated Mo Ka radiation ($\lambda = 0.71073$ Å). For compound **1** a total of 2012 independent reflections (*Rint* = 0.0330) were collected in the range $1.61 < \theta < 26.46^{\circ}$. For compound **2** a total of 1877 independent reflections (*Rint* = 0.0608) were collected in the range $2.52 < \theta < 25.49^{\circ}$. X-Ray data were collected at 100K for **1** and a 296K for **2**. The frame width was set to 0.5 deg for data collection with a crystal-to-detector distance of 3.5 cm. Absorption corrections (SADABS)¹ were applied to the collected data. The raw intensity data frames were integrated with the SAINT program,² which also applied corrections for Lorentz and polarization effects. The software package Bruker SHELXTL was used for space group determination, structure solution and refinement.³ The space group determination was based on a check of the Laue symmetry and systematic absences were confirmed using the structure solution. The structures were solved by direct methods (SHELXS-97), completed with different Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 minimizing ω (F₀² - F_c²)2.^{4,5} Weighted *R* factors (R_w) and all goodness of fit *S* are based on F²; conventional *R* factors (*R*) are based on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atom positions were calculated

geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic U. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library. The crystal structures of **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 942724 and 942725, respectively.

2. Synthetic Procedures

2.1. Synthesis of 1-cyanomethylferrocene FcCH₂CN (1) (Fc = $(\eta^5-C_5H_5)Fe(\eta^5-C_5H_4)$). Monofunctional FcCH₂CN was synthesized in two steps from N,N,N-trimethylferrocenylmethyl-amonium iodide, by adapting the literature procedures.^{6,7} 20 g (0.052 mol) of N,N,N-(ferrocenylmethyl)trimethylammonium iodide (Alfa Aesar) were added to a 200 mL distilled water solution of KCN (Fluka) (21.6 g, 0.332 mol). The mixture was vigorously stirred under reflux during 5 h, over the course of which trimethylamine evolved and a color change was observed, from orange to deep red. As the mixture was refluxed, an oily product was separated progressively from the solution. The reaction mixture was allowed to cool to room temperature and stirred overnight. During this time, the brown oil solidified. The solid product was separated by filtration and dissolved in diethyl ether, while the filtrate was extracted with diethyl ether (3 x 200 mL). The organic layers were combined, washed with water and dried over Na₂SO₄. After solvent removal, a solid was formed which was purified by recrystallization in *n*-hexane. 1-Cyanomethylferrocene was obtained as a bright crystalline yellow solid. Yield: 8.5 g (73%). Anal. Calcd for C₁₂H₁₁Fe₁N₁: C, 63.99; H, 4.93; N, 6.22. Found: C, 64.24; H, 4.75; N, 6.53. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 3.42 (s, 2H, CH₂-CN), 4.17, 4.25 (m, 4H, C₃H₄), 4.24 (s, 5H, C₅H₅). ¹³C {¹H} NMR (CDCl₃, 75 MHz, ppm): δ 19.0 (CH₂-CN), 68.1, 68.4 (C₅H₄), 69.3 (C₅H₅), 118.0 (CH₂-CN). IR (KBr, cm⁻¹): ν (C–H) 3104, 2957, 2924, ν (C=N) 2246.

2.2. Procedure for the SiO₂-Mediated Mechanochemical Synthesis of 1-Cyanocarbonylferrocene FcC(O)CN (2) (Fc = $(\eta^5 - C_5H_5)Fe(\eta^5 - C_5H_4)$. In an agate mortar, a mixture of 1-cyanomethylferrocene 1 (0.05 g, 0.222 mmol) and silica gel (0.07 g) (70-230 mesh, Sigma Aldrich) were ground together, with a pestle. The solid mixture was ground at room temperature in the open air until homogeneous. After 10 min of grinding the color of the mixed powder changed from yellow to purple. The reaction mixture was left for 60 minutes, after which it was ground for another 10 min to ensure efficient mixing. The reaction was monitored by ¹H NMR and FT-IR spectroscopy. The IR spectrum indicated the progressive disappearance of the sharp absorption of C=N bond of the starting solid cyanomethylferrocene 1 at 2246 cm⁻¹ and the appearance of a new strong ν (CO) carbonyl absorption at 1641 cm⁻¹ together with a sharp band at 2216 cm⁻¹ for the acylcyanide functional group (see Figure S4). In addition, ¹H NMR of the crude mixture was taken in CDCl₃ to confirm the formation of the cyanocarbonylferrocene derivative (Figure S5). The work-up of the reaction involved washing the silica gel with a CH_2Cl_2 followed by concentration and subsequent crystallization in *n*-hexane. 1-Cyanocarbonylferrocene (2) was obtained as an analytically pure, air-stable purple crystalline solid. Yield: 28 mg (53%). Anal. Calcd for C₁₂H₉Fe₁N₁O₁: C, 60.25; H, 3.80; N, 5.86. Found: C, 60.06; H, 3.89; N, 5.54. ¹H NMR (CDCl₃, 300 MHz, ppm): δ 4.40 (s, 5H, C₅H₅), 4.88, 5.02 (m, 4H, C₅H₄). ¹³C{¹H} NMR (CDCl₃, 75 MHz, ppm): δ 66.4 (*ipso*-Fc), 71.2, 76.1(C_5H_4), 71.6, (C_5H_5), 108.8 (CO-CN), 162.9 (CO-CN). IR (KBr, cm⁻¹): ν (C-H)_{Ar} 3098, ν (C=N) 2216, v(C=O) 1641. MS (EI): m/z 239.0 [M⁺].

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3. Structural Characterization of Compounds 1 and 2.



Figure S1. ¹H NMR spectrum (in CDCl₃, 300 MHz) of 1 (inset: expanded view of cyclopentadienyl region).



Figure S2. ¹³C NMR spectrum (in CDCl₃, 75 MHz) of 1 (inset: expanded view of cyclopentadienyl region).

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Figure S3. IR spectrum (in KBr) of compound 1. The assignment of the IR bands has been made on the basis of the DFT theoretical studies (see S7).



Figure S4. FT IR spectra (in KBr) of a powered mixture of 1 and SiO₂, measured at different times of grinding.

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Figure S5. Comparison of the ¹H NMR spectra (in CDCl₃, 300 MHz) of pure **1**, reaction of **1** + **SiO**₂ (after 1h of grinding, extracted with CDCl₃) and pure **2**.



Figure S6. ¹H NMR spectrum (in CDCl₃, 300 MHz) of **2**, (inset: expanded view of cyclopentadienyl region).



Figure S7. ¹³C NMR spectrum (in CDCl₃, 75 MHz) of compound 2, (inset: view of cyclopentadienyl region).



Figure S8. IR spectrum (in KBr) of compound 2. The assignment of the IR bands has been made on the basis of the DFT theoretical studies (see Section 7).

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Figure S9. Mass spectrometry characterization by EI for compound 2.



Figure S10. Isotopic distribution of the $[M^+]$ peak of **2**.

3. UV-Visible Measurements



Figure S11. Comparison of the UV-Visible spectra (in CH₂Cl₂ solution) of: FcCH₂CN (1), FcC(O)CN (2), FcCN (3) and unsubstituted ferrocene (FcH).

5. Crystallographic Data for Compounds 1 and 2

Compound 1

A clear yellow prismatic-like specimen of **1**, approximate dimensions 0.16 mm x 0.19 mm x 0.21 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 1784 frames were collected. The total exposure time was 14.87 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 16941 reflections to a maximum θ angle of 26.46° (0.80 Å resolution), of which 2012 were independent (average redundancy 8.420, completeness = 99.7%, R_{int} = 3.30%, R_{sig} = 1.91%) and 1818 (90.36%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.0855(17) Å, b = 7.5248(9) Å, c = 10.2932(11) Å, $\beta = 104.676(6)^\circ$, volume = 980.5(2) Å³, are based upon the refinement of the XYZ-centroids of 8240 reflections above 20 $\sigma(I)$ with 6.437° < $2\theta < 52.67^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.877. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7000 and 0.8000.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, $C_{12}H_{11}FeN$. The final anisotropic full-matrix least-squares refinement on F^2 with 127 variables converged at $R_1 = 2.34\%$, for the observed data and $wR_2 = 8.86\%$ for all data. The goodness-of-fit was 1.002. The largest peak in the final difference electron density synthesis was 0.558 e⁻/Å³ and the largest hole was -0.243 e⁻/Å³ with an RMS deviation of 0.083 e⁻/Å³. On the basis of the final model, the calculated density was 1.525 g/cm³ and F(000), 464 e⁻.



Figure S12. Thermal ellipsoid plot (at 50% probability) of compound 1.

Sample and crystal data for 1.				
$C_{12}H_{11}FeN$				
225.07				
100(2) K				
0.71073 Å				
0.16 x 0.19 x 0.21 mm				
clear yellow prismatic				
monoclinic				
$P 2_1/c$				
a = 13.0855(17) Å	$\alpha = 90^{\circ}$			
b = 7.5248(9) Å	$\beta = 104.676(6)^{\circ}$			
c = 10.2932(11) Å	$\gamma = 90^{\circ}$			
980.5(2) Å ³				
4				
1.525 Mg/cm ³				
1.491 mm ⁻¹				
464				
	C ₁₂ H ₁₁ FeN 225.07 100(2) K 0.71073 Å 0.16 x 0.19 x 0.21 mm clear yellow prismatic monoclinic $P 2_1/c$ a = 13.0855(17) Å b = 7.5248(9) Å c = 10.2932(11) Å 980.5(2) Å ³ 4 1.525 Mg/cm ³ 1.491 mm ⁻¹ 464			

Sample and crystal data for 1

Data collection and structure refinement for 1.		
Theta range for data collection	1.61 to 26.46°	
Index ranges	-16<=h<=16, -9<=k<=9, -12<=l<=12	
Reflections collected	16941	
Independent reflections	2012 [R(int) = 0.0330]	
Coverage of independent reflections	99.7%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8000 and 0.7000	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	2012 / 0 / 127	
Goodness-of-fit on F ²	1.002	
Δ/σ_{max}	0.001	
Final R indices	1818 data; I> $2\sigma(I) R_1 = 0.0234, wR_2 = 0.0722$	
	all data $R_1 = 0.0292, wR_2 = 0.0886$	
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0695P) ² +0.2059P] where P=(F_o^2 +2 F_c^2)/3	
Largest diff. peak and hole	0.558 and -0.243 eÅ ⁻³	
R.M.S. deviation from mean	0.083 eÅ ⁻³	



Figure S13. View of the crystal packing along the *b* axis where double layers parallel to the *bc* plane assembled through van der Waals forces can be seen.

Compound 2

A dark purple prismatic-like specimen of **2**, approximate dimensions 0.04 mm x 0.10 mm x 0.18 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 528 frames were collected. The total exposure time was 17.60 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 5228 reflections to a maximum θ angle of 25.49° (0.83 Å resolution), of which 1877 were independent (average redundancy 2.785, completeness = 98.5%, R_{int} = 6.08%, R_{sig} = 8.23%) and 1426 (75.97%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.612(6) Å, b = 10.349(9) Å, c = 13.003(10) Å, volume = 1024.3(14) Å³, are based upon the refinement of the XYZ-centroids of 1860 reflections above 20 $\sigma(I)$ with 6.202° < 20 < 47.16°. Data were corrected for absorption effects using the multi-scan method (TWINABS). The ratio of minimum to maximum apparent transmission was 0.781. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7817 and 0.9447.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_12_12_1$, with Z = 4 for the formula unit, $C_{12}H_9FeNO$. The final anisotropic full-matrix least-squares refinement on F^2 with 127 variables converged at $R_1 = 5.37\%$, for the observed data and $wR_2 = 14.12\%$ for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.332 e⁷/Å³ and the largest hole was -0.691 e⁷/Å³ with an RMS deviation of 0.106 e⁷/Å³. On the basis of the final model, the calculated density was 1.550 g/cm³ and F(000), 488 e⁷.



Figure S14. Thermal ellipsoid plot (at 50% probability) of compound 2.

Sample and crystal data for 2.		
Chemical formula	C ₁₂ H ₉ FeNO	
Formula weight	239.05	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal size	0.04 x 0.10 x 0.18 mm	
Crystal habit	dark purple prismatic	
Crystal system	orthorhombic	
Space group	$P 2_1 2_1 2_1$	
Unit cell dimensions	a = 7.612(6) Å	$\alpha = 90^{\circ}$
	<i>b</i> = 10.349(9) Å	$\beta = 90^{\circ}$
	c = 13.003(10) Å	$\gamma = 90^{\circ}$
Volume	1024.3(14) Å ³	
Z	4	
Density (calculated)	1.550 Mg/cm^3	
Absorption coefficient	1.439 mm^{-1}	
F(000)	488	

Data collection and structure refinement for 2.

Theta range for data collection	2.52 to 25.49°
Index ranges	-8<=h<=9, -12<=k<=12, -12<=l<=15
Reflections collected	5228
Independent reflections	1877 [R(int) = 0.0608]
Coverage of independent reflections	98.5%
Absorption correction	multi-scan
Max. and min. transmission	0.9447 and 0.7817
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1877 / 0 / 127
Goodness-of-fit on F ²	1.000
Final R indices	1426 data; I> 2σ (I) R1 = 0.0537, wR2 = 0.1250
	all data $R1 = 0.0799, wR2 = 0.1412$
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0805P) ² +0.0000P] where P=(F_o^2 +2 F_c^2)/3
Largest diff. peak and hole	0.332 and -0.691 eÅ ⁻³
R.M.S. deviation from mean	0.106 eÅ ⁻³



Figure S15. View of the crystal packing along the *a* axis where van der Waals forces between columns of molecules parallel to the *a* axis can be seen.

6. Electrochemistry of Compounds 1 and 2



Figure S16. CV responses of compound 1 (10^{-3} M) recorded in CH₃CN containing 0.1 M TBAPF₆, at different scan rates. Plots of I_{pa} and I_{pc} against scan rate^{1/2}.



Figure S17. SWV response of compound 1 (10^{-3} M) recorded in CH₃CN containing 0.1 M TBAPF₆.



Figure S18. CV responses of compound 2 (10^{-3} M) recorded in CH₃CN containing 0.1 M TBAPF₆, at different scan rates. Plots of I_{pa} and I_{pc} against scan rate^{1/2}.



Figure S19. SWV response of compound 2 (10^{-3} M) recorded in CH₃CN containing 0.1 M TBAPF₆.



Figure S20. Comparison of the CV responses, recorded in CH_3CN solution containing 0.1 M TBAPF₆, at 100 mVs⁻¹ of: FcCH₂CN (1), FcC(O)CN (2), FcCN (3), ferrocene (FcH) and decamethylferrocene (Fc*).

7. Theoretical Studies⁸

7. 1. UV-Visible theoretical spectra of compounds 1 and 2. As mentioned in the main article, the absorption spectra of compounds 1 and 2 considering vertical excitations from the ground state were calculated by means of Time-Dependent linear response Theory (TD-DFT). This methodology, with a careful previous assessment, can provide accurate results for large systems that are not affordable with other more expensive methods as for example CASPT2. TD-DFT single-point calculations were carried out with different density functionals B3LYP, PBE0 and BPW91, finding out that BPW91 correctly predicts the experimental results, the HOMO-LUMO gap for ferrocene derivatives being within the expected range of values. All-electron Pople's 6-311+G(df,p) basis set was used. Solvent effects were also evaluated by means of the polarizable continuum model of Tomasi and co-workers (PCM), although vacuum calculations gave better agreement. The electronic spectra were simulated by means of the SWizard program package. This program calculates the absorption profile as a sum of Gaussian functions using the formula:

$$\varepsilon(\omega) = 2.174 * 10^8 \sum_{i} \frac{f_i}{\Delta_{y_2}} \exp(-2.773 \frac{(\omega - \omega_i)^2}{\Delta_{y_2}^2})$$

where ε is the molar absorbance in units of mol⁻¹ cm⁻¹ L, the index sum runs over the number of computed excitation energies ω_i (expressed in cm⁻¹) with corresponding oscillator strengths f_i , and $\Delta_{1/2}$ is the half-weight bandwidth assumed constant. With these computational tools it is possible to analyze the composition of the observed absorption bands, which in the case of the deep-purple band of compound **2** (the one around 516 nm) is formed mainly by two contributions, one arising from a HOMO-2 -> LUMO transition (63%) and a second one from a HOMO-1 -> LUMO transition (32%). HOMO-2, HOMO-1 and HOMO are very close in energy, as shown in the following figures below this text. Compound **1** presents a HOMO-LUMO gap of 2.93 eV, whereas compound **2** has a much shorter value of 1.83 eV. Looking at the molecular orbital pictures of compound **2**, it is easy to appreciate that LUMO has a very important contribution from the acylcyano subunit. There is a kind of charge transfer from the ferrocene moiety to the substituent in that characteristic deep-purple band of compound **2**.



Figure S21. UV-Visible theoretical spectra obtained with TD-DFT at the BPW91/6-311+G(df,p) level of theory in vacuum. The curves are 30 nm blue-shifted to favor the comparison with the experimental spectra in solution.



Figure S22. Molecular orbital relative energies in atomic units of compound **2** at the BPW91/6-311+G(df,p) level of theory.



Figure S23. LUMO, HOMO, HOMO-1 and HOMO-2 of compound 2 at the BPW91/6-311+G(df,p) level of theory.

7.2. AIM Structural differences of compounds 1-2. Atoms in Molecules theory is a very useful tool based on the topological analysis of the electron density. By obtaining the molecular graph of a given system, the strength and nature of bonding can be measured looking at the values of the density at the bond critical points (BCPs), which are first-order saddle points of the electron density. Other points of chemical interest are ring critical points (RCPs) and cage critical points (CCPs). AIM calculations revealed a different nature on the ferrocene moieties of compounds 1 and 2. Cp units in compound 2 present two RCP and one CCP which are not present in compound 1. Also, density values on Cp-Fe bonds are slightly smaller in compound 2. These changes reveal the substitution effect on the ferrocene unit, changes that have direct consequences on the optical properties.



Figure S24. Molecular graphs of compounds 1-2. Green dots are BCPs, red dots RCPs and blue dots CCPs. Electron density values on BCPs are plotted on the bond pathways.

7.3. Ionization energy of compound 2. Vertical and adiabatic ionization energies were calculated with B3LYP, PBE0, LC-BPW91 and BPW91 density functionals. The vertical value of ferrocene obtained through photoelectron spectroscopy technique was taken as reference (6.90 eV) to calibrate the functionals. Once again BPW91 showed an excellent agreement (6.93 eV). Using the ionization energy definition itself (not the Koopman's theorem) calculations in vacuum, dichloromethane and water were carried out, resulting in 7.57 eV (vertical, vacuum), 7.44 eV (adiabatic, vacuum), 5.86 eV (adiabatic, dichloromethane) and 5.64 eV (adiabatic, water). Using the procedure followed by Winget and co-workers, the half-potential $E_{1/2}$ vs SCE is then 0.96 eV.

8. References

- 1. Sheldrick, G. M. *SADABS* Version 2.03, Program for Empirical Absorption Correction; University of Göttingen: Germany, 1997-2001.
- 2. *SAINT+NT* Version 6.04; SAX Area-Detector Integration Program; Bruker Analytical X-ray Instruments: Madison, WI, 1997-2001.
- 3. Bruker AXS. *SHELXTL* Version 6.10, Structure Determination Package; Bruker Analytical X-ray Instruments: Madison, WI, 2000.
- 4. Sheldrick, G. M. Acta Crystallogr. A, 1990, 46, 467.
- 5. Sheldrick, G. M. SHELXL97, Program for Crystal Structure Refinement; Göttingen: Germany, 1997.
- 6. D. Lednicer and C. R. Hauser, Organic Syntheses, 1973, 5, 578.
- 7. K. E. Gonsalves, R.W. Lenz, M.D. Rausch, Appl. Organomet. Chem., 1987, 1, 81.
- Electronic structure calculations were carried out with Gaussian 09 code: Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009. Harmonic frequency calculations were used in the harmonic frequency calculations.

Time-Dependent-Density Functional Theory (TD-DFT) references: (a) R. Bauernschmitt, R. Ahlrichs. *Chem. Phys. Lett.* **1996**, *256*, 454-464; (b) A. Dreuw, M. Head-Gordon. *Chem. Rev.* **2005**, *105*, 4009-4037. BPW91 references: exchange functional A. D. Becke *Phys. Rev. A* **1988**, *38*, 3098-3100; correlation functional: J. Perdew (**1991**) In: Ziesche P, Eschrig H (eds) Electronic structure of solids. Verlag, Berlin.

AIM theory references: (a) R. F. W. Bader (1990) Atoms in Molecules. A Quantum Theory. Clarendon, Oxford. (b) A. D. Becke, K. E. Edgecombe. *J. Chem. Phys.* 1990; *92*, 5397-5403.].

Other functionals: B3LYP: (a) A. D. Becke. *J Chem Phys* **1993**, *98*, 5648–5652; (b) C. Lee, W. Yang, R. Parr. *Phys Rev B*, **1988**, *37*, 785–789.

PBE0 (a) C. Adamo, V. Barone. *J Chem Phys* **1999**, *110*, 6158–6169; (b) J. P. Perdew, K. Burke, M. Ernzerhof *Phys Rev Lett* **1996**, *77*, 3865–3868; **LC-BPW91** (Hirao correction): I. Iikura, T. Tsuneda, T. Yanai, K. Hirao. *J Chem Phys.* **2001**, *115*, 3540–3544.

SWizard program: S. I. Gorelsky. *SWizard program*, http://www.sg-chem.net/, University of Ottawa, Ottawa, Canada, 2010. S. I. Gorelsky and A. B. P. Lever. *J. Organomet. Chem.* 2001; 635, 187-196.

Half-potential: P. Winget, E. J. Weber, C. J. Cramer, D. Truhlar. Phys. Chem. Chem. Phys. 2000, 2, 1231-1239.