

Effect of Fluorinated Ligand on the Electrochemical Properties of (Diphosphine)Pt(*p*-SC₆HF₄)₂

Su-Kyung Lee and Dong-Youn Noh*

Department of Chemistry, Seoul Women's University, Seoul 01797, Korea.

*E-mail: dynoh@swu.ac.kr

(Received October 13, 2017; Accepted December 13, 2017)

Key words: P₂PtS₂ Core, Group Electronegativity, Fluorobenzene, Electrochemistry

INTRODUCTION

Heteroleptic (diphosphine)Pt(dithiolate) complexes have been investigated for their versatile properties, especially for diversity of redox behavior in solution state depending on functionality of ligands.^{1–3} These complexes are usually stable in solution state mainly due to thermodynamic stability obtained by the chelate effect of the two bi-dentate ligands, diphosphine and dithiolate.⁴ Conversely, monothiolate derivatives are expected to be less stable in solution state than dithiolate due to lack of stability caused by dithiolate-induced chelate effect.

In previous studies on electrochemistry of (dppf)Pt(BzT)₂ complexes (dppf: 1,1'-bis(diphenylphosphino)ferrocene; BzT: benzene-thiolate such as benzenethiolate(BT) and 2,3,5,6-tetrafluorobenzenethiolate(TFBT)),⁵ revealed different redox behavior depending on BzT-ligands. It was tentatively suggested to be concerned with group electronegativity (GEN)^{6,7} of the monothiolate ligand: On anodic scanning, the (dppf)Pt(BT)₂ complex (*Scheme 1*) reveals irreversible anodic peak before reversible redox cycle corresponding to [dppf]⁺⁰ is observed at higher potential region. Conversely, (dppf)Pt(TFBT)₂ complex with fluoride substituents on benzenethiolate ligand reveals no irreversible peak at low potential region.

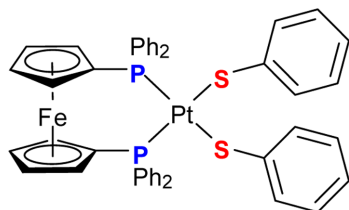
In the coupling reaction of (P2)Pt(BzT)₂ complexes (P2: 1,2-bis(diphenylphosphino)-1',2'-dimethyltetrafulval-

ene),⁸ the (P2)Pt(BT)₂ complex undergoes oxidative coupling reaction to produce [(P2)Pt{μ-(BT)₂}Pt(P2)]²⁺ dimerization.⁹ Being opposed to this result, (P2)Pt(TFBT)₂ complex did not afford the coupling product under the same reaction conditions. In this study, UV-Vis, CV and spectroelectrochemistry of (P2)Pt(TFBT)₂ complex are investigated and compared with those of (P2)Pt(BT)₂ and (P2)PtCl₂ complexes based on electronegativity differences of ligands, with a view to explain the difference of redox behavior and product of coupling reaction.

EXPERIMENTAL

First grade organic solvents were purchased and used without further purification. They are degassed by bubbling Ar prior to use. All reactions involving Pt(II) complexes were conducted under protection from light and air. Melting points were determined using a Stuart SMP3 (Barloworld Scientific Ltd.). MALDI-TOF mass spectra were measured with a Voyager-DETM STR Biospectrometry Workstation (Applied Biosystems Inc.). Infrared spectra were recorded by the KBr pellet method on a Perkin Elmer Spectrum 100 in the range of 4000–400 cm⁻¹. The ¹H/¹⁹F/³¹P NMR measurements were conducted at room temperature using an Avance 500 (Bruker, 500 MHz) with samples dissolved in CDCl₃. Positive chemical shifts are reported downfield from external standards, viz. 85% H₃PO₄ for ³¹P{¹H} resonances and CFCl₃ for ¹⁹F resonances. UV/Vis spectra were obtained on an HP 8452A diode array spectrophotometer in CH₂Cl₂.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were conducted at room temperature with a CHI 620A Electrochemical Analyzer (CHI Instrument Inc.) in 3 mL of CH₂Cl₂ solution containing 1 mM of the sample, using 0.1 M *n*-Bu₄N⁺PF₆⁻ as supporting electrolyte, Ag/AgCl as reference electrode, a



Scheme 1. Schematic structure of (dppf)Pt(BT)₂.

Pt button working electrode, a Pt wire as the counter electrode and with scan rate of 50 mV s⁻¹. All redox potentials were referenced against Fc/Fc⁺ redox couple ($E_{1/2}$ = 0.565 V). *In-situ* measurements of UV-Vis and CV (UV-Vis spectroelectrochemistry: UV-Vis SEC)¹⁰ were measured on the same conditions described above, except for a Pt grid working electrode with a scan rate of 10 mV s⁻¹ and a referenced Fc/Fc⁺ redox potential ($E_{1/2}$ = 0.530 V).

Preparation of (P2)Pt(TFBT)₂

A CH₂Cl₂ solution (25 mL) of (P2)PtCl₂ (0.2 mmol, 173 mg),¹ triethylamine (0.8 mmol, 81 mg) and 2,3,5,6-tetrafluorobenzeneethiol (H(TFBT): 0.4 mmol, 73 mg) was stirred for 24 h at room temperature under argon atmosphere (*Scheme 2*). Red-orange solution was evaporated and solid residue was purified by column chromatography (SiO₂, CH₂Cl₂). Red-orange products were recrystallized from CH₂Cl₂/MeOH. Yield: 82% (190 mg); m.p. > 250 °C (decomp.); Anal. Calc. for C₄₄H₂₈F₈P₂PtS₆: C 45.63; H 2.44. Found: C 45.74; H 2.47%; ¹H NMR (500 MHz, CDCl₃, TMS): δ = 7.82 (m, 8H, Ph), 7.56 (t, 4H, Ph), 7.50 (t, 8H, Ph), 6.50 (m, 2H, SC₆F₄H), 1.89 ppm (s, 6H, CH₃ in TTF); ³¹P NMR (202 MHz, CDCl₃, 85% H₃PO₄): δ = 32.40 ppm ($J_{\text{Pt-P}}$ = 2987 Hz); ¹⁹F NMR (282 MHz, CDCl₃, CFCI₃): -133.4 (m, *o*-F), -142.2 ppm (m, *m*-F); FT-IR (KBr): 3061 (Ar C-H), 2918, 2850 (-CH₃), 1625, 1484, 1436, 1428 (Ar C=C), 1219, 1168 (Ar C-F str), 1101 (P-Ph),

1011 (Ar C-H ip def), 910 (C-F def), 887 (asym S-C-S), 743, 713, 690 (Ar C-H oop def), 550, 519, 480 cm⁻¹ (Ar ring oop def); UV/Vis (CH₂Cl₂): λ_{max} = 232 (s), 276 (m), 320 (sh), 460 nm (w); MALDI-TOF MS: *m/z*(%) 975.9736 (100) [M⁺-SC₆F₄H].

Preparation of (P2)Pt(BT)₂

This compound was prepared according to the established process.⁹

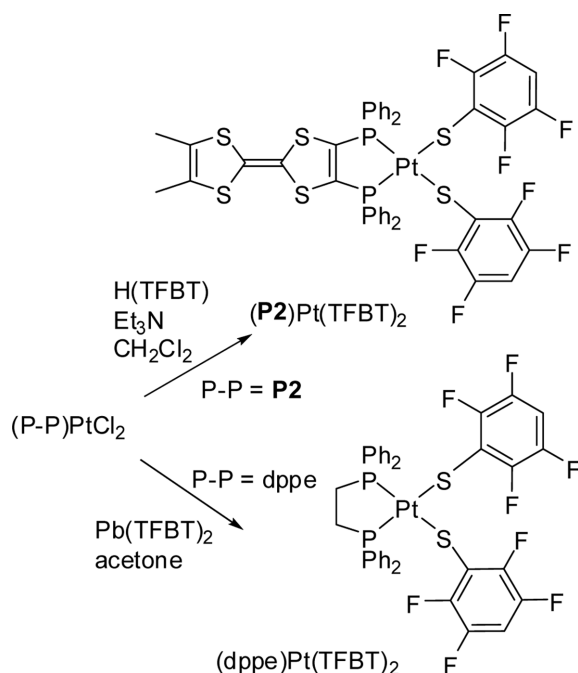
Preparation of (dppe)Pt(TFBT)₂

An acetone solution (5 mL) of Pb(TFBT)₂ (0.1 mmol, 57 mg)¹¹ was added to acetone suspension (5 mL) of (dppe)PtCl₂ (0.1 mmol, 66 mg) with stirring for 24 h at room temperature (*Scheme 2*). PbCl₂ precipitate was separated by filtration and the purified product was recrystallized from acetone/pentane. Yield: 39% (37 mg); m.p. > 275 °C (decomp); Anal. Calc. for C₃₈H₂₆F₈P₂PtS₂: C 47.75; H 2.74. Found: C 47.24; H 2.78%; ¹H NMR (300 MHz, CDCl₃, TMS): δ = 7.78 (m, 8H, Ph), 7.49 (m, 12H, Ph), 6.50 (m, 2H, SC₆F₄H), 2.15 ppm (m, 4H, PCH₂CH₂P); ³¹P NMR (202 MHz, CDCl₃, 85% H₃PO₄): δ = 45.60 ppm ($J_{\text{Pt-P}}$ = 2986 Hz); ¹⁹F NMR (282 MHz, CDCl₃, CFCI₃): δ = -132.7 (m, *o*-F), -142.5 ppm (m, *m*-F); FT-IR (KBr): 3057 (Ar C-H), 1626, 1484, 1437, 1427 (Ar C=C), 1218, 1167 (Ar C-F str), 1104 (P-Ph), 1000 (Ar C-H ip def), 910 (C-F def), 888 (asym S-C-S), 746, 712, 690 (Ar C-H oop def), 535, 482 cm⁻¹ (Ar ring oop def); UV/Vis (CH₂Cl₂): λ_{max} = 232 (s), 260 (m), 340 nm (w).

RESULTS AND DISCUSSION

(P2)Pt(TFBT)₂ was synthesized from metathesis reaction of the corresponding (P2)PtCl₂ and H(TFBT) in the presence of NEt₃ (*Scheme 2*). Column chromatographic purification afforded the product in a high yield of 82%. Comparatively, the (dppe)Pt(TFBT)₂ complex was prepared from (dppe)PtCl₂ and Pb(TFBT)₂ affording a lower yield of 39%, but it allows convenient purification of the desired product by precipitating out the side-product (PbCl₂) from the reaction mixture. Both (diphosphine)Pt(TFBT)₂ complexes were spectroscopically characterized.

UV-Vis spectra of P2 and its Pt(II) complexes were obtained in CH₂Cl₂ with 62.5 mM samples, and are demonstrated in *Fig. 1*. Spectrum of P2 reveals three intense bands in the short wavelength region, concerned with the phenyls in diphosphine ligand.¹² The weak band observed at 418 nm (8 times expanded) is obviously attributed to the π-π* transition in TTF moiety.¹³ This band, however, shifts to



Scheme 2. Syntheses of (diphosphine)Pt(TFBT)₂.

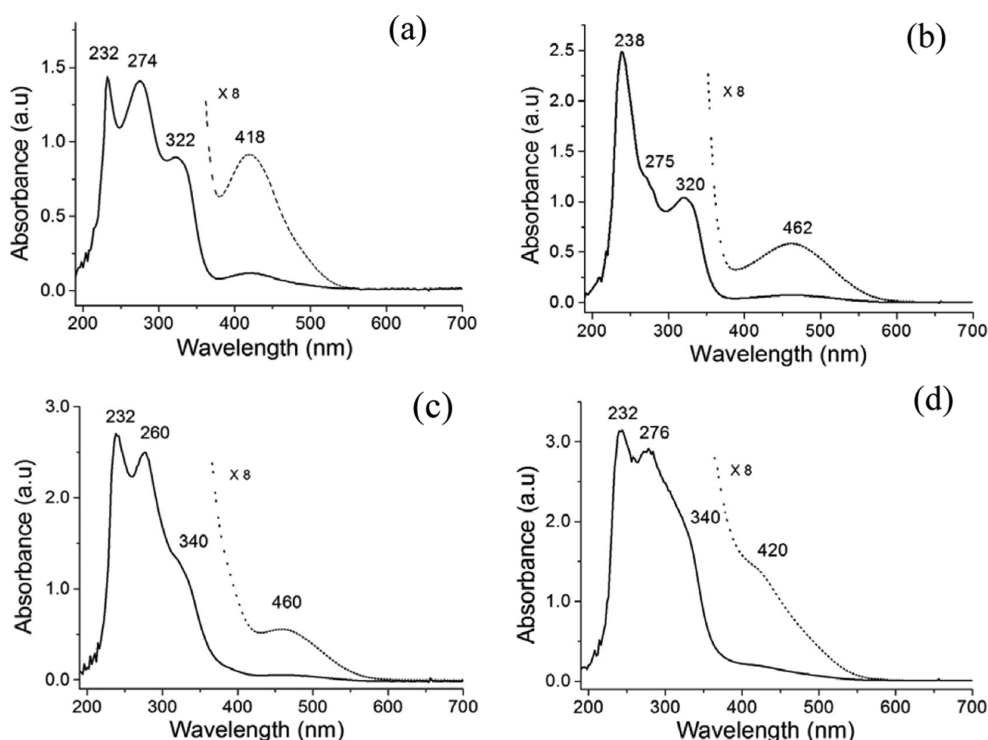


Figure 1. UV-Vis spectra of (a) **P2**, (b) (**P2**)PtCl₂, (c) (**P2**)Pt(TFBT)₂ and (d) (**P2**)Pt(BT)₂.

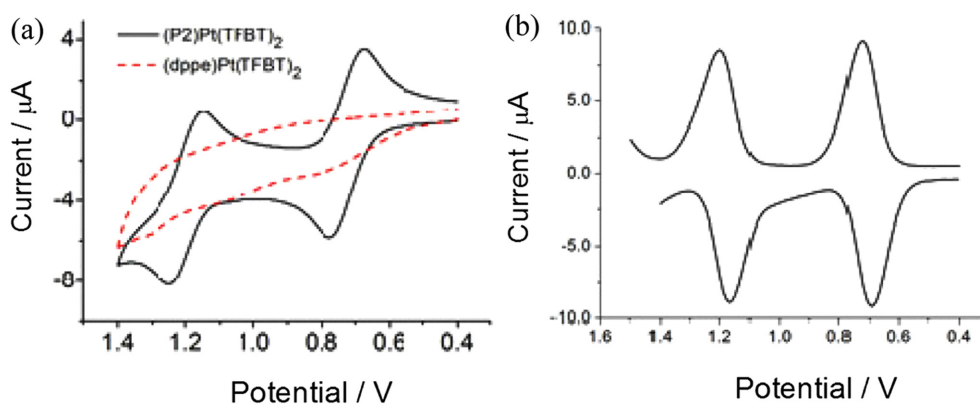


Figure 2. (a) CVs of (**P2**)Pt(TFBT)₂ and (dppe)Pt(TFBT)₂, and (b) DPV of (**P2**)Pt(TFBT)₂ (CH₂Cl₂, Fc/Fc⁺ = 0.565 V).

462 nm and 460 nm for (**P2**)PtCl₂ and (**P2**)Pt(TFBT)₂, respectively. To the contrary, it stays almost unchanged at 420 nm for (**P2**)Pt(BT)₂. Differences between both (**P2**)Pt(monothiolate)₂ complexes are in line with the electron-withdrawing character of the BT (non-fluorinated) and TFBT (fluorinated) ligands, known as ‘group electronegativity’ of functional groups.⁶ It is also comparable with the electronegative Cl[−] anion from this point of view. Therefore, more electronegative TFBT ligand impacts UV-Vis absorption of TTF moiety in **P2** ligand, while non-fluorinated BT ligand does less. These observations are further

discussed below, associated with electrochemical results.

CV and DPV of (**P2**)Pt(TFBT)₂ (Fig. 2) exhibit two reversible cycles in the potential region measured, unambiguously attributable to successive one-electron redox processes of TTF core in **P2** ligand.⁹ From Fig. 2a, compared to the CV of (**P2**)Pt(TFBT)₂, TTF-free (dppe)Pt-(TFBT)₂ complex reveals no redox cycle in this potential region. Half-wave potentials ($E_{1/2}$) for the two redox cycles of (**P2**)Pt(TFBT)₂ are 0.725 and 1.199 V (Table 1). Potentials are close to those of (**P2**)PtCl₂ (0.734 and 1.206 V), contrary to un-coordinated **P2** ($E_{1/2}$ = 0.422 and 0.899 V).

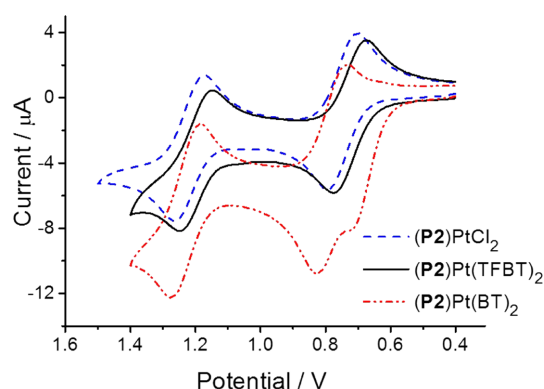
Table 1. CV data for **P2** and its Pt(II) complexes^a

Complexes	E_{pa}^1	E_{pa}^2	E_{pa}^3	E_{pc}^2	E_{pc}^3	$E_{1/2}^{2[b]}$	$E_{1/2}^{3b}$
P2		0.527	0.964	0.396	0.834	0.422	0.899
(P2)PtCl ₂ ^c		0.777	1.245	0.691	1.166	0.734	1.206
(P2)Pt(TFBT) ₂		0.775	1.248	0.675	1.149	0.725	1.199
(P2)Pt(BT) ₂ ^[c]	0.732	0.827	1.276	0.733	1.184	0.780	1.230

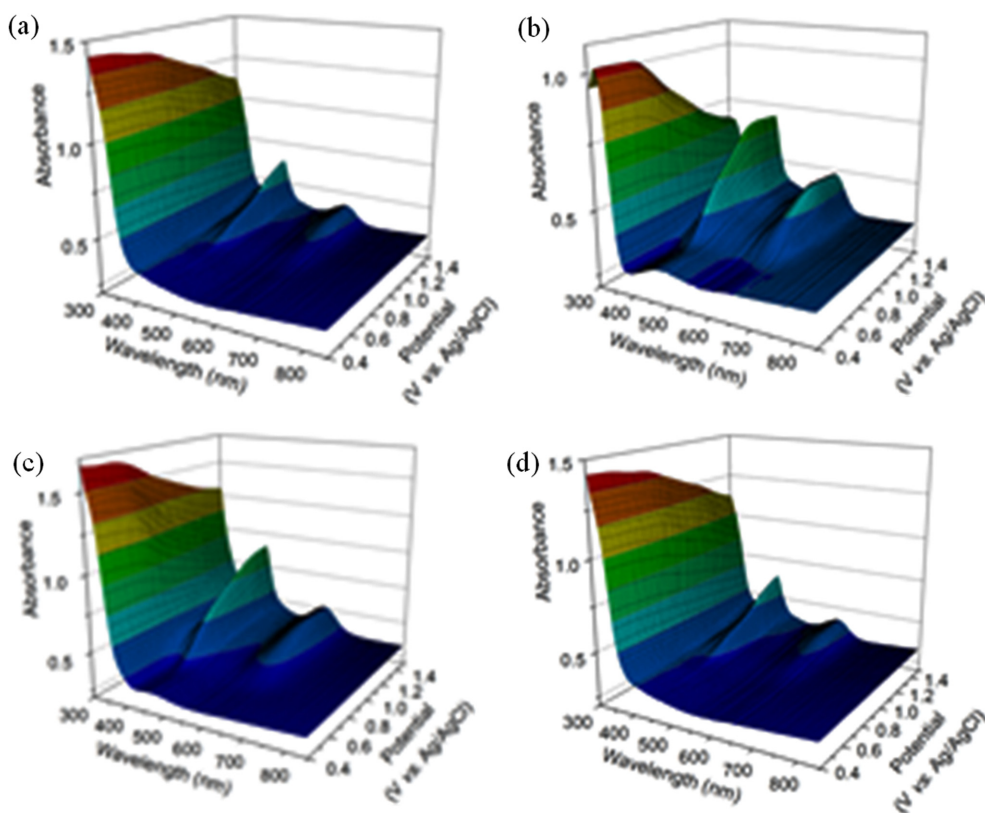
^a50 mV s⁻¹ scan rate; Supporting electrolyte: 0.1 M *n*-Bu₄N-PF₆; Working electrode: Pt disk; Counter electrode: Pt wire; Ref. electrode: Ag/AgCl; 1 mM samples in CH₂Cl₂; $E_{1/2} = 0.565$ V for Fc⁺/Fc.

^b $E_{1/2} = (E_{pa} + E_{pc}) / 2$.

^cref. 9.

**Figure 3.** CVs of (**P2**)PtCl₂, (**P2**)Pt(TFBT)₂ and (**P2**)Pt(BT)₂ measured in CH₂Cl₂ (Fc⁺/Fc = 0.565 V).

Half-wave potentials of (**P2**)Pt(BT)₂, however, appear at more anodic potential region ($E_{1/2} = 0.780$ and 1.230 V). Moreover, it reveals an additional irreversible wave at $E_{pa} = 0.732$ V (Fig. 3). This irreversible wave is rationalized as that associated with thiolate ligand oxidation, leaving a cationic species [(**P2**)Pt(BT)]⁺.⁹ Cationic species is revealed as a key intermediate in the dimerization process to [(**P2**)Pt(μ-BT)₂Pt(**P2**)]²⁺. A noteworthy point in these electrochemical results is that such a thiolate ligand oxidation process is not identified in the CV of (**P2**)Pt(TFBT)₂. That is, redox behavior of (**P2**)Pt(TFBT)₂ is almost identical with that of (**P2**)PtCl₂, rather than that of (**P2**)Pt(BT)₂ (Fig. 3). Such electrochemical behavior were also revealed in different

**Figure 4.** UV-Vis SEC spectra of (a) **P2**, (b) (**P2**)PtCl₂, (c) (**P2**)Pt(TFBT)₂ and (d) (**P2**)Pt(BT)₂.

diphosphine system such as (dppf)Pt(TFBT)₂ and (dppf)Pt(BT)₂.⁵ Considered together with UV-Vis results, differences in redox behavior between (P2)Pt(TFBT)₂ and (P2)Pt(BT)₂ arise from electronegativities of TFBT and BT ligands.

Oxidized state of (P2)Pt(TFBT)₂ was investigated by UV-Vis SEC and compared with those of related complexes shown in Fig. 4. UV-Vis SEC was conducted between 0.4 and 1.4 V, considering oxidation potentials of complexes. Weak absorption band of (P2)Pt(TFBT)₂ at 460 nm (0.4 V) intensifies from approximately 0.7 V, and final absorption bands are observed at 413(sh), 448 and 624 nm when the applying potential is 1.4 V.^{1c} Almost the same results are obtained for (P2)PtCl₂ (416(sh), 448 and 625 nm) and (P2)Pt(BT)₂ (420(sh), 450 and 625 nm), except that the absorption band for (P2)Pt(BT)₂ starts to intensify at approximately 0.8 V. It suggests that oxidation of coordinated P2 ligand shifts to higher potential region (*ca.* about 0.1 V) by thiolate ligand oxidation.

In summary, overall redox behavior of UV-Vis SEC, as well as the CV results, for (P2)Pt(TFBT)₂ are close to that of (P2)PtCl₂, but much different from those of (P2)Pt(BT)₂ even though both complexes belong to the (P2)Pt(benzenethiolate)₂ category. It results from the difference of 'group electronegativity' of the benzene-thiolate ligands (TFBT and BT). Consequently, this difference can prevent oxidative dimerization reaction of (P2)Pt(TFBT)₂, contrary to the case of (P2)Pt(BT)₂.

Acknowledgments. This work was supported by a sabbatical year research grant from Seoul Women's University (2017). A part of this study was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (NRF2010-0011478). We gratefully thank Dr. M. Fourmigué (CNRS-Univ. Rennes 1, France) for the supply of P2 compound.

REFERENCES

- (a) Lee, S. K.; Shin, K. S.; Noh, D. Y.; Jeannin, O.; Barrière, F.; Bergamini, J. F.; Fourmigué, M. *Chem. Asian J.* **2010**, *5*, 169. (b) Shin, K. S.; Jung, Y. J.; Lee, S. K.; Fourmigué, M.; Barrière, F.; Bergamini, J. F.; Noh, D. Y. *Dalton Trans.* **2008**, 5869. (c) Noh, D. Y.; Shin, K. S.; Lee, S. K. *Bull. Korean Chem. Soc.* **2009**, *30*, 3069.
- (a) Shin, K. S.; Han, Y. K.; Noh, D. Y. *Bull. Korean Chem. Soc.* **2003**, *24*, 235. (b) Noh, D. Y.; Seo, E. M.; Lee, H. J.; Jang, H. Y.; Choi, M. G.; Kim, Y. H.; Hong, J. *Polyhedron* **2001**, *20*, 1939.
- (a) Jeon, S.; Suh, W.; Noh, D. Y. *Inorg. Chem. Comm.* **2017**, *81*, 43. (b) Jeon, H.; Suh, W.; Noh, D. Y. *Inorg. Chem. Comm.* **2012**, *24*, 181.
- (a) Calvin, M.; Wilson, K. W. *J. Am. Chem. Soc.* **1945**, *67*, 2003. (b) Calvin, M.; Bailes, R. H. *J. Am. Chem. Soc.* **1946**, *68*, 949. (c) Duffield, R. B.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 557. (d) Calvin, M.; Melchior, N. C. *J. Am. Chem. Soc.* **1948**, *70*, 3270.
- Lee, S. K.; Noh, D. Y. *Inorg. Chem. Comm.* **2010**, *13*, 183.
- (a) Huheey, J. E. *J. Phys. Chem.* **1965**, *69*, 3284. (b) Huheey, J. E. *J. Phys. Chem.* **1966**, *70*, 2086.
- (a) Herrera-Álvarez, C.; Gómez-Benítez, V.; Redón, R.; García, J. J.; Hernández-Ortega, S.; Toscano, R. A.; Morales-Morale, D. *J. Organomet. Chem.* **2004**, *689*, 2464. (b) Garner-O'Neale, L. D.; Bonamy, A. F.; Meek, T. L.; Patrick, B. G. *J. Mol. Struct. (Theochem)* **2003**, *639*, 151.
- (a) Fourmigué, M.; Batail, P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 29. (b) Fourmigué, M.; Uzelmeier, C. E.; Boubekeur, K.; Bartley, S. L.; Dunbar, K. R. *J. Organomet. Chem.* **1997**, *529*, 343. (c) Avarvari, N.; Martin, D.; Fourmigué, M. *J. Organomet. Chem.* **2002**, *643/644*, 292. (d) Uzelmeier, C. E.; Smucker, B. W.; Reinheimer, E. W.; Shatruck, M.; O'Neal, A. W.; Fourmigué, M.; Dunbar, K. R. *Dalton Trans.* **2006**, 5259. (e) Devic, T.; Batail, P.; Fourmigué, M.; Avarvari, N. *Inorg. Chem.* **2004**, *43*, 3136.
- Lee, S. K.; Jeannin, O.; Fourmigué, M.; Suh, W.; Noh, D. Y. *J. Organomet. Chem.* **2012**, *716*, 237.
- Kaim, W.; Klein, A. *Spectroelectrochemistry*, RSC Publishing, Cambridge, **2008**.
- (a) Appleton, S. E.; Briand, G. G.; Decken, A.; Smith, A. S. *Dalton Trans.* **2004**, 3515. (b) Peach, M. E. *Can. J. Chem.* **1968**, *46*, 2699.
- Fourmigué, M.; Batail, P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 29.
- Tian, J.; Ding, Y.; Zhou, T.; Zhang, K.; Zhao, X.; Wang, H.; Zhang, D.; Liu, Y.; Li, Z. *Chem. Eur. J.* **2014**, *20*, 575.