КООРДИНАЦИОННЫЕ СОЕДИНЕНИЯ

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PALLADIUM(II)-DPPE-ARYLAZOIMIDAZOLE COMPLEXES: SYNTHESIS, AND SPECTROSCOPIC CHARACTERIZATION

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Reaction of $[\text{Pd}(\text{dppe})\text{Cl}_2/\text{Br}_2]$ with AgOTf in a dichloromethane medium followed by ligand addition led to $[\text{Pd}(\text{dppe})(\text{OSO}_2\text{CF}_3)_2]$ and then $[\text{Pd}(\text{dppe})(\text{RaaiR})(\text{OSO}_2\text{CF}_3)_2]$ [$\text{RaaiR}' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R'}$, (**1–3**), abbreviated as a N,N'-chelator, where N(imidazole) and N(azo) are represented by N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**1**), CH_2CH_3 (**2**), CH_2Ph (**3**), OSO_2CF_3 is the triflate anion, dppe = 1,2-bis-(diphenylphosphinoethane)]. ^{31}P $\{^1\text{H}\}$ NMR confirmed that due to the two phosphorus atom interaction in the azoimine symmetrical environment one sharp peak was formed. The ^1H NMR spectral measurements suggest that azo-imine link with lot of phenyl protons in the aromatic region. ^{13}C (^1H) NMR spectrum, ^1H – ^1H COSY and ^1H – ^{13}C HMQC spectrum assign the solution structure and stereo-retentive conformation in each complex.

Keywords: Nickel(II), arylazoimidazole, ^1H , ^{13}C (^1H), ^{31}P (^1H), ^1H – ^1H COSY, ^1H – ^{13}C HMQC NMR, ESI mass, IR spectra.

INTRODUCTION

Understanding photo-induced electron transfer is a major scientific objective and is of technological importance for the design of synthetic molecular devices [1–3]. It is clear that the ability to mimic the natural photosynthesis process in the laboratory would have great technological significance in terms of solar energy conversion and storage. Synthetic porphyrin-based assemblies have been extensively used as models for molecular organization and energy/electron transfer processes [4–8]. Many clever and ingenious reaction center models have been prepared, and it is clear that the sophistication of synthetic multicomponent species that mimic the primary events of natural photosynthesis has increased tremendously. However, as the types and numbers of components are increased, the level of complexity also expands, and model systems become more difficult to prepare. To a large extent, progress in this area is still significantly synthesis limited. Most of the existing model systems are linked through organic spacers [5–7]. The synthetic methods for these systems typically are multistep processes, and yields are often extremely low. Recently some attempts have been turned to developing new strategies for designing assemblies that can achieve sequential multistep electron transfer processes. Sessler *et al.* have prepared model systems that linked donors and acceptors through hydrogen bonds [9, 10]. Sauvage *et al.* have designed bis(terpyridyl)porphyrins and utilized the terpyridyl group to build donor/acceptor array. In this paper,

the reaction of RaaiR' with lower case Palladium(II) dppe derivatives was examined and the products, $[\text{Pd}(\text{dppe})(\text{RaaiR}')](\text{OTf})_3$ [$\text{RaaiR}' = p\text{-R-C}_6\text{H}_4\text{-N=N-C}_3\text{H}_2\text{-NN-1-R'}$, (**1–3**), abbreviated as a N,N'-chelator, where N(imidazole) and N(azo) are represented by N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and R' = Me (**1**), CH_2CH_3 (**2**), CH_2Ph (**3**), OSO_2CF_3 is the triflate anion] were isolated. The complexes were well characterized by IR, ^1H NMR (1D & 2D) and mass spectrometry.

EXPERIMENTAL

Published methods were used to prepare RaaiR' and $[\text{Pd}^{\text{II}}(\text{dppe})(\text{Cl})_2]$ [7–21]. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of solvents was done following the literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. IR spectra were obtained using a JASCO 420 spectrophotometer ($4000\text{--}200\text{ cm}^{-1}$). The ^1H NMR spectra in CDCl_3 were obtained on a Bruker 500 MHz FT NMR spectrometer using SiMe_4 as an internal reference and CFCl_3 (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}\text{ M}$ in acetonitrile. Mass spectra were recorded on a VG Autospec ESI-mass spectrometer. Electrochemical work was carried out using an EG & G PARC Versastat

computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298 K using a Pt-disk milli working electrode at a scan rate of 50 mV s^{-1} . All results were referenced to a saturated calomel electrode (SCE).

Preparation of the complexes, {diphenylphosphinoethane}{1-(ethyl)-2-(phenylazo)imidazole-(palladium(II))}, [Pd(dppe)(HaaiEt)](OTf)₂, (2a). To an dichloromethane colourless solution (15 cm^3) of [Pd(dppe)Cl₂] (0.583 g, 0.1 mmol) was added stoichiometric amount of AgOTf (0.514 g, 0.2 mmol) and the mixture filtered off. To this filtrate was added dichloromethane solution of 1-(ethyl)-2-(phenylazo)imidazole (0.190 g, 0.1 mmol) slowly, dropwise, and the mixture was stirred in 343–353 K for 4 h. The solution formed, was concentrated (4 cm^3) and kept in a refrigerator for 1 h. The addition of hexane to the above orange solution gave precipitate, which was collected by filtration, washed thoroughly with hexane to remove excess ligand and then dried *in vacuo* over pump overnight. Analytically pure complexes were obtained. The yield was 70–80%.

Analysis of [Pd(dppe)(HaaiEt)](OTf)₂, (2a), Found, C: 62.42, H: 4.91, Calcd for [C₃₇H₃₆N₄PdP₂](OSO₂CF₃)₂: C: 62.41, H: 4.91, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1610 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, 755, 695 cm^{-1} ; ESI MS: 704.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.5 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], –0.7(90), –0.68(90), –0.81(80).

Analysis of [Pd(dppe)(MeaaiEt)](OTf)₂, (2b), Found, C: 62.81, H: 5.19, Calcd for [C₃₈H₃₈N₄PdP₂](OSO₂CF₃)₂: C: 63.01, H: 4.99, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1610 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, 755 cm^{-1} ; ESIMS: 718.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.66 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.75(90), –0.58(90), –0.86(80).

Analysis of [Pd(dppe)(ClaaiEt)](OTf)₂, (2c), Found, C: 59.41, H: 4.61, Calcd for [C₃₇H₃₅N₄PdClP₂](OSO₂CF₃)₂: C: 59.42, H: 4.61, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1612 cm^{-1} , $\nu(\text{N}=\text{N})$ 1305 cm^{-1} , $\nu(\text{C}=\text{N})$ 1566 cm^{-1} ν (dppe), 1102, $759, 699 \text{ cm}^{-1}$; ESIMS: 739(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.5 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.65(90), –0.62(90), –0.91(80).

Analysis of [Pd(dppe)(HaaiMe)](OTf)₂, (1a), Found, C: 62.11, H: 4.71, Calcd for [C₃₆H₃₄N₄PdP₂](OSO₂CF₃)₂: C: 62.14, H: 4.91, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1613 cm^{-1} , $\nu(\text{N}=\text{N})$ 1307 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, $755, 695 \text{ cm}^{-1}$;

ESIMS: 690.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.71 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.73(90), –0.61(90), –0.88(80).

Analysis of [Pd(dppe)(MeaaiMe)](OTf)₂, (1b), Found, C: 62.62, H: 4.91, Calcd for [C₃₇H₃₆N₄PdP₂](OSO₂CF₃)₂: C: 62.49, H: 4.91, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1614 cm^{-1} , $\nu(\text{N}=\text{N})$ 1312 cm^{-1} , $\nu(\text{C}=\text{N})$ 1565 cm^{-1} ν (dppe), 1112, $755, 695 \text{ cm}^{-1}$; ESIMS: 704.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.5 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.72(90), –0.61(90), –0.88(80).

Analysis of [Pd(dppe)(ClaaiMe)](OTf)₂, (1c), Found, C: 59.14, H: 4.41, Calcd for [C₃₆H₃₃N₄PdClP₂](OSO₂CF₃)₂: C: 59.14, H: 4.44, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1610 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, $754, 695 \text{ cm}^{-1}$; ESIMS: 725(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.15 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.7(90), –0.68(90), –0.81(80).

Analysis of [Pd(dppe)(HaaiBz)](OTf)₂, (3a), Found, C: 65.43, H: 4.81, Calcd for [C₄₂H₃₈N₄PdP₂](OSO₂CF₃)₂: C: 65.42, H: 4.81, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1617 cm^{-1} , $\nu(\text{N}=\text{N})$ 1306 cm^{-1} , $\nu(\text{C}=\text{N})$ 1566 cm^{-1} ν (dppe), 1112, $759, 695 \text{ cm}^{-1}$; ESIMS: 766.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.5 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.75(90), –0.60(90), –0.8(80).

Analysis of [Pd(dppe)(MeaaiBz)](OTf)₂, (3b), Found, C: 65.84, H: 4.95, Calcd for [C₄₃H₄₀N₄PdP₂](OSO₂CF₃)₂: C: 65.83, H: 4.91, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1614 cm^{-1} , $\nu(\text{N}=\text{N})$ 1308 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, $755, 695 \text{ cm}^{-1}$; ESIMS: 780.5(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.5 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.70(90), –0.60(90), –0.89(80).

Analysis of [Pd(dppe)(ClaaiBz)](OTf)₂, (3c), Found, C: 62.44, H: 4.51, Calcd for [C₄₂H₃₇N₄PdClP₂](OSO₂CF₃)₂: C: 62.43, H: 4.52, IR (KBr disk): $\nu(\text{C}=\text{C})$ 1615 cm^{-1} , $\nu(\text{N}=\text{N})$ 1300 cm^{-1} , $\nu(\text{C}=\text{N})$ 1560 cm^{-1} ν (dppe), 1102, $755, 695 \text{ cm}^{-1}$; ESIMS: 801(M-OTf); ³¹P {¹H} NMR (CDCl₃): –36.55 ppm; ¹⁹F {¹H} NMR (CDCl₃): –78 ppm; Lower case Cyclic Voltammetry [E/V (ΔE_p /mV)], 0.72(90), –0.62(90), –0.82(80).

¹H-NMR spectral data, δ (J/Hz), ppm in CDCl₃ of the complexes

Compd	4-H ^c	5-H ^c	7.11-H ^c	8.10-H	N-CH ₃	N-CH ₂	dppe
(1a) ^a	7.55 (7.5)	7.46(7.5)	8.03 (8.1)	7.75 (8.1) ^d	2.09 ^f		7.15–7.22
(1b)	7.58 (7.5)	6.96(7.5)	8.07 (8.1)	7.84 (8.1) ^c	2.17 ^f		7.11–7.32
(1c)	7.3 (8.1)	7.42(8.1)	8.05 (7.8)	7.85 (7.8) ^c	2.16 ^f		7.01–7.33
(2a) ^a	7.4 (7.5)	7.00(7.5)	8.01 (7.8)	7.75 (8.1) ^d	1.52(8.1) ^d	4.62,4.65 (10.0) ^e	7.00–7.22
(2b)	7.53 (8.1)	7.24(8.1)	8.01 (7.5)	7.72 (7.5) ^c	1.58(8.1) ^d	4.64,4.56 (10.0) ^e	7.01–7.17
(2c)	7.34 (8.1)	7.36(8.1)	8.04 (7.5)	7.76 (7.5) ^c	1.55(8.1) ^d	4.64,4.53 (11.0) ^e	7.01–7.33
(3a) ^a	7.56 (7.8)	7.48(7.8)	8.08 (8.1)	7.78 (8.1) ^d		5.68,5.73 (15.0) ^g	7.11–7.33
(3b)	7.47 (8.1)	6.99(8.1)	8.01 (8.1)	7.70 (8.1) ^c		5.46,5.73 (17.0) ^g	7.01–7.33
(3c)	7.11 (7.8)	7.32(7.8)	8.15 (8.1)	7.78 (8.1) ^c		5.44,5.70 (18.0) ^g	7.11–7.23

^a δ(9-H) 7.45 ppm(m), ^b δ (9-Me), ^c doublet, ^d triplet, ^e AB type sextet, ^f 1-Me, singlet, ^g AB type quartet, ^h Phenyl-H.

RESULTS AND DISCUSSION

Reaction of [Pd(dppe)(Cl)₂] with AgOTf gave [Pd(dppe)(OTf)₂], which was followed by addition of arylazoimidazole in dichloromethane medium led to [Pd(dppe)(RaaiR)] (**1–3**), [RaaiR' = *p*-R-C₆H₄-N=N-C₃H₂-NN-1-R', abbreviated as a N,N'-chela- tor, where N(imidazole) and N(azo) are represented by N and N', respectively; R = H (**a**), Me (**b**), Cl (**c**) and

R' = Me (**1**), CH₂CH₃ (**2**), CH₂Ph (**3**) and OSO₂CF₃ is the triflate anion]. All these complexes were obtained in a very good yield (**Scheme 1**, nearly 75%). All these nine diphosphines are yellow to orange color. All the complexes were supported by elemental analysis and well characterised by IR, multinuclear NMR (¹H, ¹³C, ³¹P, ¹⁹F, ¹H ¹H COSY and ¹H ¹³C HMQC) and lower case ESI mass Spectrophotometrically.

Scheme 1.

IR spectra of the complexes show a 1 : 1 correspondence to the spectra of the dichloro and dibromo analogues, except the appearance of intense stretching in 1605–1650 and 1290–1350 cm⁻¹ with concomitant loss of ν(Pd–Cl) or Ni–Br in 380–340 cm⁻¹. They were assigned to ν(C=C) and ν(N=N), which appear near in 1600 and 1300 cm⁻¹, respectively.

The ESI mass spectrum of a MeCN solution in a positive ion mode is structurally enlightening, since it displays a series of characteristic signals. The ¹H NMR

spectra of the complexes were assigned (measured in CDCl₃, Figure, Table) on comparison with the free and parent ligand [7, 9, 10]. Aromatic portion shows a broad peak mostly from 7.22–7.66 region for the phenyl protons of the dppe ligands. Whereas the complex shows a sharp peak near in 4 ppm due to the ethyl substitution on RaaiR group. The complexes **1c**, **2c**, **3c**, show a broad peak in 4.6–4.8 due to CH₂ of the benzyl group whereas **1b**, **2b**, **3b** complexes show peaks near in 2.16 ppm due to the methyl group of RaaiEt. The aryl protons (7–H–11–

^1H NMR of complex 2a, H H COSY & ^{31}P (^1H) NMR of complex 2a.

H) of are downfield shifted by 0.1–0.7 ppm as compared to those of the parent derivatives [7–9]. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position (isomers A & B). Phosphorous NMR (measured in CDCl_3) gave direct information about the complex formation and the complex nature. All the complexes show one sharp singlet signal near -36.5 ppm. Fluorine NMR, ^{19}F $\{^1\text{H}\}$ NMR, (measured in CDCl_3) shows a sharp peak for the triflate ion in near -78 in case of all the complexes. The COSY (measured in CDCl_3) reveals the ^1H - ^1H coupling interactions in the molecule. The cross peaks along both the sides of the diagonal iden-

tify the nuclei that are coupled to each other. On the contrary, the protons that are decoupled from the adjacent ones due to the lack of α -protons will show no coorelation in the spectrum. Extending horizontal and vertical lines from $\delta = 7.32$ and 7.68 ppm [$\text{C}(\text{dppe})\text{H}$] encounter cross peaks at $\delta = 7.12$ and 7.23 ppm, where the $\text{C}(\text{imidazole})\text{H}$ resonances are merged into multiplets along with the phenyl ring proton resonances. This also helps to accurately assign phenyl and arylazo moiety protons to their respective values, and these protons interact with dppe-moiety. The evidence for the presence of protons attached to the different types of carbon atoms in the spectrum was obtained from the ^1H - ^{13}C HMQC spectrum. The ^1H - ^{13}C heteronuclear multiple-quantum co-

herence (HMQC) spectrum provides information (measured in CDCl_3) regarding the interaction between the protons and the carbon atoms to which they are directly attached. The peaks observed at $\delta = 134$, 131, 135.6 and 137.6 ppm assign them to the phenyl of arylazo carbon atoms respectively (C7, C11; C8, C10), due to their interaction with H resonance at $\delta = 7.42\text{--}7.5$, 7.55, 7.82, 7.80 and 7.38 ppm.

In conclusion, this work describes the isolation of a novel series of lower case Palladium(II) arylazoimidazole complexes with a dppe link and their spectral and elemental characterisation. ^1H NMR study suggests azoimine and dppe-linkage. ^{31}P $\{^1\text{H}\}$ NMR shows one sharp signal which is lower than those of parent dichloro and dibromo complexes. ^{19}F $\{^1\text{H}\}$ NMR suggests the presence of triflate ion. ^{13}C , $^1\text{H}\text{--}^{13}\text{C}$ COSY spectrum as well as the contour peaks in the $^1\text{H}\text{--}^{13}\text{C}$ HMQC spectrum of the present complexes, confirms their assignment of accurate structure and solution proton-proton interaction.

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REFERENCES

1. Seth J., Palaniappan V., Johnson T.E. et al. *J. Am. Chem. Soc.*, **1994**, *116*, 10578.
2. (a) Prathapan S., Johnson T.E., Lindsey J.S. *J. Am. Chem. Soc.*, **1993**, *115*, 7519, (b) Lindsey J.S., Prathapan S., Johnson T.E., Wagner R.W. *Tetrahedron*, **1994**, *50*, 8941.
3. Fox M.A., Jones W.E., Jr., Watkins D.M. *Chem. Eng. News*, **1993**, *71* (11), 38.
4. Wagner R.W., Lindsey J.S. *J. Am. Chem. Soc.*, **1994**, *116*, 9759.
5. Wasielewski M.R., Gaines G.L., III, Wiederrecht G.P. et al. *J. Am. Chem. Soc.*, **1993**, *115*, 10442.
6. (a) Helms A., Heiler D., McLendon G. *J. Am. Chem. Soc.*, **1992**, *114*, 6227, (b) Helms A., Heiler D., McLendon G. *J. Am. Chem. Soc.*, **1991**, *113*, 4325. (c) McLendon G. *Acc. Chem. Res.*, **1988**, *21*, 160.
7. (a) Sessler J.L., Johnson M.R., Creager S.E. et al. *J. Am. Chem. Soc.*, **1990**, *112*, 9310, (b) Sessler J.L., Capuano V.L., Harriman A. *J. Am. Chem. Soc.*, **1993**, *115*, 4618.
8. (a) Osuka A., Maruyama K. *J. Am. Chem. Soc.*, **1988**, *110*, 4454, (b) Nagata T., Osuka A., Maruyama K. *J. Am. Chem. Soc.*, **1990**, *112*, 3054.
9. (a) Sessler J.L., Wang B., Harriman A. *J. Am. Chem. Soc.*, **1993**, *115*, 10418, (b) Sessler J.L., Wang B., Harriman A. *J. Am. Chem. Soc.*, **1995**, *117*, 704.
10. (a) Odobel F., Sauvage J.P., Harriman A. *Tetrahedron Lett.*, **1993**, *34*, 8113, (b) Harriman A., Odobel F., Sauvage J.P. *J. Am. Chem. Soc.*, **1994**, *116*, 5481.