**Oxygen atom transfer from pyridyltetrazine chelated oxorhenium(V) reagents to diphosphines: twin isomerization, effects of diphosphine spacer length and metal oxidation state**

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**ABSTRACT**

The bimolecular reaction of ReOCl$_3$(dptz), 1, where dptz is 3,6-di(2-pyridyl)-1,2,4,5-tetrazine with excess diphosphine Ph$_3$P(CH$_2$)$_x$PPh$_2$ (x = 1-4) has furnished ReO(OOPPh$_3$(CH$_2$)$_x$PPh$_2$)Cl(dptz), 2 with a dangling phosphine function which is spontaneously converted in solution to ReO(OOPPh$_3$(CH$_2$)$_x$P(O)PPh$_2$)Cl(dptz), 3. The complex 2 (x = 1) on reaction with excess 1 affords mononuclear ReO(OOPPh$_3$(CH$_2$)$_x$P(O)PPh$_2$)Cl(dptz), 4 while for x = 2-4 binuclear complex (dptz)ClReO(OOPPh$_3$(CH$_2$)$_x$P(O)PPh$_2$O)ReOCl$_3$(dptz), 5 is obtained. Rate studies of the twin isomerization (linkage-cum-geometrical) reaction 2 → 3 revealed that the reaction is intramolecular in nature. It is initiated by the nucleophilic attack of the metal by the dangling phosphine function. The process slows down nearly exponentially as the diphosphine spacer length x increases. The oxidized complex (ReO(OOPPh$_3$(CH$_2$)$_x$PPh$_2$)Cl(dptz))ReOCl$_3$, 6 does not isomerize.

**Keywords:** Oxygen atom transfer, Twin isomerization, Pyridyltetrazine, Rhenium

1. INTRODUCTION

This work has originated from our interest in oxygen atom transfer reaction between monooxorhenium(V) reagents and tertiary phosphines (Chakravorty et al., 2005; Abram et al., 2004; Sengupta et al., 2006; Gangopadhyay et al., 2002; Seymore et al., 2000; Bryan et al., 1987; Rowbottom et al., 1972). The available results primarily concern monophosphines. Diphosphines are potentially interesting but have attracted only limited attention so far (Bhattacharyya et al., 2000; Bhattacharyya et al., 2001; Sengupta et al., 2006; Fowles et al., 1991). Recently we reported oxochehalte ReOCl$_3$(dptz), 1, where dptz is 3,6-di(2-pyridyl)-1,2,4,5-tetrazine which underwent facile bimolecular oxygen atom transfer reaction with triphenyl phosphine furnishing the corresponding phosphine oxide complex ReO(OOPPh$_3$Cl) as shown in eqn (1) (Sengupta et al., 2013).

\[ \text{ReOCl}_3(\text{dptz}) + \text{PPh}_3 \rightarrow \text{ReO(OOPPh}_3\text{Cl(dptz)}} \] (1)

The present work was initiated to scrutinize the transfer reactions of 1 with a group of linear diphosphines bearing a polymethylene spacer of variable length. Attention has been focused on the transfer of one oxygen atom only so that phosphine oxide complexes ReO(OOPPh$_3$(CH$_2$)$_x$PPh$_2$)Cl(dptz), 2 (x = 1-4) with a dangling phosphine function are generated. The latter function could be a potential nucleophile that might attack the metal site within the same molecule. Such reactivity has indeed been observed providing an opportunity to scrutinize the effects of diphosphine spacer length and metal oxidation state. Oxygen atom transfer to the pendant phosphine function of 2 occurs upon reacting it with excess of 1. To model the observed phenomenon the results of monophosphorus species of type ReO(OOPPh$_3$), ReO(OOPPh$_3$) and ReO(PPh$_2$) have been compared (Sengupta et al., 2012; Sengupta et al., 2003; Sengupta et al., 2006). The complexes have been characterized with the help of microanalyses, spectral and electrochemical data and the factors controlling the reactivity are scrutinized.

2. EXPERIMENTAL

Four diphosphines Ph$_3$P(CH$_2$)$_x$PPh$_2$ (x = 1-4) have been employed in the present work. In order to achieve transfer of only one oxygen atom to the diphosphines, excess phosphine was reacted (eqn (2)) with 1 in dichloromethane solution furnishing the species of type ReO(OOPPh$_3$(CH$_2$)$_x$PPh$_2$)(dptz), 2. The rate of the reaction of eqn (2) has been determined spectrophotometrically in dichloromethane solution at 308 K for the x = 4 case where the subsequent isomerization proceeds very slowly. In the presence of excess diphosphine the rate of transfer is proportional to the concentration of 1 and the observed rate constant is proportional to the concentration of phosphine implying a second order rate law.

\[ \text{ReOCl}_3(\text{dptz}) + \text{PPh}_3(\text{CH}_2)_x\text{PPh}_2 \rightarrow \text{ReO(OOPPh}_3(\text{CH}_2)_x\text{PPh}_2\text{Cl(dptz)}} \] (2)

The complexes of type 2 are inherently reactive in dichloromethane solution, the dangling phosphine function displacing the coordinated phosphine oxide function furnishing ReO(OOPPh$_3$(CH$_2$)$_x$P(O)PPh$_2$Cl(dptz), 3 (eqn (3)). This linkage isomerization is simultaneously attended by meridional→facial geometrical isomerization; the net result is twin isomerization.

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Re(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)) → Re⁴⁺(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz))

Oxygen atom transfer to the pendant phosphine function of 2 occurs upon reacting it with excess of 1. For x = 1 only mononuclear product Re⁴⁺(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)), 4 (eqn (4)) incorporating a dangling phosphine oxide function could be isolated. No binuclear product was observable. For x=2-4 binuclear complex (dptz)Cl₃Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)O)Re⁴⁺Cl₃(dptz), 5 (eqn (5)), insoluble in all common organic solvents is obtained. Its composition and gross connectivity as in 5 is however not subject to any serious question (Bhattacharyya et al., 2000; Bhattacharyya et al., 2001).

Re(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)) + ReOCl₃(dptz) → Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)O)Cl₃(dptz) ........... (4)

Re(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)) + ReOCl₃(dptz) → Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)O)Cl₃(dptz) ........... (5)

The phospine oxide complex 2 (x=1) underwent facile metal oxidation upon treatment with dilute nitric acid in acetonitrile solution furnishing 1:1 electrolytic (N, 97 °C m⁻³ mol⁻¹ in methanol solution) (Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)O)Cl₃(dptz))/ReOCl₃, 6 (eqn (6)) as yellow solid. It is isomerically 2(Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)) → (Re⁴⁺(OPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz))ReOCl₃)

2.1. Materials

The ReOCl₃(dptz), 1 complex was prepared as before (Sengupta et al., 2013). HPLC grade acetonitrile was used for electrochemical work and all other chemicals and solvents were of reagent grade and were used as received.

2.2. Physical measurements

UV-vis spectral measurements were carried out with a Shimadzu UVPC 1601 spectrometer fitted with thermostatted cell compartments. IR spectra (4000-100 cm⁻¹) were recorded in KBr disk with the help of Perkin Elmer L-1100 and Nicolet Magna IR 750 Series II spectrometers. Proton NMR spectra were recorded on a Bruker FT 300 MHz spectrometer. In ¹H NMR the spin-spin structures are abbreviated as follows: s, singlet; d, doublet; t, triplet; m, multiplet and b, broad. Electrochemical measurements were performed under nitrogen atmosphere on a CH 620A electrochemical analyzer, using a platinum working electrode. The supporting electrolyte was tetraethylammonium perchlorate (TEAP), and the cell voltage was measured in methanol (~10⁻³ M solution) with a Philips PR 9500 bridge using a platinumized electrode (cell constant of 1.05). Room-temperature magnetic susceptibilities of powders were measured with a model 155 PAR vibrating sample magnetometer.

2.3. Synthesis

2.3.1. Synthesis of Re(PPPh₂(CH₂)₂P(PPPh₂)Cl₃(dptz)), 2

These were prepared by a general procedure: Reaction of Re⁴⁺OCl₃(dptz) with excess Ph₃P(CH₂)₂PPh₃ (x = 1-4) in dichloromethane solution. Details are given below for a representative case. Re(PPPh₂(CH₂)₂PPh₃Cl₃(dptz)). To 65 mg (0.12 mmol) of complex 1 in dichloromethane solution was added 138 mg (0.36 mmol) of PPPh₂(CH₂)₂PPh₃ and the solution was stirred magnetically at room temperature for 3 h. During the reaction the solution color changed from orange yellow to violet. The solution was subjected to chromatography on a silica gel column (25 x 1 cm, 60-120 mesh). Excess diphosphine was eluted with benzene. The violet band that followed was eluted with a benzene-acetonitrile (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded as a violet solid. Yield: 75 mg (70%); Anal. Calcd for [Re₂H₂Cl₂N₃O₂P:] C, 49.47; H, 3.36; N, 9.36. Found: C, 49.51; H, 3.31; N, 9.29. UV-vis (λ_max, nm (ε, M⁻¹ cm⁻¹), CH₂Cl₂ solution) : 816(2950), 748(3450), 610(3700), 598(2700), 485(4950). ¹H NMR 5 in (CDCl₃) : dptz, 25.12 (s, 1H), 23.21 (d, 1H, J = 7.5 Hz), 10.88 (d, 1H, J = 7.4 Hz), 9.87 (t, 1H, J = 8.6 Hz), 6.96 (d, 1H, J = 7.5 Hz), 6.84 (t, 1H, J = 6.4 Hz), 6.71 (t, 1H, J = 7.5 Hz), -2.76 (b, 1H), Ph₃P(CH₂)₂PPh₃, -2.30 (m, 2H, | P-H |).
The general procedure consisted of simply leaving a dichloromethane solution of Re(II)PPh₂Cl₂(dptz) was left for 24 h. It was then subjected to chromatography on a silica gel column. A green band was eluted with a benzene-acetonitrile (25:10) mixture. Solvent removal under reduced pressure afforded Re(II)PPh₂Cl₂(dptz) as a green solid which was dried under vacuum over fused CaCl₂. Yield: 62% (85%). Anal.Calcd for C₉₂H₁₄₀N₄O₆P₂: C, 50.03; H, 3.31; N, 9.21. Found: C, 50.10; H, 3.36; N, 9.18. UV-Vis (λmax, nm (ε, M⁻¹ cm⁻¹), CH₂Cl₂ solution) : 668(1400), 590(1700), 459(2000). Analogous NMR δ (CDCl₃): d, 1H, J = 7.2 Hz, 7.98 (t, 1H, J = 7.8 Hz), 7.88 (t, 1H, J = 7.6 Hz), 6.86 (d, 1H, J = 7.6 Hz), 3.80 (d, 1H, J = 6.2 Hz), 3.60 (m, 2H), 2.80 (m, 2H, CH₂), 17.98 (m, 1H, CH₃), 16.18 (m, 2H, 8.46 (m, 2H), 7.32 (m, 4H), 7.18 (m, 4H), 6.54 (m, 2H), 4.66 (t, 2H, J = 7.8 Hz), 4.50 (t, 2H, J = 8.2 Hz). IR (cm⁻¹): KBr disk : 311, 328, 330 (Re-Cl), 1119 (O-P), 1159 (C=N). E₁/₂ (versus SCE, CH₂CN, scan rate 50 mV s⁻¹): Re⁺⁻Re⁺, 0.68 V (ΔEₚ = 80 mV).

2.3.3. Synthesis of Re(II)PPh₂Cl₂(dptz) 4
To 52 mg (0.06 mmol) of complex Re(II)PPh₂Cl₂(dptz) in dichloromethane solution was added 33 mg (0.08 mmol) of Re(II)PPh₂Cl₂(dptz). In the solution was stirred magnetically at room temperature for 3 h. The solution was then subjected to chromatography on a silica gel column (25 x 1 cm, 60-120 mesh). A violet band was eluted with a benzene-acetonitrile (25:1) mixture. Solvent removal from the eluate under reduced pressure afforded a violet solid. The product was dissolved in a dichloromethane solution. Details are given below for a representative case.

2.3.4. Synthesis of Re(II)PPh₂Cl₂(dptz) 5
The general procedure involved simply leaving a dichloromethane solution of Re(II)PPh₂Cl₂(dptz) at room temperature for 3 h. The solution was then subjected to chromatography on a silica gel column. A green band was eluted with a benzene-acetonitrile (25:10) mixture. Solvent removal from the eluate under reduced pressure afforded a violet solid. The product was dissolved in a dichloromethane solution. Details are given below for a representative case.

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(dtz)ClRe(OPPh$_3$)(CH$_2$)$_2$PH$_2$P(OMe)$_2$ReCl(dtz). To 33 mg (0.06 mmol) of complex 1 in dichloromethane solution was added 53 mg (0.06 mmol) of Re(OPPh$_3$)(CH$_2$)$_2$PH$_2$P(OMe)$_2$Cl(dtz) and the solution was stirred magnetically at room temperature for 3 h. During the reaction a violet precipitate separated from the solution was collected by filtration, washed thoroughly with dichloromethane and dried in vacuum over fused CaCl$_2$. The precipitate was found to be insoluble in all common organic solvents and thus could only be characterized by elemental analysis and IR spectra. 

Yield : 52 mg (60%). Anal. Calcld. for C$_{58}$H$_{64}$Cl$_2$N$_2$O$_2$P$_5$Re : C, 41.22; H, 2.75; N, 5.70. Found : C, 41.27; H, 2.78; N, 5.66. IR (cm$^{-1}$, KBr disk) : 305, 307, 309, 311, 328, 328 (Re–Cl), 1128, 1131 (O–P), 1596 (C=N), 1163 (O–P), 1096 (C=N). 

2.3.5. Synthesis of (ReOPPh$_3$)(CH$_2$)$_2$P(OMe)$_2$Cl(dtz)ReO$_4$, 6. 

To 69 mg (0.08 mmol) of (ReOPPh$_3$)(CH$_2$)$_2$P(OMe)$_2$Cl(dtz) in 20 mL acetonitrile was added dilute aqueous HNO$_3$ and the solution was stirred at room temperature for 0.25 h. During this time the solution color changed from violet to yellow. Solvent removal under reduced pressure afforded (ReOPPh$_3$)(CH$_2$)$_2$P(OMe)$_2$Cl(dtz)ReO$_4$ as an yellow solid. The solid was washed thoroughly with water to remove the adherent nitric acid and then dried in vacuum over fused CaCl$_2$. Yield : 60 mg (65%). Anal. Calcld. for C$_{58}$H$_{64}$Cl$_2$N$_2$O$_2$P$_5$Re : C, 38.69; H, 2.61; N, 7.32. Found : C, 38.67; H, 2.65; N, 7.24. UV–vis (λmax, nm (ε, M$^{-1}$ cm$^{-1}$), CH$_2$Cl$_2$ solution) : 428(800), 320(990). 1H NMR 5 in (CDCl$_3$) dptz: 74.18 (1H), 12.33 (2H), 8.66 (1H), 2.98 (2H), 64.76 (1H), 151.18 (1H); PPH$_3$(CH$_2$)PPh$_3$, 9.12 (2H), 7.82 (4H), 7.65 (4H), 7.51 (4H), 5.68 (4H), 4.88 (2H). IR (cm$^{-1}$, KBr disk) : 328, 333, 338 (Re–Cl), 1118 (O–P), 1596 (C=N), 904 (Re=O). $\Delta$E$_{gg}$ (versus SCE, CH$_3$CN, scan rate 50 mVs$^{-1}$). $\Delta$E$_{gg}$ 0.30 V (ΔE$_{gg}$ = 80 mV), AM = 98 Ω$^{-1}$ cm$^{-2}$ mol$^{-1}$. 

2.4. Rate measurements. 

The rate of the single oxygen atom transfer reaction of eqn (2) was determined spectrophotometrically (quartz cell. path length 1 cm) in the case of Ph$_3$P(RePh$_2$)$_2$P(OMe)$_2$. A known excess of the diphasphine was added to a solution of (ReOCl$_3$(dtz)) (1.25 x 10$^{-4}$ M) in dichloromethane at 78 K and the absorbance $A_t$ monitored for the peak at 742 nm as a function of time (t). The time dependent spectra are characterised by isosbestic point. The absorbance $A_t$ at 742 nm at the end of the reaction (6 h) was also monitored. The calculations were performed using Microcal Origin V 6.0 (E. Northampton, Microcal Origin Inc., 1991). The observed rate constants $k_{obs}$ were determined from the slope of the linear plot of ln($A_t$ - $A_0$) versus t. The rate constant $k_{obs}$ was obtained from the linear plot of $k_{obs}$ versus concentration of the diphasphine. The rate of the twin isomerization process of eqn (3) was also followed spectrophotometrically at 308 K. Time dependent absorbances $A_t$ were measured at 598 nm and $A_0$ values were obtained at the end of the reaction (1 to 7 days depending on x). Rate constants were determined from the linear plots of -ln($A_t$ - $A_0$) versus t. Variable concentration (1 x 10$^{-4}$ M) studies carried out in the cases of x = 1 revealed that the rate constants were independent of concentration consistent with first order kinetics. The plot of rate constants against diphosphine spacer length (x) follows a single exponential decay pattern with reduced $\chi^2$ value of $= 10^{-1}$. 

3. RESULTS AND DISCUSSION 

3.1. Spectra.

In the visible region (400-900 nm) 2-4 display multiple transitions of moderate intensity (ε, 1000-5000 dm$^3$ mol$^{-1}$ cm$^{-1}$) in the form of peaks and shoulders. The most prominent feature occurs around 750 nm for 2 and around 665 nm for 3. An idealized $^1$I$_{2g}$(Re) $\to ^2$s(dptz) MLCT assignment is consistent with the observed shift to higher energy in going from phosphine oxide (2, 4) to the phosphine coordination (3) which stabilizes the $t_{2g}$ shell via back-bonding. This is also reflected in the significant increase of the $\Re^{II}$/Re$^{III}$ reduction potentials. The thienium(V) species 6 in which MLCT transitions are expected to shift to much higher energies, does not display any band in the visible region except for a weak one at 428 nm. Two or three Re–Cl stretches in the range 300-340 cm$^{-1}$ occur in the complexes of type 2, 3, 4, 6 while more signals occur for dimeric type 5 complexes. The coordinated P–O stretch in 2, 4, 5 is observed near 1130 cm$^{-1}$ as compared to $\sim$1190cm$^{-1}$ characterizing uncoordinated P–O (3, 4) (Bhattacharyya et al., 2000; Bhattacharyya et al., 2001; Nakamoto et al., 1997). In 6 the oxidized metal weakens the P–O bond and the vibration frequency drops to 1118 cm$^{-1}$. A characteristic Re–O stretch of the ReO$_4$ anion in 6 occur near 904 cm$^{-1}$. The complex of the type 2-4 have magnetic moment near 2 μB as in several other thienium(III) species (Chakraborty et al., 2005; Bhattacharyya et al., 2001; Sengupta et al., 2006; Sengupta et al., 2013; Chakraborty et al., 1999). All the complexes display paramagnetically shifted $^1$H NMR lines. Well-resolved spin–spin structures are seen for 2-4 but not for 6.

Table 1: Rate constants for the reaction of (ReOCl$_3$(dtz)) + PPh$_3$(CH$_2$)$_2$P(OMe)$_2$ $\to$ (ReOPPh$_3$(CH$_2$)$_2$P(OMe)$_2$Cl(dtz)) in dichloromethane solution.

<table>
<thead>
<tr>
<th>T, K</th>
<th>10$^{-4}$[PPh$_3$(CH$_2$)$_2$P(OMe)$_2$, M</th>
<th>10$^{-4}$k$_{obs}$ (s$^{-1}$)</th>
<th>10$^{-4}$k$_{obs}$ (M$^{-1}$ s$^{-1}$)</th>
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<td>16.11</td>
<td>16.05 (0.08)</td>
</tr>
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<td></td>
<td>1.40</td>
<td>21.63</td>
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</tr>
<tr>
<td></td>
<td>2.00</td>
<td>31.20</td>
<td></td>
</tr>
</tbody>
</table>

*The initial concentration of (ReOCl$_3$(dtz)) is 1.25x10$^{-4}$ M. Least-squares deviations are given in parentheses.

Table 2: Rate constants for the reaction Re(OPPh$_3$(CH$_2$)$_2$P(OMe)$_2$Cl(dtz)) $\to$ Re(PPh$_3$(CH$_2$)$_2$P(O)Ph$_3$Cl(dtz) in dichloromethane solution.

<table>
<thead>
<tr>
<th>x</th>
<th>T, K</th>
<th>10$^{-4}$[Re(OPPh$_3$(CH$_2$)$_2$P(OMe)$_2$Cl(dtz), M</th>
<th>10$^{-4}$k$_{obs}$ (s$^{-1}$)</th>
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<tbody>
<tr>
<td>1</td>
<td>308</td>
<td>1.25</td>
<td>26.83 (0.04)</td>
</tr>
<tr>
<td>1</td>
<td>308</td>
<td>2.50</td>
<td>26.87 (0.05)</td>
</tr>
<tr>
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<tr>
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<td>1.25</td>
<td>16.12 (0.03)</td>
</tr>
<tr>
<td>2</td>
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<td>1.25</td>
<td>12.93 (0.02)</td>
</tr>
<tr>
<td>3</td>
<td>308</td>
<td>1.25</td>
<td>5.075 (0.02)</td>
</tr>
<tr>
<td>4</td>
<td>308</td>
<td>1.25</td>
<td>1.70 (0.02)</td>
</tr>
</tbody>
</table>

*Least-squares deviations are given in parentheses.

3.2. Metal redox

The complexes uniformly display a nearly reversible Re(IV)/Re0 couple in acetonitrile solution, the cyclic voltammetric peak-to-peak separation being 60–80 mV. The reduction potentials lie near 0.30 V vs SCE in 2 and 4 and near 0.67 V in 3. The sizeable difference of reduction potentials makes it possible to observe the isomerization of 2 to 3 electrochemically as shown in Figure 1. Cylindrical isomerization studies are however best made spectrophotometrically. The phosphine oxide ligand is a pure donor and optimal metal ligand bonding is achievable in the meridional geometry, there being no bonding advantage for the sterically unfavourable facial disposition of ligands. It is thus logical that 2, 4, 5 assumes meridional geometry. Upon substitution of OPPPh2(CH2)3PPh2 by PPh2(CH2)3P(O)2Ph3, the bonding situation changes considerably due to phosphine σ-acidity, the concerned orbitals being a mixture of 3dπ and P-C σ’ components (Cotton et al., 1988). There are thus two good σ-acceptors in the phosphine complexes dptz and PPh2(CH2)3P(O)2Ph3. The back-bonding effect is maximized in the facial disposition which ensures minimum competition between the two ligands for identical metal orbitals. The observed geometrical selectivity is strong and exclusive. The strong geometrical discrimination by phosphine oxide and phosphine ligands is emerging as a general phenomenon (Sengupta et al., 2006; Chakraborty et al., 1999; Sengupta et al., 2013) for ReCl3(NH) complexes where NH is a chelated σ-acidic ligand. The present dipyridyltetrazine complexes augment this class. The voltammograms of 5 (initial scan cathodic) are virtually superimposable on those of the corresponding 2 species (initial scan anodic). The 1b2 shell in 3 is stabilized by back-bonding to phosphorus and an increase of the reduction potential is indeed expected in going from phosphine oxide to phosphine coordination (Sengupta et al., 2006; Sengupta et al., 2003; Sengupta et al., 2013).

3.3. Oxygen atom transfer

The rate of the reaction of eqn (2) has been determined spectrophotometrically in dichloromethane solution at 308 K for the x = 4 case where the subsequent isomerization proceeds very slowly. Time evolution spectra characterized by isosbestic point is shown in Figure 2. In the presence of excess diphenylphosphine (under pseudo-first order condition), the rate (kobs) of transfer is proportional to the concentration of the 1 and the observed rate constant, kobs, is proportional to the concentration of phosphine implying a second order rate law (eqn (7)). Rate data are listed in Table 1.

\[
\text{Rate} = \frac{k_{\text{obs}}[\text{ReOCl}_3(\text{dptz})]}{[\text{PPPh}_2(\text{CH}_2)_3\text{PPh}_2]} \quad (7)
\]

Oxygen atom transfer to the both ends of PPh2(CH2)3PPh2 has been achieved by reacting the phosphine oxide complexes 2 (having dangling phosphine function) with excess ReOCl3(dptz), 1 in dichloromethane. In the x = 1 case only the mononuclear product, 4 (eqn (4)) incorporating a dangling phosphine oxide function could be isolated. No binuclear product was observable. The reaction of 2 (x = 2–4) with excess 1, in dichloromethane solution furnished the binuclear complex 5, eqn (5) insoluble in all common organic solvents.

3.4. Twin isomerization

The spontaneous twin isomerization reaction of eqn (3) was studied spectrophotometrically in dichloromethane solution for x = 1–4. A representative time evolution spectra is shown in Figure 3. The reaction followed a first-order rate law eqn (8) implying that the reaction is intramolecular. Rate data are listed in Table 2. The variable temperature measurement of rate constants for x = 1 complex followed Eyring equation eqn (9) and the activation parameters ΔH* and ΔS* are 15.18(0.01) kcal mol⁻¹ and 26.13 (0.04) cal K⁻¹ mol⁻¹.

\[
\text{Rate} = \left(\frac{k_0}{h}\right)[\text{ReOCl}_3(\text{dptz})] \exp(-\Delta H^*/RT) \exp(\Delta S^*/R) \quad (8)
\]

\[
\Delta H^* = \Delta H - R\ln K \quad (9)
\]

It is logical to assume that the transformation is initiated via nucleophilic attack of the metal by the dangling phosphorus atom. The attack is stabilized in 7. The transformation can then proceed via edge displacement (Bhattacharyya et al., 2000; Bhattacharyya et al., 2001, Sengupta et al., 2006; Sengupta et al., 2003), of a chloride ligand resulting in relay substitutions: Re-OP by Re-Cl and of Re-Cl by Re-P. The net effect is twin isomerization (7). An alternative pathway involving direct transfer of oxygen from phosphorus to phosphorus is energetically highly unlikely since it requires the synchronous dissociation of both P-O and Re-O bonds. The process is depicted in 7 evidently involves considerable ordering consistent with the large negative entropy of activation (-26.13 cal K⁻¹ mol⁻¹).

The rate of the twin isomerization reaction decreases rapidly as the spacer length increases from x = 1 to x = 4. Indeed the dependence of rate on x is exponential to a good degree as illustrated in the plots of Figure 4. The data fits approximately with the relation given in eqn(10) where A0 is a constant characteristic of the dptz ligand system. The values of the constants derived from the
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Figure 4
Exponential plot of rate constant versus diphosphine spacer length for the isomerization reaction of
Re(OPPh₂(CH₂)₈PPh₂)Cl₂(dptz). (x = 1-4) in dichloromethane solution at 308 K.

4. CONCLUSION
It is demonstrated that the family Re₃(OPPh₂(CH₂)₈PPh₂)Cl₂(dptz), 2 with
dangling phosphate function formed from Re₆OCl₂(dptz), 1 and
PPh₂(CH₂)₈PPh₂ (where x = 1-4) undergoes spontaneous intramolecular linkage-

Suman Sengupta et al.,
Oxygen atom transfer from pyridyltetrazine chelated oxorhenium(V) reagents to diphosphines: twin isomerization, effects of diphosphine spacer length and metal oxidation state,
http://www.discovery.org.in/ijis.htm
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