Oxygen atom transfer from Re^{V}O to tertiary diphosphines: spacer length and chemical differentiation of products
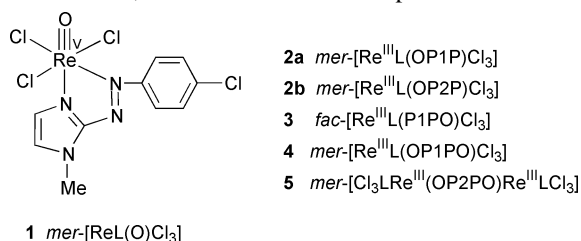
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The reaction of *mer*-[ReL(O)Cl$_3$], [L = 2-(*p*-chlorophenylazo)-1-methylimidazole] with Ph$_2$P(CH$_2$)$_n$PPh$_2$ (abbreviated P*n*P) affords [ReL(OP1P)Cl$_3$] **2a**, [ReL(OP1PO)Cl$_3$] **4** and [ReL(OP2P)Cl$_3$] **2b**, [Cl$_3$LRe(OP2PO)ReLCl$_3$] **5**, all having *mer* geometry; unlike **2b** which is stable in solution, **2a** spontaneously isomerizes to *fac*-[ReL(P1PO)Cl$_3$] *via* an associative pathway; the origin of the observed differentiation (**2a** *vs.* **2b** and **4** *vs.* **5**) is scrutinized in terms of structures and reaction models.

Tertiary phosphines are model oxygen atom acceptors from oxo moieties such as Re^{V}O.[1,2] Chelation by the π-acidic azoimidazole L as in **1**, facilitates the transfer process.[3] This work

2a *mer*-[Re^{III}L(OP1P)Cl$_3$]
2b *mer*-[Re^{III}L(OP2P)Cl$_3$]
3 *fac*-[Re^{III}L(P1PO)Cl$_3$]
4 *mer*-[Re^{III}L(OP1PO)Cl$_3$]
5 *mer*-[Cl$_3$LRe^{III}(OP2PO)Re^{III}LCl$_3$]

1 *mer*-[ReL(O)Cl$_3$]

concerns the species **2–5** formed from **1** and Ph$_2$P(CH$_2$)$_n$PPh$_2$ (abbreviated P*n*P, *n* = 1, 2)[4] directly or *via* subsequent transformations. The differentiation referred to in the title relates to the pairs **2a, 2b** and **4, 5** in which the length of the spacer –(CH$_2$)$_n$– varies.

With P*n*P in excess, stereoretentive one-atom transfer [eqn. (1)] afforded† **2a** and **2b** (Fig. 1).‡ Both are stable in the solid state and **2b** is also stable in solution. In contrast, **2a** undergoes spontaneous linkage-*cum*-geometrical isomerization [eqn. (2)] in solution furnishing† **3** (Fig. 2).‡
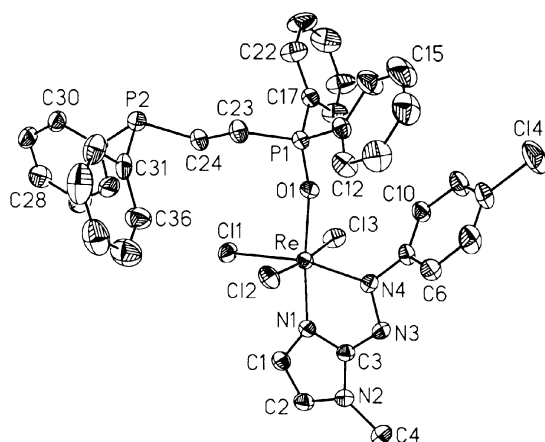
$$R\equiv O + PnP \rightarrow Re-OPnP \quad (1)$$

$$Re-OP1P \rightarrow Re-P1PO \quad (2)$$

Fig. 2 Perspective view of *fac*-[Re^{III}L(P1PO)Cl$_3$] **3**. Selected bond distances (Å) and angles (°): Re–N(1) 2.050(8), Re–N(4) 2.055(8), Re–Cl(2) 2.351(3), Re–Cl(1) 2.372(3), Re–Cl(3) 2.401(3), Re–P(1) 2.476(3); N(1)–Re–Cl(2) 176.7(2), N(4)–Re–Cl(1) 162.9(2), Cl(3)–Re–P(1) 174.9(1).

The reaction follows§ the rate law of eqn. (3). Variable temperature rate constants (10^3 *k*/min^{-1}: 308 K, 5.30; 313 K, 7.78; 318 K, 10.06; 323 K, 12.75) correspond to the activation parameters Δ*H*,‡ 12.3 kcal mol^{-1} and Δ*S*,‡ −38.2 cal K^{-1} mol^{-1}. The reaction is thus intramolecular and strongly associative in nature.

$$\mathbf{2a} \xrightarrow{\;k\;} \mathbf{3} : \text{rate} = k[\mathbf{2a}] \quad (3)$$
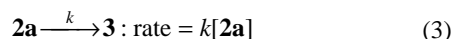
Oxygen atom transfer to the pendent phosphine function of **2** occurs† upon reacting it with an excess of **1** [eqn. (4) and (5)]. While **2a** furnishes **4** (Fig. 3),‡ **2b** yields insoluble **5** in which both the phosphine oxide functions are coordinated, the metal atoms presumably having *mer* geometry.[5]
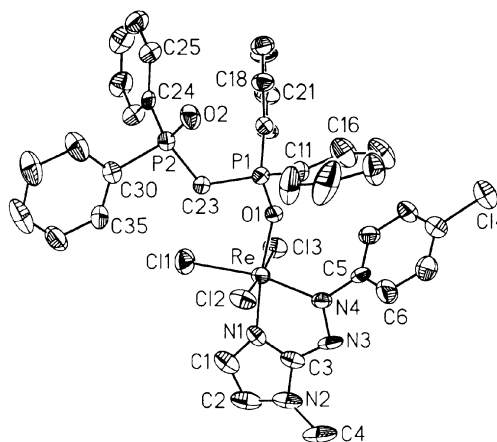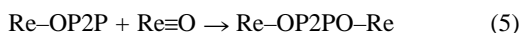

Fig. 1 Perspective view of *mer*-[Re^{III}L(OP2P)Cl$_3$] **2b**. Selected bond distances (Å) and angles (°): Re–N(1) 2.000(6), Re–N(4) 2.002(7), Re–O(1) 2.048(5), Re–Cl(3) 2.355(2), Re–Cl(2) 2.372(2), Re–Cl(1) 2.375(2); N(1)–Re–O(1) 173.9(2), Cl(3)–Re–Cl(2) 174.67(8), N(4)–Re–Cl(1) 166.9(2), P(1)–O(1)–Re 164.0(4).

Fig. 3 Perspective view of *mer*-[Re^{III}L(OP1PO)Cl$_3$] **4**. Selected bond distances (Å) and angles (°): Re–N(4) 1.985(10), Re–N(1) 1.993(11), Re–O(1) 2.033(7), Re–Cl(3) 2.356(4), Re–Cl(2) 2.370(4), Re–Cl(1) 2.377(4), P(1)–O(1) 1.523(8), P(2)–O(2) 1.459(8); N(1)–Re–O(1) 172.7(4), Cl(3)–Re–Cl(2) 174.4(1), N(4)–Re–Cl(1) 168.0(3), P(1)–O(1)–Re 147.5(5).

$$Re\text{–}OP1P + Re\equiv O \rightarrow Re\text{–}OP1PO \qquad (4)$$

$$Re\text{–}OP2P + Re\equiv O \rightarrow Re\text{–}OP2PO\text{–}Re \qquad (5)$$

The remarkable double isomerization of **2a** can be rationalized. **2a** did not afford single crystals but the structure of **4** provides a credible geometrical model in which the pendent P(1)C(23)P(2) fragment is positioned near the Cl(1)Cl(2)O(1) face. A simple rotation around the P(1)–C(23) bond brings the P(2) atom to within 2.6 Å of the face as in **6** which is a plausible

6   **7**
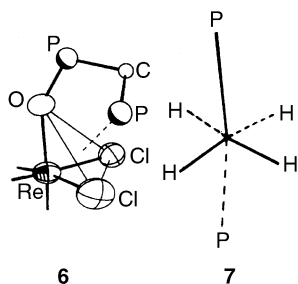
model for the associative transition state of the reaction. The attack by P(2) can progress *via* edge displacement[6] of a chloride ligand with concomitant Re–OP(1) bond cleavage leading to **3**, [eqn. (6)]. The *fac* geometry of **3** is sustained by concerted

$$(6)$$

2a   **3**
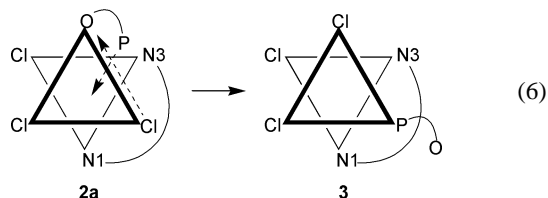
Re–L and Re–P back-bonding as in *fac*-[ReL(PPh₃)Cl₃].[3] In **2b** the PCH₂CH₂P fragment has the *anti* conformation **7**. The potentially reactive *gauche* conformation is not accessible due to the bulk of PPh₂, and accordingly **2b** fails to isomerize.

The conformation **7** is, however, ideally suited for sustaining binucleation as in **5**.[5] On the other hand only the dangling phosphine oxide function is preserved in **4** as a vestige of transient binucleation. The environment of the O(2) atom in **4** is crowded [O(2)···P(1) 3.57 Å, O(2)···C(11) 3.55 Å] and model building has confirmed that the $n = 1$ analog of **5** is not sterically viable.

In summary, there is a strong chemical differentiation between the $n = 1$ and 2 products formed in both one-atom (**2a**, **2b**) and two-atom (**4**, **5**) transfer from **1** to P*n*P. The applicability of the observed structural and dynamical features to other systems is under scrutiny.

Notes and references

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4 The $n = 1–3$ cases have been examined but only $n = 1, 2$ are reported here as $n = 2, 3$ constitute a similar pair.

5 The similarly prepared binuclear complex [Cl₃L′Re(OP2PO)ReL′Cl₃], where L′ is the Schiff base of pyridine-2-carbaldehyde and *p*-toluidine has been structurally characterized. It is centrosymmetric with the PCH₂CH₂P fragment having *anti* and the metals having *mer* geometry. S. Bhattacharyya, I. Chakraborty, B. K. Dirghangi and A. Chakravorty, unpublished work.

6 N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, 1972, **17**, 391.