

Oxygen atom transfer from Re^{VO} to tertiary diphosphines: spacer length and chemical differentiation of products

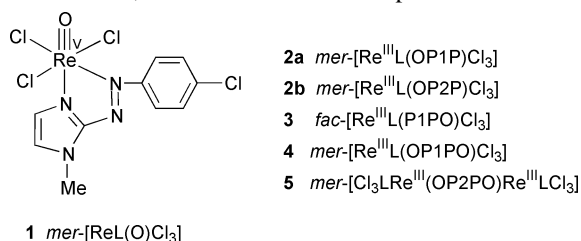
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The reaction of $\text{mer-}[\text{ReL}(\text{O})\text{Cl}_3]$, $[\text{L} = 2\text{-}(p\text{-chlorophenyl-azo})\text{-1-methylimidazole}]$ with $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (abbreviated PnP) affords $[\text{ReL}(\text{OP1P})\text{Cl}_3]$ **2a**, $[\text{ReL}(\text{OP1PO})\text{Cl}_3]$ **4** and $[\text{ReL}(\text{OP2P})\text{Cl}_3]$ **2b**, $[\text{Cl}_3\text{LRe}(\text{OP2PO})\text{ReLCl}_3]$ **5**, all having mer geometry; unlike **2b** which is stable in solution, **2a** spontaneously isomerizes to $\text{fac-}[\text{ReL}(\text{P1PO})\text{Cl}_3]$ **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^{VO} .^{1,2} Chelation by the π -acidic azoimidazole **L** as in **1**, facilitates the transfer process.³ This work



concerns the species **2–5** formed from **1** and $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ (abbreviated PnP , $n = 1, 2$)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 $-(\text{CH}_2)_n-$ varies.

With PnP 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).‡

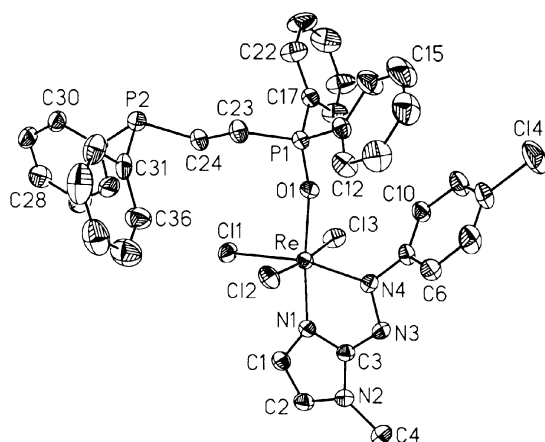


Fig. 1 Perspective view of $\text{mer-}[\text{Re}^{\text{III}}\text{L}(\text{OP2P})\text{Cl}_3]$ **2b**. Selected bond distances (Å) and angles (°): $\text{Re-N}(1)$ 2.000(6), $\text{Re-N}(4)$ 2.002(7), $\text{Re-O}(1)$ 2.048(5), $\text{Re-Cl}(3)$ 2.355(2), $\text{Re-Cl}(2)$ 2.372(2), $\text{Re-Cl}(1)$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

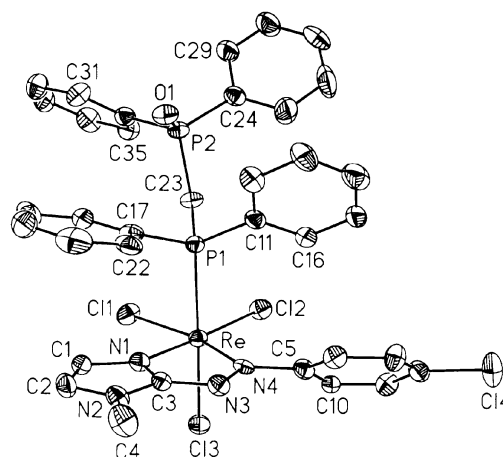
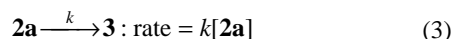


Fig. 2 Perspective view of $\text{fac-}[\text{Re}^{\text{III}}\text{L}(\text{P1PO})\text{Cl}_3]$ **3**. Selected bond distances (Å) and angles (°): $\text{Re-N}(1)$ 2.050(8), $\text{Re-N}(4)$ 2.055(8), $\text{Re-Cl}(2)$ 2.351(3), $\text{Re-Cl}(1)$ 2.372(3), $\text{Re-Cl}(3)$ 2.401(3), $\text{Re-P}(1)$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

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



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

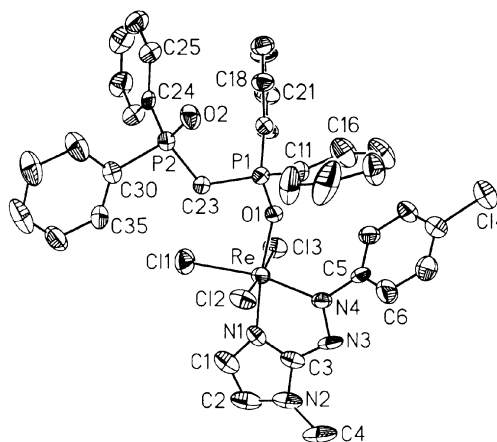
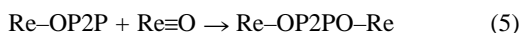
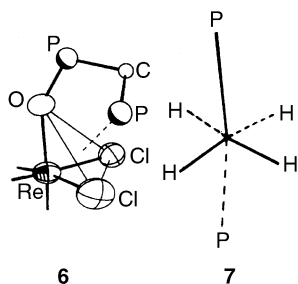


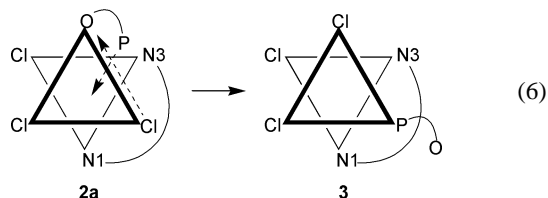
Fig. 3 Perspective view of $\text{mer-}[\text{Re}^{\text{III}}\text{L}(\text{OP1PO})\text{Cl}_3]$ **4**. Selected bond distances (Å) and angles (°): $\text{Re-N}(4)$ 1.985(10), $\text{Re-N}(1)$ 1.993(11), $\text{Re-O}(1)$ 2.033(7), $\text{Re-Cl}(3)$ 2.356(4), $\text{Re-Cl}(2)$ 2.370(4), $\text{Re-Cl}(1)$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



model for the associative transition state of the reaction. The attack by P(2) can progress *via* edge displacement⁶ 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



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 PnP. The applicability of the observed structural and dynamical features to other systems is under scrutiny.

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Notes and references

† **2a** was prepared from PIP (0.6 mmol) and **1** (0.2 mmol) in CH₂Cl₂ solution followed by rapid solvent removal, washing with hexane and drying; **2b** was similarly prepared; **3** was made by leaving **2a** in C₆H₆ for 8 h and **4** was prepared from **2a** (0.1 mmol) and **1** (0.2 mmol) in C₆H₆; for each, purification was carried out by chromatography on a silica gel column using C₆H₆–MeCN mixtures as eluents. Reaction of **2b** (0.1 mmol) and **1** (0.1 mmol) in C₆H₆ afforded insoluble **5**. The yields in all cases were in the range 75–85% and satisfactory elemental analyses were obtained for all. Selected spectral data: UV–VIS (C₆H₆): λ_{max}/nm (ε/dm³ mol^{−1} cm^{−1}): **2a**, 660(610), 454(5680), 355(7570); **2b**, 658(450), 460(3550), 348(4970); **3**, 660(840), 468(5530), 362(9510); **4**, 655(510), 450(5230), 358(6910). IR (KBr, cm^{−1}): **2a**, 300, 310 (Re–Cl), 1120 (O–P), 1330 (N=N); **2b**, 310, 320 (Re–Cl), 1120 (O–P), 1330 (N=N); **3**, 310, 320 (Re–Cl), 1190 (P–O), 1325 (N=N); **4**, 310, 320 (Re–Cl), 1120 (O–P), 1200 (P–O), 1335 (N=N); **5**, 300, 320 (Re–Cl), 1120 (O–P), 1335 (N=N).

‡ Crystal data for **2b**·1.5C₆H₆: C₄₅H₄₂Cl₄N₄O₂Re, *M* = 1044.77, triclinic, space group *P*1, *a* = 11.957(4), *b* = 12.383(3), *c* = 17.046(6) Å, α = 88.36(2), β = 74.21(2), γ = 84.10(2)°, *U* = 2415.8(12) Å³, *Z* = 2, *T* = 293 K, μ(Mo–Kα) = 2.84 mm^{−1}, 7237 reflections measured, 7109 unique, 5904 observed [*I* > 2σ(*I*)], *R*₁ = 0.0467, *wR*₂ = 0.1273; **3**·1.5C₆H₆: C₄₄H₄₀Cl₄N₄O₂Re, *M* = 1030.74, triclinic, space group *P*1, *a* = 10.110(6), *b* = 10.668(5), *c* = 20.760(7) Å, α = 89.47(3), β = 80.08(4), γ = 81.41(4)°, *U* = 2181(2) Å³, *Z* = 2, *T* = 293 K, μ(Mo–Kα) = 3.143 mm^{−1}, 6515 reflections measured, 6424 unique, 5198 observed [*I* > 2σ(*I*)], *R*₁ = 0.0542, *wR*₂ = 0.1279; **4**: C₃₅H₃₁Cl₄N₄O₂P₂Re, *M* = 929.58, monoclinic, space group *C*2/*c*, *a* = 35.353(11), *b* = 12.730(6), *c* = 16.840(7) Å, β = 104.68(3)°, *U* = 7332(5) Å³, *Z* = 8, *T* = 293 K, μ(Mo–Kα) = 3.73 mm^{−1}, 5705 reflections measured, 5422 unique, 3386 observed [*I* > 2σ(*I*)], *R*₁ = 0.0585, *wR*₂ = 0.1060. CCDC 182/1746. See <http://www.rsc.org/suppdata/cc/b0/b004565i/> for crystallographic files in .cif format.

§ UV–VIS spectra of thermostatted isomerizing benzene solutions of **2a** displayed well defined isosbestic points at 482, 422 and 307 nm. The rate was followed at 360 nm. The first order rate constants were obtained from the slope of linear plot of −ln(*A*_∞ − *A*_{*t*}) vs. time *t* where *A*_{*t*} is the absorbance at time *t* and *A*_∞ is the absorbance at the completion of reaction (after 24 h).

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