

Ready Deprotonation of the Protic Solvento Species

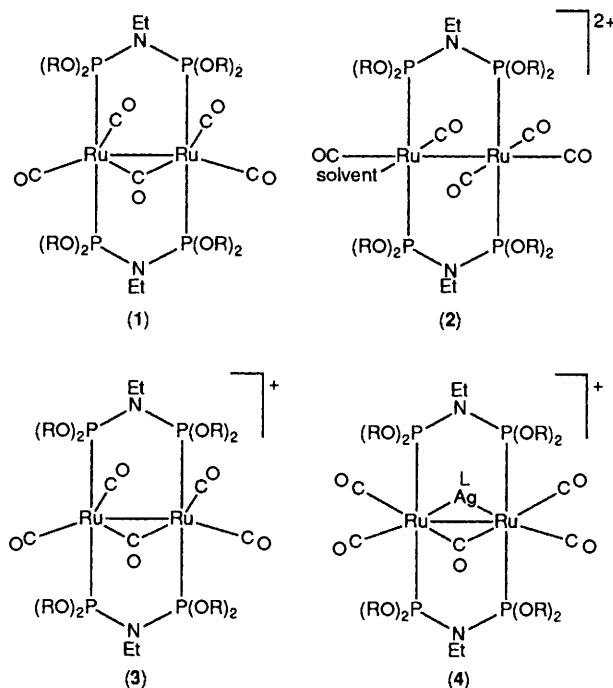
$[\text{Ru}_2(\text{CO})_5(\text{R}'\text{OH})\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^{2+}$ ($\text{R} = \text{Me}$ or Pr^i ; $\text{R}' = \text{H}, \text{Me}, \text{Et}, \text{etc.}$) and the Formation of $[\text{Ru}_2\{\mu\text{-OC}(\text{O})\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ containing Carbon Dioxide in a Bridging Co-ordination Mode

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Treatment of $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ ($\text{R} = \text{Me}$ or Pr^i) with silver(I) salts in the presence of protic solvents of the type $\text{R}'\text{OH}$ ($\text{R}' = \text{H}, \text{Me}, \text{Et}, \text{etc.}$) leads to the formation of the solvento species $[\text{Ru}_2(\text{CO})_5(\text{R}'\text{OH})\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^{2+}$ which is readily deprotonated and rearranges to afford $[\text{Ru}_2\{\mu\text{-OC}(\text{OR}')\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^+$; $[\text{Ru}_2\{\mu\text{-OC}(\text{OH})\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^+$ can be deprotonated further to give $[\text{Ru}_2\{\mu\text{-OC}(\text{O})\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ containing a bridging carbon dioxide group, confirmed X-ray crystallographically.

We have established previously from cyclic voltammetric studies that the one-electron oxidation of the electron-rich derivative $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]$, (**1**; $\text{R} = \text{Me}$), in weakly co-ordinating solvents such as acetone or benzonitrile, is irreversible with the one-electron oxidised product participating in a chemical process involving solvent attack and the product of the attack being immediately oxidised to the dicationic solvento species $[\text{Ru}_2(\text{CO})_5(\text{solvent})\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]^{2+}$ (solvent = acetone or benzonitrile) (**2**; $\text{R} = \text{Me}$).¹ On the other hand the one-electron oxidation of $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]$ (**1**; $\text{R} = \text{Pr}^i$) in these solvents was found to be reversible on the time-scale of the experiment although further oxidation of the oxidised product $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]^+$ (**3**; $\text{R} = \text{Pr}^i$) also proved to be irreversible, again leading to the formation of a solvento dication, viz. $[\text{Ru}_2(\text{CO})_5(\text{solvent})\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]^{2+}$ (**2**; $\text{R} = \text{Pr}^i$).¹ We have also established that $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ ($\text{R} = \text{Me}$ or Pr^i) (**1**) can be chemically oxidised to the solvento species $[\text{Ru}_2(\text{CO})_5(\text{solvent})\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^{2+}$ (**2**) in non-protic solvents.² More specifically it has been shown that oxidation by silver(I) salts occurs *via* the inner-sphere intermediate $[\text{Ru}_2(\mu\text{-AgL})(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^+$ ($\text{L} = \text{acetone}, \text{etc.}$) (**4**) with this silver(I) adduct degrading, with loss of elemental silver, to $[\text{Ru}_2(\mu\text{-$



$\text{CO}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2\}^+$ (**3**);³ the latter, in turn, spontaneously disproportionates in solution to $[\text{Ru}_2(\text{CO})_5(\text{solvent})\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]^{2+}$ (**2**) and $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ (**1**).³ It has now been established that a different reactivity pattern is observed

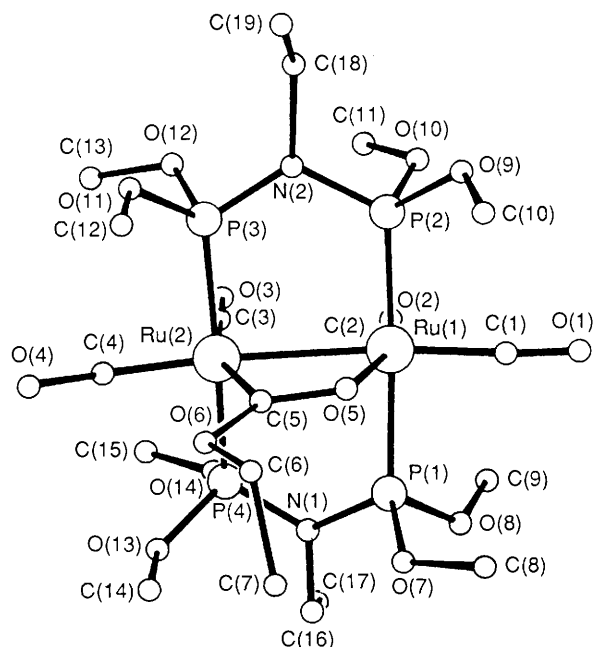


Figure 1. The stereochemistry of $[\text{Ru}_2\{\mu\text{-OC(OEt)}\}(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]^+$ showing the atom labelling scheme. Relevant interatomic distances: Ru(1)–Ru(2), 2.777(1); Ru(1)–P(1), 2.325(3); Ru(1)–P(2), 2.324(3); Ru(2)–P(3), 2.306(3); Ru(2)–P(4), 2.318(3); Ru(2)–C(5), 2.091(12); Ru(1)–O(5), 2.140(8); C(5)–O(5), 1.268(14) Å.

when the oxidation by silver salts is carried out either in, or in the presence of, protic solvents of the type $\text{R}'\text{OH}$.

Treatment of $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]$ ($\text{R} = \text{Me}$ or Pr^i) (**1**) with silver(I) hexafluoroantimonate (2 mol. equiv.) in methanol or ethanol ($\text{R}'\text{OH}$) was found to afford a product characterised as $[\text{Ru}_2\{\mu\text{-OC}(\text{OR}')\}(\text{CO})_4\{\mu\text{-(RO)}_2\text{PN}(\text{Et})\text{P}(\text{OR})_2\}_2]\text{SbF}_6$ (**5**, SbF_6^-). This formulation was confirmed through crystal structure determinations on both $[\text{Ru}_2\{\mu\text{-OC}(\text{OMe})\}(\text{CO})_4\{\mu\text{-(MeO)}_2\text{PN}(\text{Et})\text{P}(\text{OMe})_2\}_2]\text{SbF}_6$ and $[\text{Ru}_2\{\mu\text{-OC}(\text{OEt})\}(\text{CO})_4\{\mu\text{-(MeO)}_2\text{P}(\text{OMe})_2\}_2]\text{SbF}_6$

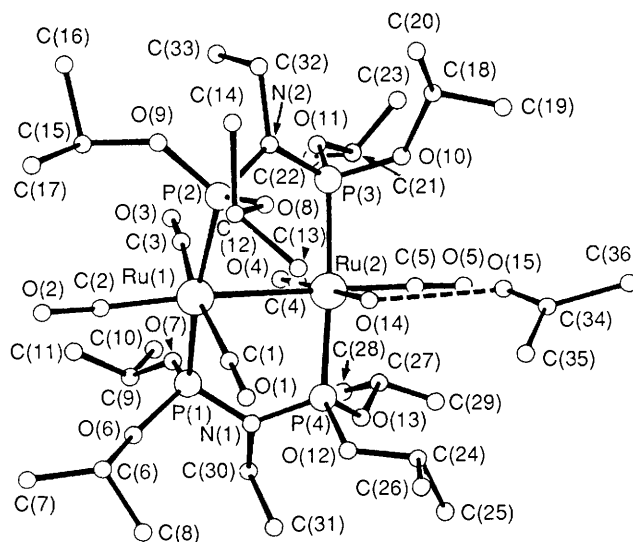
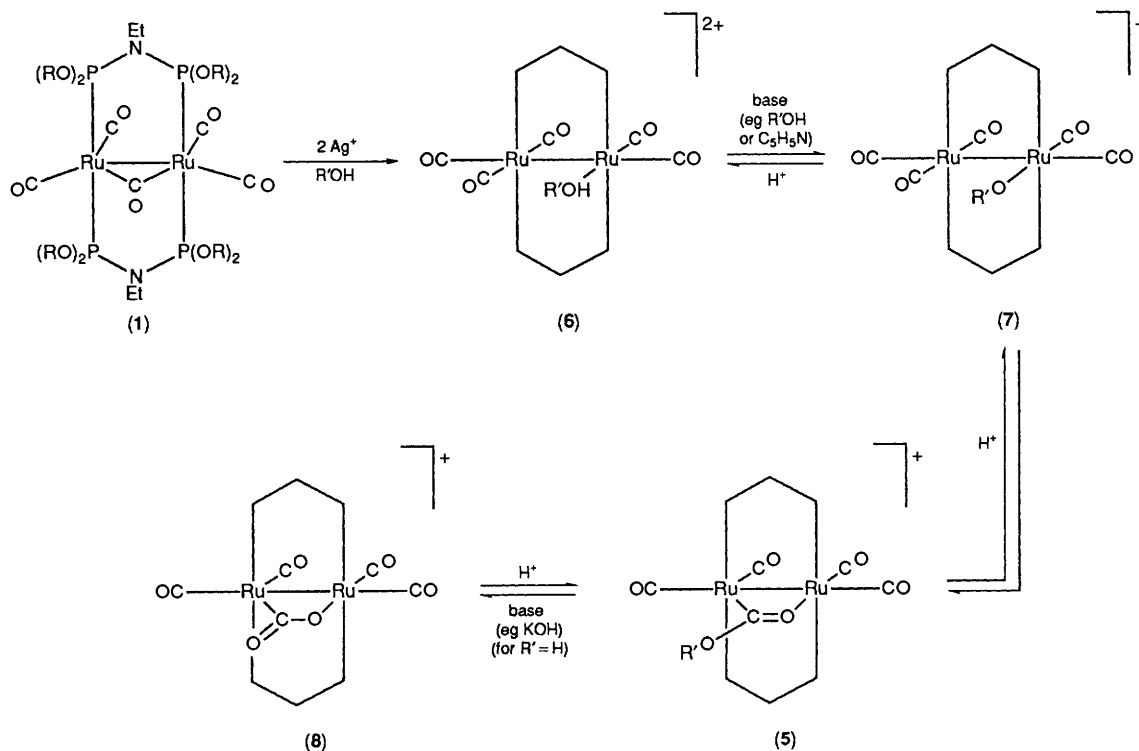


Figure 2. The stereochemistry of $[\text{Ru}_2(\text{CO})_5(\text{H}_2\text{O})\{\mu\text{-(Pr}^i\text{O)}_2\text{PN}(\text{Et})\text{P}(\text{OPr}^i)_2\}_2]^{2+} \cdot \text{Me}_2\text{CO}$ showing the atom labelling scheme. Relevant interatomic distances: Ru(1)–Ru(2), 2.871(1); Ru(1)–P(1), 2.332(3); Ru(1)–P(2), 2.343(3); Ru(2)–P(3), 2.349(3); Ru(2)–P(4), 2.353(3); Ru(2)–O(14), 2.212(8); O(14) \cdots O(15), 2.656 Å.



Scheme 1

PN(Et)P(OMe)₂]₂SbF₆; the stereochemistry of the cation of the latter is illustrated in Figure 1.† The notable feature of these structures is the presence of a bridging OC(OR') (R' = Me or Et) group giving rise to a four-membered Ru₂OC ring. These results are interpreted in terms of the oxidation of (1) by silver(I) salts in alcohols such as methanol or ethanol leading to the formation of the alcohol solvento species [Ru₂(CO)₅(R'OH){μ-(RO)₂PN(Et)P(OR)₂}]²⁺ (R' = Me or Et) (6), with these alcohols being sufficiently basic to effect at least partially the deprotonation of (6) to [Ru₂(OR')(CO)₅{μ-(RO)₂PN(Et)P(OR)₂}]⁺ (7), and of the alkoxide ligand in the latter migrating on to a co-ordinated carbonyl group, as summarised in Scheme 1.

Consistent with this interpretation, reaction of [Ru₂(μ-CO)(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}] (1) with AgSbF₆ (2 mol. equiv.) in acetone or tetrahydrofuran (thf) in the presence of water was observed to produce the aquo derivative [Ru₂(CO)₅(H₂O){μ-(RO)₂PN(Et)P(OR)₂}]₂(SbF₆)₂, characterised crystallographically as well as by conventional methods.† The interesting feature of the structure of the tetra-isopropoxydiphosphazane derivative crystallised from acetone-toluene *viz.* [Ru₂(CO)₅(H₂O){μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}]₂(SbF₆)₂·Me₂CO was the presence of an acetone molecule hydrogen-bonded to the co-ordinated water (Figure 2).

The co-ordinated water in [Ru₂(CO)₅(H₂O){μ-(RO)₂PN(Et)P(OR)₂}]₂(SbF₆)₂ is readily deprotonated by weak bases such as pyridine or an equimolar amount of triethylamine to afford a product established to be the dimetallo-carboxylic acid species [Ru₂{μ-OC(OH)}(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]₂SbF₆.‡ This compound can be deprotonated further by stronger bases such as potassium hydroxide or an excess of triethylamine to give a neutral product characterised as

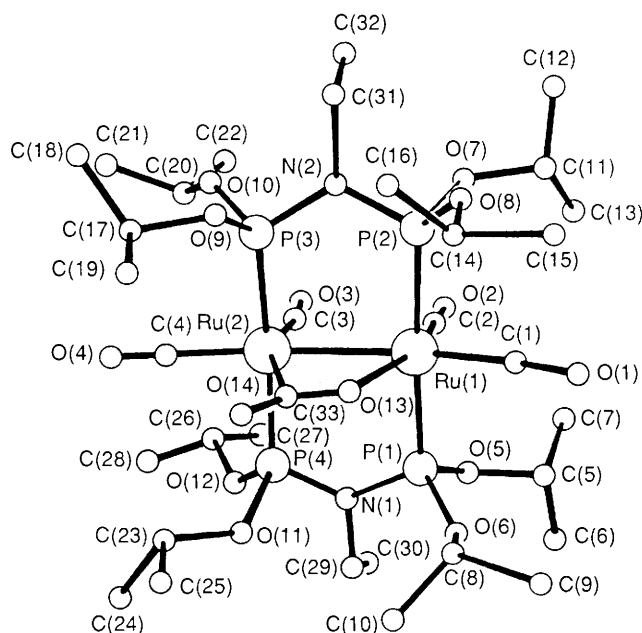


Figure 3. The stereochemistry of [Ru₂(μ-OC(O))(CO)₄{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}] showing the atom labelling scheme. Relevant interatomic distances and angles: Ru(1)–Ru(2), 2.800(1); Ru(1)–P(1), 2.315(3); Ru(1)–P(2), 2.323(3); Ru(2)–P(3), 2.318(3); Ru(2)–P(4), 2.319(3); Ru(1)–O(13), 2.23(1); Ru(2)–C(33), 2.04(2); C(33)–O(13), 1.25(2); C(33)–O(14), 1.13(2) Å; Ru(2)–C(33)–O(13), 120.0(14); Ru(1)–O(13)–C(33), 102.8(12); Ru(2)–C(33)–O(14), 139(2); O(13)–C(33)–O(14), 101(2)°.

† *Crystal data:* C₁₉H₃₉F₆N₂O₁₄P₄Ru₂Sb, *M* = 1081.4, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 11.492(8), *b* = 15.698(5), *c* = 21.542(8) Å, β = 103.09(4)°, *U* = 3785.28 Å³, *D*_c = 1.90 g cm⁻³, *Z* = 4, Mo-*K*_α radiation, λ = 0.71069 Å, μ = 18.27 cm⁻¹. Nonius CAD4 diffractometer, 3770 unique reflections with *I* > 3σ(*I*) in the range 3 ≤ θ ≤ 23°. Structure solved from a Patterson synthesis and successive Fourier maps and refined to *R* = 0.070 (338 parameters).

C₃₃H₆₈F₁₂N₂O₁₄P₄Ru₂Sb₂·(CH₃)₂CO, *M* = 1572.6, monoclinic, space group *P*2₁/*n* (No. 14), *a* = 12.181(2), *b* = 23.389(2), *c* = 22.901(2) Å, β = 99.552(11)°, *U* = 6434.3 Å³, *D*_c = 1.62 g cm⁻³, *Z* = 4, Mo-*K*_α radiation, λ = 0.71069 Å, μ = 15.70 cm⁻¹. Nonius CAD4 diffractometer, 5987 unique reflections with *I* > 3σ(*I*) in the range 3 ≤ θ ≤ 23°. Structure solved from a Patterson synthesis and successive Fourier maps and refined to *R* = 0.083 (336 parameters).

C₃₃H₆₆N₂O₁₄P₄Ru₂, *M* = 1041.0, orthorhombic, space group *Pbca* (No. 61), *a* = 16.858(4), *b* = 17.994(2), *c* = 31.602(5) Å, *U* = 9586.1 Å³, *D*_c = 1.44 g cm⁻³, *Z* = 8, Mo-*K*_α radiation, λ = 0.71069 Å, μ = 8.07 cm⁻¹. Nonius CAD4 diffractometer, 4602 unique reflections with *I* > 3σ(*I*) in the range 3 ≤ θ ≤ 23°. Structure solved from a Patterson synthesis and successive Fourier maps and refined to *R* = 0.072 (356 parameters).

For all structures atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

‡ Ru₂{μ-OC(OH)}(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]₂SbF₆ was characterised by microanalysis and by IR and ¹H and ³¹P NMR spectroscopy as were all other new compounds synthesised in this study. The presence of an AA'BB' pattern of peaks, centred at 139.9 ppm for R = Prⁱ (in CDCl₃, relative to H₃PO₄) in the ³¹P{¹H} NMR spectrum of this compound is consistent with the CO₂H group bridging the two ruthenium atoms unsymmetrically but its co-ordination as an OC(OH) rather than as an HOC(O) ligand is a proposal based on the structures established for [Ru₂{μ-OC(OR')}](CO)₄{μ-(MeO)₂PN(Et)P(OMe)₂}]₂SbF₆ (R = Me and Et).

[Ru₂{μ-OC(O)}(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]₂ (8). A crystal structure determination of the tetra-isopropoxydiphosphazane derivative [Ru₂{μ-OC(O)}(CO)₄{μ-(PrⁱO)₂PN(Et)P(OPrⁱ)₂}]₂ revealed a ligated carbon dioxide with an unusual mode of co-ordination; as illustrated in Figure 3 the carbon dioxide bridges the two ruthenium atoms through its carbon and one of its oxygen atoms.†

This mode of co-ordination for carbon dioxide to a dinuclear centre has not been reported previously although an analogous one in which a carbon dioxide molecule bridges three metal atoms through its carbon and both of its oxygen atoms has recently been reported, the compound in question being [OsRh₂(μ-H)₂(μ₃-CO₂)(C₈H₁₂)₂(PMe₂Ph)₃].⁴ Furthermore it has been proposed that the complex [Co(Prⁿ-salen)K(CO₂)(thf)] {salen = *N,N'*-ethylenebis(salicylidene-aminato) dianion} adopts a structure in solution whereby one of the oxygen atoms of the CO₂, co-ordinated to the cobalt through its carbon atom, is weakly bound to the potassium ion.⁵

Significantly these deprotonation reactions are reversible and treatment of [Ru₂{μ-OC(OR')}](CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]⁺ (R' = Me, Et, or H) with HBF₄-Et₂O in acetone was found to produce the acetone solvento species [Ru₂(CO)₅(Me₂CO){μ-(RO)₂PN(Et)P(OR)₂}]₂²⁺. Likewise protonation of [Ru₂{μ-OC(O)}(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]₂ in acetone was found to give rise stepwise to [Ru₂{μ-OC(OH)}(CO)₄{μ-(RO)₂PN(Et)P(OR)₂}]₂⁺ and [Ru₂(CO)₅(Me₂CO){μ-(RO)₂PN(Et)P(OR)₂}]₂²⁺; clearly the co-ordinated R'OH ligand in [Ru₂(CO)₅(R'OH){μ-(RO)₂PN(Et)P(OR)₂}]₂²⁺ is displaced by the acetone solvent,

present in very large excess. These reactions are summarised in Scheme 1.

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