Novel Synthesis of a Phosphinidene Oxide-κ*P* (RP=O, R = $\mathrm{Bu^tCH_2}$–) Complex of Rhenium(I) from a Phosphaalkyne Precursor. Crystal and Molecular Structure of $[\mathrm{ReCl(Ph_2PCH_2CH_2PPh_2)_2\{P(O)CH_2Bu^t\}}]$

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The first example of the transformation of a phosphaalkyne to a phosphinidene oxide-κ*P* ligand is reported.

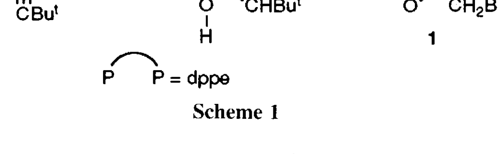
Tervalent phosphorus compounds having the two-coordinate structure RP=O are rare and highly reactive species, which readily undergo cyclic head-to-tail trimerisation.[1] Compounds of the type X–P=O (X = F, Cl, Br) have been generated by the action of silver on appropriate phosphorus oxide trihalides at high temperatures and low pressures, and the gaseous products characterised by mass, photoelectron or IR spectroscopy. Alkyl- and aryl-phosphinidene oxides, RP=O (R = Ph, $\mathrm{Bu^t}$), can be generated by several methods and trapped with a variety of reagents;[1] however, examples of metal complexes containing RP=O ligands are extremely rare.

Generation and stabilisation of RP=O (R = $\mathrm{Pr^i_2N}$) within the coordination sphere of a transition metal was first reported by Niecke *et al.*[2] by the treatment of $\mathrm{Pr^i_2NP{=}NBu^t}$ with $[\mathrm{Cr(CO)_6}]$ followed by treatment with $\mathrm{SO_2}$, and the *P*-bonded (κ*P*) ligating mode was confirmed by a single-crystal X-ray diffraction study. Marinetti and Mathey[3] proposed the intermediacy of a κ*P*-tungsten pentacarbonyl complex $[\mathrm{W(CO)_5\text{-}P(O)Ph}]$ in the thermal fragmentation of the phosphinidene complex $[\mathrm{W(CO)_5PPh}]$ in the presence of phenyloxirane, but its low stability prevented full characterisation.

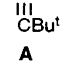
We now report a stable *P*-bonded phosphinidene oxide complex of rhenium(I), which results from a completely different route to any previously described. It was formed upon $\mathrm{N_2}$ replacement by $\mathrm{P{\equiv}CBu^t}$[4–7] from *trans*-$[\mathrm{ReCl(N_2)(dppe)_2}]$ (dppe = $\mathrm{Ph_2PCH_2CH_2PPh_2}$) in tetrahydrofuran (thf), presumably followed by addition of $\mathrm{H_2O}$ across the activated P≡C triple bond of the phosphaalkyne-κ*P* coordinated to the bulky rhenium centre (Scheme 1).

In previous work,[8] we described the synthesis of the iron(II) complex **A** and reported that its tetrafluoroborate salt readily underwent addition of HF across the P≡C triple bond in $\mathrm{CH_2Cl_2}$ to afford the fluorophosphaalkene-κ*P* complex: $[\mathrm{FeH(dppe)_2PF{=}CHBu^t}]^+$, which was characterised by a single crystal X-ray study.

In the current study, the phosphaalkyne-κ*P* ligand at the rhenium(I) site also appears to be susceptible to nucleophilic attack, to give the phosphinidene oxide-κ*P* product. Interestingly, this type of reactivity of the phosphaalkyne ligand contrasts with that observed[9] for related N- or C-unsaturated ligands, such as nitriles, isocyanides, vinylidenes or η^2-phenylallene, which are activated by the same rhenium(I) centre towards β-protonation. The phosphinidene oxide complex **1** was isolated as an orange-yellow crystalline solid. Its $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum [in $\mathrm{CD_2Cl_2}$ δ rel. $\mathrm{P(OMe)_3}$] exhibits a quintet at $\delta\mathrm{P^A}$ $[\mathrm{P(O)CH_2Bu^t}]$ +199.1 and a doublet at $\delta\mathrm{P^B}$ (dppe) −116.1, both with J_{AB} 25.6 Hz; in the ^{1}H NMR spectrum, the resonances at δ 0.21 (s, 9H) and −0.24 (s, br, 2H) are assigned respectively to the $\mathrm{Bu^t}$ and the methylene protons of the phosphinidene oxide ligand.



Scheme 1



A

The molecular structure of **1** (Fig. 1)† confirms that the phosphinidene oxide, $\mathrm{Bu^tCH_2P{=}O}$, is coordinated to the rhenium atom *via* the phosphorus lone-pair electrons and is

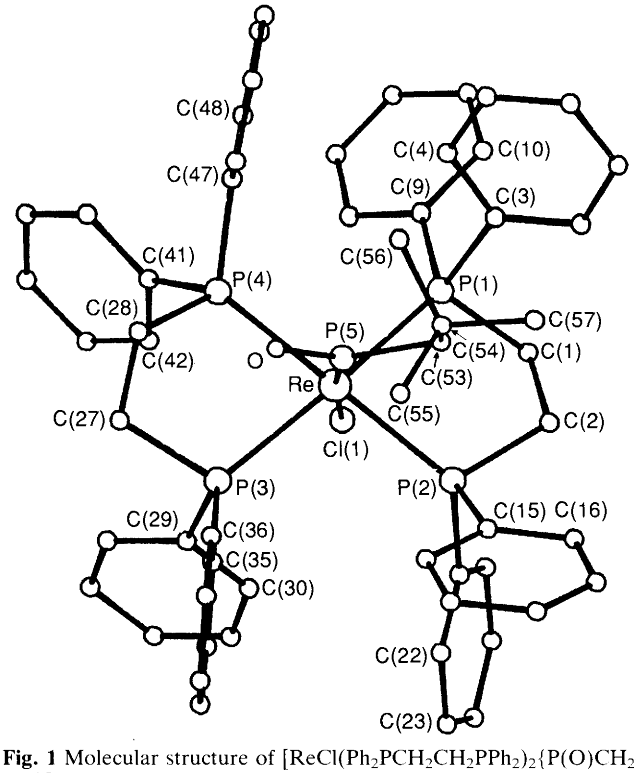


Fig. 1 Molecular structure of $[\mathrm{ReCl(Ph_2PCH_2CH_2PPh_2)_2\{P(O)CH_2\text{-}Bu^t\}}]$. Selected bond lengths and angles: Re–Cl(1) 2.540(1); Re–P(1) 2.425(1); Re–P(2) 2.446(1); Re–P(3) 2.437(1); Re–P(4) 2.426(1); Re–P(5) 2.203(1); P(5)–C(53) 1.843(5); P(5)–O 1.499(3) Å; Cl(1)–Re–P(5) 174.23(4); Re–P(5)–O 130.8(1); O–P(5)–C(53) 104.9(2)°.

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† *Crystal data*: $\mathrm{C_{57}H_{59}ClP_5Re\cdot CH_2Cl_2}$, M = 1221.6, monoclinic, space group $P2_1/n$, a = 16.740(2), b = 14.724(7), c = 22.530(4) Å; β = 100.60(1)°, U = 5458.5 Å^3, Z = 4, D_c = 1.49 g cm^{-3}, $F(000)$ = 2472. Monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 25.9 cm^{-1}. Data were collected using a crystal (*ca.* 0.35 × 0.3 × 0.3 mm) on an Enraf–Nonius CAD4 diffractometer. Cell dimensions were derived from the setting angles for 25 reflections with $7.3 < \theta < 8.6°$. Intensities were measured by an ω–2θ scan for 7256 reflections with $+h +k \pm l$ and $2 < \theta < 22°$, of which 6993 were unique (R_{int} = 0.014), and 5819 reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = \{\sigma^2(I) + (0.04I)^2\}^{\frac{1}{2}}/L_{\mathrm{P}}$, were used in the full-matrix least-squares refinement. Final parameters were R = 0.027, R_w = 0.037, S = 1.2, for 613 variables, 5819 observed reflections. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.[10,11]

trans to the chloride. As expected the P atom of the phosphinidene oxide is trigonal planar with a P=O bond length [1.499(3) Å] which is only slightly longer than that found[2] in $[Cr(CO)_5P(O)NPr^i_2]$ (1.475 Å). The IR spectrum of **1** shows ν(P=O) at 1097 cm^{-1} {*cf.* 1200 cm^{-1} for $[Cr(CO)_5P(O)NPr^i_2]$}. The Re–P distance [2.203(1) Å] for the coordinated phosphinidene oxide is significantly shorter than the corresponding Re–P(dppe) distances [Re–P average 2.433(1) Å], reflecting the smaller sp^2 hybridised phosphorus radius of the RP=O ligand. To our knowledge this is the shortest rhenium(I)–phosphorus distance so far observed in any coordination complex.

This new synthetic route to a stabilised phosphinidene oxide, starting from *P*-bonded ligated phosphaalkyne, may possibly be extended to the formation of other chalcogeno derivatives, RP=E (E = S, Se), or imido derivatives, (E = NR), at metal centres, and this is currently under investigation.

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