Novel Phosphaalkyne/Benzoyldiazenido Ligand Coupling forming the First η^2-Phosphidocarbene Complex. Synthesis and Molecular Structure of $[ReCl_2\{\eta^4\text{-}N(NCOPh)PCBu^tPCBu^t\}(PPh_3)]$

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Treatment of $[ReCl_2(NNCOPh)(PPh_3)_2]$ with $P{\equiv}CBu^t$, in benzene, affords $[ReCl_2(NNCOPh)(P{\equiv}CBu^t)(PPh_3)_2]$ and subsequently through an unprecedented phosphaalkyne/hydrazido coupling, $[ReCl_2\{\eta^4\text{-}N(NCOPh)PCBu^tPCBu^t\}(PPh_3)]$, the structure of which, authenticated by an X-ray diffraction analysis, contains the novel η^2-phosphidocarbene $Re{=}C(Bu^t)P\text{–}$ fragment.

The chemistry of compounds containing phosphorus–carbon multiple bonds has been expanding rapidly in the last few years and a wide variety of reactivity towards metal centres has been established.[1,2]

The coordination chemistry of phosphaalkynes at dinitrogen-binding metal sites has received little attention, although we previously reported the very rare η^1-ligation mode at *trans*-$[M(dppe)_2]$, (M = Mo or W, dppe = $Ph_2PCH_2CH_2PPh_2$),[3] *trans*-$[FeH(dppe)_2]^{+}$[4] and *trans*-$[ReCl(dppe)_2]$,[4] centres which are known[5] to bind only linear ligands, such as N_2 and isocyanides in the axial positions.

We have now extended our studies to the chelate benzoylhydrazido(3−)† rhenium(v) complex $[ReCl_2(NNCOPh)(PPh_3)_2]$ **1** which is a known[7] precursor for a variety of benzoyldiazenido(1−) and derived dinitrogen complexes. Thus treatment of a benzene solution of **1** with $P{\equiv}CBu^t$ at 40 °C, leads *via* ring opening and addition of one phosphaalkyne to the formation of the benzoyldiazenido complex $[ReCl_2(NNCOPh)(P{\equiv}CBu^t)(PPh_3)_2]$ **2**. This complex was isolated as a red solid and its ^{31}P $\{^1H\}$ NMR spectrum (in CD_2Cl_2, δ rel. to H_3PO_4) exhibits the expected AB_2 pattern: δ P^A $(P{\equiv}CBu^t)$ −63.3 (t, $J_{P_AP_B}$ 11 Hz) and $\delta P^B(PPh_3)$ −1.42 ppm (d, $J_{P_AP_B}$ 11 Hz), while in the ^1H NMR spectrum, the Bu^t resonance occurs as a singlet at δ 0.84.

$[ReCl_2(NNCOPh)(PPh_3)_2]$
1

$[ReCl_2(NNCOPh)(P{\equiv}CBu^t)(PPh_3)_2]$
2

$[ReCl_2\{\eta^4\text{-}N(NCOPh)PCBu^tPCBu^t\}(PPh_3)]$
3

A second product **3** containing two $Bu^tC{\equiv}P$ units was also isolated as a dark red crystalline material and its molecular structure, which is shown in Fig. 1, was established by a single crystal X-ray diffraction study.‡ The structure of **3** is particularly interesting since it reveals the presence of three metallacycles, two of which are five-membered rings, one being derived from the hydrazido ring and the other, a $N\text{–}\dot{P}{=}C\text{–}P$ containing cycle. The latter results from an unprecedented addition of a phosphaalkyne to the N(α) atom of the diazenido ligand and further coupling with a second phosphaalkyne molecule which also binds the metal *via* an

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† This chelating ligand, $=N\text{–}N{=}C(Ph)O\text{–}$, can also be considered[6] as a benzoyldiazenido(1−) species, $\text{–}N{=}N\text{–}C(Ph){=}O{\rightarrow}$.

‡ *Crystal data for* **3**: $C_{35}H_{28}Cl_2N_2OP_3Re{\cdot}C_6H_6$, M_r = 920.8, triclinic, space group $P\bar{1}$ (No. 2), a = 11.157(2), b = 11.537(2), c = 16.368(2) Å, α = 97.09(3), β = 95.93(3), γ = 98.78(2)°, V = 2050.1 Å^3, Z = 2, D_c = 1.49 cm^{-3}, $F(000)$ = 912. Monochromated Mo-Kα radiation, λ = 0.71069 Å, μ = 32.8 cm^{-1}. Data were collected using a crystal 0.12 × 0.08 × 0.05 mm on an Enraf-Nonius CAD4 diffractometer. A total of 7208 unique reflections were measured for $2<\theta<25°$ and $+h\pm k\pm l$, and 4392 reflections with $|F^2|>3\sigma(F^2)$ were used in the refinement. The structure was solved by routine heavy atom methods. There is disorder of two of the phenyl groups. Final residuals were R = 0.034, R' = 0.038. Programmes from the Enraf-Nonius SDP-Plus package were run on a microVAX computer. 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.

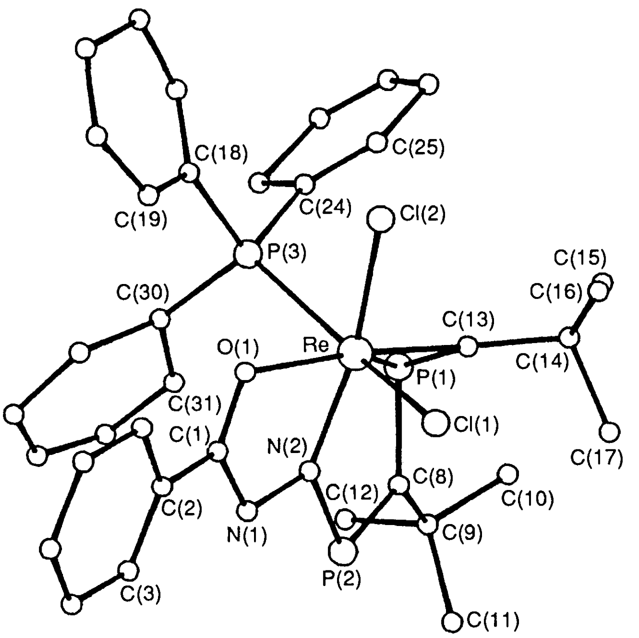


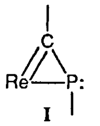
Fig. 1 Molecular structure of [ReCl$_2${η^4-N(NCOPh)PCBu^t-PCBu^t}(PPh$_3$)] **3**, showing the atom numbering scheme

η^2-coordination mode to afford a novel type of three-membered metallacycle (*vide infra*).

Some π-delocalisation is evident within the phosphaalkyne and benzoylhydrazido-derived rings, with a conceivable stabilizing effect and, *inter alia*, the N(1)–N(2) bond length, 1.371(8) Å, is intermediate between a single and a double bond[8] and the corresponding ligand appears to have partial diazene-type character. Furthermore, the C(1)–N(1) distance, 1.345(11) Å, also indicates considerable double bond character.

The most remarkable metallacycle, however, is the three-membered ring resulting from η^2-coordination of the terminal phosphaalkyne unit. It lies out of the plane of the N–P=C–P containing cycle and contains a remarkably short rhenium–carbon distance, 1.893(7) Å, which is even shorter than that expected for a Re=C double bond (1.91 Å).[9] Moreover, it is significantly shorter than those known for the related η^2-vinyl [1.947(6) and 2.193(6) Å][10] or vinylidene [2.046(8) Å][11] ligands in *trans*-[ReCl{η^2-C(CH$_2$Ph)CH$_2$}(dppe)$_2$]$^+$ or *trans*-[ReCl(=C=CHPh)(dppe)$_2$], respectively. The P(1)–C(13) bond length [1.797(8) Å] of the phosphametallacycle, corresponds to a significant elongation of the η^2-phosphaalkyne bond and it approaches that expected for a single bond [*cf.* 1.815(8) Å for P(1)–C(8)]. Such a metallacycle can be mainly represented by the η^2-carbenic structure **I** which, to our knowledge, provides the first example of an η^2-phosphidocarbene, which can alternatively also be viewed as a metalla-1*H*-phosphirene. This η^2-carbene is isoelectronic with an η^2-vinyl species and also behaves as a three-electron donor. It can also be related to the recently described ligated η^2-phosphinocarbene, η^2-CHPMe$_2$, which can be considered as a rare example of an η^2-λ^5-phosphaalkyne (HC≡PMe$_2$) derived from C–H activation of PMe$_3$ in the complexes [TaH$_2$(η^5-C$_5$Me$_5$)(η^2-CHPMe$_2$)(PMe$_3$)][12] and [Ta(η^2-CH$_2$PMe$_2$)(η^2-CHPMe$_2$)(PMe$_3$)$_3$].[13] However, in these cases, a significant contribution of the non-carbenic structure **II** has been recognised since the P–C distances, 1.714(9) and 1.760(6) Å, are shortened, and the ligand behaves formally as a 2-electron donor (or a 4-electron donor in the carbenic form).

As expected two separate Bu^t resonances (δ 1.45 and 1.48) are observed in the ^{1}H NMR spectrum of **3**, while a very low field doublet (δ 346.3) in the ^{31}P {^{1}H} NMR spectrum§ is attributed to P(2), the phosphorus directly bonded to N. Low-field ^{31}P resonances, although not so extensively shifted, have also been reported for other species containing the =P–N moiety, such as 1,2,3,4-triaza-[14] or 1,2,3-diaza-phospholes[15] (δ *ca.* 160–180).



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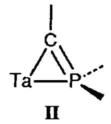

II

The formation of the η^2-carbene in **3** reflects the high tendency of rhenium to form multiple bonds to carbon,[5] but the novel phosphaalkyne/hydrazido coupling is surprising in view of the known[16] stability of the chelating benzoylhydrazido ligand towards electrophiles such as H$^+$. Although the mechanism of this reaction has not yet been elucidated, it can be formally regarded as being similar to the known[14] formation of a triazaphosphole through a [3 + 2] cycloaddition reaction between a phosphaalkyne and an azide.

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§ ^{31}P {^{1}H} NMR data (rel. to H$_3$PO$_4$): δ P(1) 17.2 (dd, $J_{\mathrm{P^1P^2}}$ 16, $J_{\mathrm{P^1P^3}}$ 9 Hz), δ P(2) 346.3 (d, $J_{\mathrm{P^1P^2}}$ 14 Hz), δ P(3) 26.6 (d, $J_{\mathrm{P^1P^3}}$ 9 Hz).