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Insertion of sodium phosphaethynolate, Na[OCP], into a zirconium-benzyne complex[†]

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Reaction of the zirconium–benzyne complex $[Cp_2Zr(PMe_3)(C_6H_4)]$ with sodium phosphaethynolate, Na[OCP], affords a zircono-phosphaalkene complex. Notably, unlike reactions of other transition metal complexes with Na[OCP] that yield the products of simple salt metathesis, this transformation represents novel Na[OCP] insertion chemistry and formation of an unusual solid state coordination polymer. The polymer is disrupted upon addition of Me₃SiCl to afford a silyl-capped dimer that retains the zirconophosphaalkene functionality. Protonation of either form of zirconophosphaalkenes results in the formation of benzoylphosphine, PhC(=O)PH₂.

The development of convenient and scalable routes to the phosphorus analogue of the cyanate anion, $[OCP]^-$, has spawned renewed interest in the chemistry of this fundamental 3-atom building block.¹ An attractive aspect of this synthon is that through its three dominate resonance structures, $[O-C = P]^-$, $[O=C = P]^-$, and $[O = C \rightarrow P]^-$, a wide range of reactivity may be realized. Indeed, recent reports have shown that this material exhibits novel [4+2] and [2+2] cycloaddition chemistry and may serve as a means to transfer [P]⁻ or a [OCP]⁻ unit.^{2–7} Furthermore, the stability and scalability of Na[OCP] as a common synthon has led to the development of phosphorus analogs of important small molecules, such as urea and cyanuric acid.^{8,9} Heterocycles **a–e** (Scheme 1) serve as an indication of the applicability of Na[OCP] towards important developments in main-group chemistry.

The reactivity of the phosphaethynolate anion towards transition metal complexes, however, has remained relatively unexplored, with only a handful of isolated products known (Fig. 1).¹⁰⁻¹² In these cases the scope of reported reactions to produce the





[OCP]-metal complex can be described as salt metathesis reactions where $[OCP]^-$ acts as a pseudo-halide. Conversely, phosphaalkynes $(R-C \equiv P)$ have rich chemistry with transition metal complexes, especially for insertion and oligomerization reactions.¹³⁻¹⁶



Fig. 1 Representative metal complexes derived from Na[OCP].^{10–12}

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It is noteworthy that a number of phosphaalkynes are highly reactive and cannot be stored for long periods of time.^{15,17} Alternatively, utilization of Na[OCP], a remarkably stable salt, provides opportunities for the isolation of organometallic products that were previously inaccessible.

We have been interested in the chemistry of 1,3-benzoxaphospholes and related molecules as fluorescent conjugated materials that feature $p\pi$ - $p\pi$ P=C bonds.¹⁸⁻²¹ During our studies we have sought new routes to these important species and recognized that a 9-atom heterocyclic system might be assembled by reaction of the phosphaethynolate anion with benzyne (Scheme 2), similar to a previously reported reaction between benzyne and organic azides.²² Our initial efforts to generate benzyne in the presence of phosphaethynolate anion, followed by trapping reactions with electrophiles, did not yield the desired product. As ascertained by ³¹P NMR spectroscopy, reactions produced numerous products which is the result of direct reactions of Na[OCP] with typical benzyne precursors, even combining Na[OCP] with the relatively mild precursor 2-trimethylsilylphenyl triflate resulted in oxidative tetramerization of [OCP]⁻ after a few minutes.²³ Herein, we describe the synthesis, structure, and reactivity of a novel zirconophosphaalkene (2). Notably, formation of compound 2 represents the first example of insertion of Na[OCP] into a metal-carbon bond.

Addition of Na[OCP] (dioxane)_{2.5} to a solution of the zirconium benzyne complex [Cp₂Zr(C₆H₄)(PMe₃)] (1)²⁴ produces a dark red solution from which an insoluble red microcrystalline solid (2) can be isolated in 43% yield (Scheme 3). The solid state ³¹P MAS NMR spectrum of 2 reveals a singlet at $\delta = 50.6$ ppm. Red crystals of 2 suitable for a single crystal X-ray study were obtained by layering a THF solution of Na[OCP] on top of a solution of 1 in THF in a thin glass tube. Fig. 2 reveals that insertion of the CP unit of Na[OCP] into one of the zirconium–carbon bonds has occurred to afford an unusual polymeric structure consisting of [Cp₂Zr{ κ -C, κ ²-P-C₆H₄C(O)P}] dimers bridged by [Na(THF)₂] cations. Interestingly, despite the oxophilicity of zirconium, the resulting product has formed Zr–P instead of Zr–O bonds and



Scheme 3 Synthesis of 2 and 3.



Fig. 2 Molecular structure of **2** (ellipsoids set at 50% probability; hydrogen atoms, co-crystallized THF, and second coordination polymer chain omitted for clarity). Selected bond distances [Å] and angles [°]: P1–Zr1: 2.6151(14); P1–Zr1: 2.7010(14); P1–P1': 2.548(2); P1–C11: 1.743(5); Zr1–C13: 2.406(5); O1–C11: 1.276(6); C11–C12: 1.488(8); P1–Zr1–C13: 71.04(14); Zr1–P1–Zr1': 122.75(5); Zr1–P1–C11: 109.37(19); Zr1'–P1–C11: 127.22(19); P1–C11–O1: 125.6(4).

represents an unusual example of a cyclic bridging metallophosphaalkene.^{14,26,27} The structure also contains a second crystallographically inequivalent [Cp₂Zr{ κ -C, κ ²-P-C₆H₄C(O)P}] unit (and corresponding coordination polymer chain) as well as co-crystallized THF molecules.

Within each dimer the two halves are related by an inversion center and the $[Zr_2{C_6H_4C(O)P_{2}}]$ array is essentially coplanar. The average P=C bond length of 1.742 Å is similar to other P-zirconophosphaalkenes,²⁵ however the expected opening of the Zr-P-C angle is not observed due to the cyclic structure of the phosphaalkene unit.^{25–27} The insertion of Na[OCP] follows a pathway similar to that reported for reaction of a zirconium benzyne with acetonitrile,²⁸ however the difference in electronic properties between $R-C \equiv P$ and $[O-C \equiv P]^-$ results in Zr-P bond formation instead of the Zr-C bond found in the insertion of *t*-butylphosphaalkyne.^{29,30}

Addition of Me₃SiCl to a suspension of 2 in THF results in the formation of a new red-orange species 3 as the sole product by ³¹P NMR spectroscopy (δ = 194.0 ppm), which could be isolated in 96% yield (Scheme 3). Analysis of orange single crystals of 3 grown from a saturated benzene solution revealed silvlation of the oxygen atoms has occurred to replace the bridging sodium atoms of 2 (Fig. 3). The metallo-phosphaalkene core is retained, although there is some loss of planarity of the [Zr₂{C₆H₄C(O)P₂] array. A slight shortening of the P=C bond is observed (1.7046(19) Å) compared to that in 2 (1.743(5) Å), as well as ca. 0.05 Å lengthening of the Zr-P bonds. This change in P-C and P-Zr bond distances combined with a lengthening of the C-O bond between 2 (1.276(6) Å) and 3 (1.372(2) Å) suggest that the oxygen atoms in 2 donate a significant amount of electron density into the π -system, as shown in resonance form 2d (Scheme 4). A similar effect was previously observed in the structure of metallophosphaalkenes that contained nitrogen in a trans-orientation to the metal atom.³¹ This increased electron density around phosphorus also explains the significant difference observed between the ³¹P resonances of 2 (δ = 50.6 ppm) and 3 (δ = 193.96 ppm).



Fig. 3 Molecular structure of **3** (ellipsoids set at 50% probability; hydrogen atoms omitted for clarity). Selected bond distances [Å] and angles [°]: Zr1–P1: 2.6721(6); Zr1′–P1: 2.7608(6); Zr1–C11: 2.3873(19); P1–C17: 1.7046(19); Si1–O1: 1.6708(16); O1–C17: 1.372(2); P1–Zr1–P1': 59.276(19); P1–Zr1–C11: 71.22(5); Zr1–P1–Zr1': 120.723(19); Zr1–P1–C17: 105.83(7); Zr1′–P1–C17: 131.39(7); P1–C17–O1: 124.03(14); Si1–O1–C17: 127.71(13).



Compounds 2 and 3 undergo protonation upon addition of H_2O to generate a species that displays a triplet in the ³¹P NMR spectrum at -107.9 ppm (¹J_{PH} = 219.7 Hz). This material has been identified as benzoylphosphine (4) by multinuclear NMR (Scheme 5). Compound 4 was originally prepared by reaction of [K(18-crown-6)][PH₂] with benzoate esters PhC(=O)OR to give PhC(=O)P{K}H, which was subsequently protonated to produce 4.³² Compound 4 produced by this method was unstable and converts to dibenzoylphosphine [Ph(C=O)PH(C=O)Ph] and PH₃. Compound 4 produced from 2 or 3 was shown to be indefinitely stable towards self-condensation in solution at 25 °C when observed periodically by NMR, whereas solutions of 4 produced from the original route decompose slowly at -78 °C. Attempts to isolate 4 in pure form, however, failed as samples contained small amounts of dibenzoylphosphine.

We have described the formation of a novel zirconophosphaalkene through the insertion of Na[OCP] into a zirconiumcarbon bond. We aim to expand this insertion chemistry towards the formation of other organometallics from Na[OCP], as well



Scheme 5 Protonation of zirconophosphaalkene complexes.

as the potential for using Na[OCP] towards the formation of interesting main group materials.

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