Angewandte Chemie

Phosphorus Chemistry

DOI: 10.1002/anie.200900100

New Adventures in the Molecular Chemistry of Phosphorus

*Christopher A. Russell**

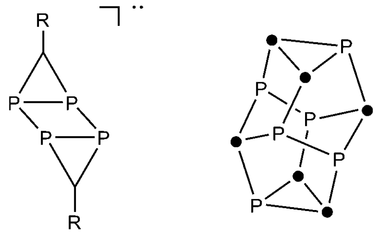
Dedicated to Prof. Michael F. Lappert on the occasion of his 80th birthday

Dötz reaction · phosphaalkynes · phosphorus · sandwich complexes · transition metals

"Phosphorus Remains Exciting!" was the title of a recent Highlight by Pfitzner[1] that focused on developments in the solid-state chemistry of the element. The same conclusion may also be drawn with regard to the molecular chemistry of phosphorus. Important developments have been reported in the chemistry of low-coordination phosphorus, where Cummins described elegant procedures whereby phosphorus-containing moieties were assembled on transition-metal scaffolds starting from terminal metal–phosphide or nitride functionalities.[2] By investigating the reactivity of these species, a preparation of P_2 under mild conditions was discovered; this has been exploited by observations of its reactivity towards both organic and inorganic systems.[3] In addition, interesting developments in phosphorus-rich cage complexes have developed from some of the above work; it should be noted that related cages have also been observed by using different strategies.[4] By using a similar approach of manipulation of a main group unit in the protective sphere of a transition metal, Grützmacher and co-workers removed the silyl group of a P-bonded silylphosphaalkyne group attached to a ruthenium center by reaction with a nucleophile, thus leading to a metal complex of the cyaphide anion.[5] This result opens the possibility of exploring the chemistry of this heavier homologue of the cyanide anion.

Given the diverse nature of progress in phosphorus chemistry, it would be easy to forget that the foundations of low-coordinate phosphorus chemistry were laid upon phosphaalkyne chemistry, which has been extensively utilized in organophosphorus and phosphaorganometallic synthesis. Given the similarity of low-coordinate phosphorus chemistry to organic chemistry, one can readily identify those compounds where the structures adopted for the phosphorus-containing isomers are structural imitations of the all-carbon molecules from which they are formally derived.[6] However, recent studies on 1,2,4-triphospholide complexes suggested that replacement of CH units for isolobal P moieties in the cyclopentadienyl framework induces changes in the electronic structure, thus giving ligands which are equipped to stabilize low-oxidation-state transition metals.[7] Hence the phosphorus atom acts as a carbon copy,[8] but with an added twist! It would be most exciting if this important selling point could be more widely exploited across research fields with which it is not commonly associated. Although phospholide complexes are the most prolific of the phosphorus heterocycles, many other sizes of phosphorus-containing rings have been realized; indeed, the formation of diphosphacyclobutadiene sandwich complexes forms part of this Highlight. In this regard, it is noteworthy that the intriguing electronic properties bestowed on heterocycles by the inclusion of one or more phosphorus atoms makes the quest for targeted syntheses of other synthetically useful ring systems a key remaining objective.

As well as examples where phosphorus shows distinct similarities to carbon, there are numerous examples where phosphorus shows different chemistry that is seemingly unrelated to the "conventional" chemistry of carbon, as seen in the preference to form cages rather than catenated chains and the important and developing role of relatively stable radical chemistry (Scheme 1).[9] In addition, substituting phosphorus atoms for carbon atoms may result in analogues of molecules hitherto unrealized in mainstream organometallic chemistry or the stabilization of species or intermediates which are mere objects of speculation in carbon-based chemistry. Whether these species are true representatives of their organic cousins is of course a matter for debate, but nevertheless, they serve to provoke active debate across a wide range of scientific circles.



Scheme 1. Examples of phosphorus-based diradicals (R = NiPr$_2$) and cage compounds (● = CtBu).

Despite the fact that the chemistry of low-coordinate phosphorus has been extensively probed in the last three

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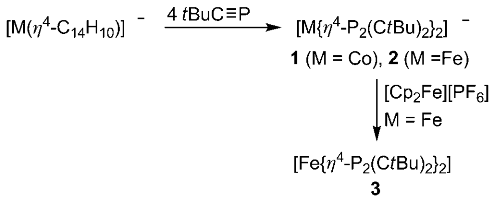
[*] Dr. C. A. Russell
School of Chemistry, University of Bristol
Cantock's Close, Bristol, BS8 1TS (UK)
Fax: (+44) 117-929-0509
E-mail: chris.russell@bris.ac.uk
Homepage: http://www.inchm.bris.ac.uk/people/russell.shtm

decades, the area still possesses ample capacity to surprise, as shown by recent reports from Lammertsma and co-workers. Homoleptic sandwich anions of diphosphacyclobutadiene were prepared for cobalt[10a] and iron[10b] using highly reactive polyarene/transition-metalate precursors;[11] furthermore, the anionic iron complex could be oxidized to give the neutral bis(1,3-diphosphacyclobutadiene)iron, **3** (Scheme 2). Notably, while transition metal complexes of cyclobutadiene have played an important part of the development of organometallic chemistry,[12] the all-carbon analogue of **3**, bis(η^4-cyclobutadiene)iron, and indeed of **1** and **2**, have not been observed to date.

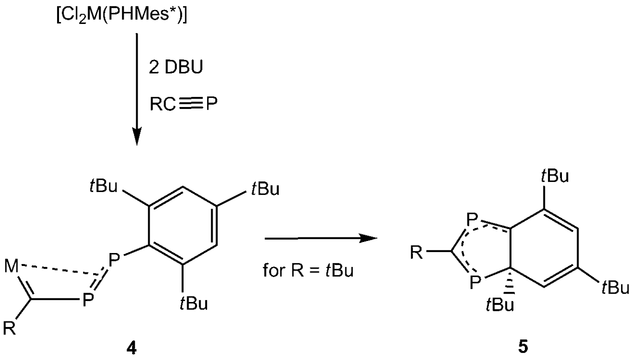


Scheme 2. Routes to diphosphacyclobutadiene sandwich moieties. Cp = cyclopentadienyl.

The solid-state structures of **1**–**3** each possess metal-containing moieties which show two approximately coplanar 1,3-diphosphacyclobutadiene units that adopt mutually staggered configurations in sandwiching a metal atom. The beautiful symmetry of each species identifies them as a welcome addition to the iconic family of sandwich compounds. Interestingly, the dimerization of the phosphaalkynes leads exclusively to the 1,3-isomer rather than the alternative 1,2-isomer—a topic which has attracted more recent interest.[13] Density functional theory calculations suggest that the dianion of **3**, containing formally an 18e Fe center, is a viable species although it is yet to be observed in the laboratory. The quest for other homoleptic diphosphacyclobutadiene complexes will doubtless expand beyond Fe and Co. In particular, with regard to the routes used to form **1** and **2**, it will be very interesting to see how the recently reported dianionic polyarene complexes of the Group 4 metals[14] react with phosphaalkynes.

To further enhance the story, the reactivity of **1** towards electrophiles was examined and the three chosen reactions gave distinct products. The reaction with H^+ showed that the proton interacted with the metal center. In contrast, the bulkier Me^+ and Ph_2P^+ groups attacked the diphosphacyclobutadiene ring with the added subtlety that Me^+ simply added to a P center whereas Ph_2P^+ was shown to insert into a P–C bond.[10a]

As alluded to above, an alternative application of the phosphorus-for-carbon substitution strategy is in stabilizing purported intermediates in important organic transformations. One such example is the Dötz benzannulation reaction, which, since its discovery in 1975, has enjoyed considerable attention from the synthetic community as it enables the regiocontrolled preparation of aromatic systems from acyclic precursors.[15] Naturally, for such a significant reaction, a thorough understanding of the mechanism is fundamentally important, as the mechanistic implications may allow for the fine tuning of the reaction, however, such information is often very challenging to acquire. Lammertsma and co-workers have used the phosphorus-for-carbon approach to isolate a metal complex of a diphospha-3*H*-indene moiety, **5**—a stable P_2-containing entity which shows a remarkable resemblance to the Wheland intermediate of the Dötz reaction.[16] This compound was prepared by the in situ formation of a metal-phosphinidene and subsequent reaction with a phosphaalkyne, RC≡P (Scheme 3). Strikingly, for R = Mes*, the isolated product is a η^3-diphosphenylcarbene complex, **4**, but for R = *t*Bu, an unprecedented rearrangement occurs to form **5**.[17]



Scheme 3. Synthesis and reactivity of η^3-diphosphenylcarbene complexes (M = (η^6-*p*Cy)Ru, (η^5-Cp*)Ir). Cp* = pentamethylcyclopentadienyl, *p*Cy = *para*-cymene, DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene, Mes* = 2,4,6-tri-*tert*-butylphenyl.

The solid-state crystal structure of a ruthenium complex of **5** clearly showed the dearomatized Mes* ring, and demonstrated the preference of the metal to bind to the diphosphabutadiene unit rather that the all-carbon butadiene unit. The mechanism of conversion **4**→**5** was examined by using density functional theory calculations. Interestingly, no simple direct pathway could be found and an alternative process involving firstly a phosphinidene complex and subsequently an η^3-phosphaalkenyl–phosphinidene complex had to be invoked.

In summary, new surprises continue to emerge from the extensively explored links between phosphorus and carbon. In both scenarios outlined above, the interplay between theory and experiment has served to enrich the respective stories. There remains a continuing challenge not only to extend the subtleties of this link but also to make the area, in particular the valuable properties conferred upon molecules by the phosphorus/carbon exchange, more accessible to a wider chemical audience.

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