



Citation for published version:

Fischer, RC, Hill, MS & Liptrot, DJ 2018, 'Philip Power at 65: An icon of organometallic chemistry', *Dalton Transactions*, vol. 47, no. 16, pp. 5529-5532. <https://doi.org/10.1039/c8dt90058b>

DOI:

[10.1039/c8dt90058b](https://doi.org/10.1039/c8dt90058b)

Publication date:

2018

Document Version

Peer reviewed version

[Link to publication](#)

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Philip Power at 65: a Living Legend in Organometallic Chemistry

Roland C. Fischer,^a Michael S. Hill,^b David J. Liptrot.^b

- a) Institut für Anorganische Chemie, Technische Universität Graz, Stremayrgasse 9, A-8010 Graz, Austria.
- b) Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK.

Professor Phil Power FRS turns 65 this month. His contributions to organometallic and inorganic chemistry over the last four decades are expansive, and he has been instrumental in the definition of several new subfields in the discipline. To date, Prof Power has contributed over 500 publications to the literature, and his lab remains an active source of novel chemistry.

Power was born in Cork, Republic of Ireland and undertook a BA in Chemistry at Trinity College, Dublin, completed in 1974. He subsequently crossed the Irish Sea, completing a PhD at the University of Sussex in 1977. This was followed by a postdoctoral stay at Stanford University and his appointment to the University of California, Davis in 1981. During his career Power has been the recipient of awards too numerous to list here, perhaps most notably the Ludwig Mond Medal of the RSC and F. A. Cotton Award of the ACS in 2005. He was appointed a Fellow of the Royal Society in this same year. Power has also shown a commitment to service to the chemical community, acting as an Associate Editor of Inorganic Chemistry, and having served on the advisory boards of twelve journals including Dalton Transactions.

Over the course of his career, a significant proportion of Power's oeuvre has been published in RSC journals, charting a course from his very earliest contributions to some of his most recent enterprises, with numerous highlights along the way. In honour of Prof Powers' birthday, we have put together a web collection of his key contributions in RSC journals. These publications are landmarks in Prof Power's career and continue to have outstanding impact in the chemical community. Alongside these, we have invited previous co-workers, collaborators and chemists whose work shares an affinity with Prof Power's to share cutting edge research close in theme to his foci in Dalton Transactions and Chemical Communications. This collection shows a chemist with wide-ranging interests and a propensity for timely research, coupled with a cerebral dedication to conceptual frameworks which have helped to unify organometallic chemistry's vibrant cutting edges.

Early Contributions

Power's first paper in the chemical literature, originating from his PhD studies under Prof Michael F Lappert, was entitled "Ready Oxidative Addition of An Alkyl or Aryl Halide to a Tin(II) Alkyl or Amide - Evidence for a Free-Radical Pathway".¹ It is the first in a plethora of papers from Power investigating the reactivity of low-coordinate tin compounds. This first work utilised the bulky alkyl and amide ligands $-E(\text{SiMe}_3)_2$ ($E = \text{CH}, \text{N}$), which Power has regularly revisited throughout the last 4 decades. Thus began a stream of related papers with Lappert,² including Power's first foray into stable radicals, the pnictyl species $\cdot[E\{\text{CH}(\text{SiMe}_3)_2\}_2]$ ($E = \text{P}, \text{As}$).³ Later work as Lappert's collaborator would identify these as "Jack-in-the-Box molecules", reflecting Power's ability to succinctly frame research areas.⁴ After graduation in 1977, Power went on to work with Prof. Richard H. Holm, yielding his first forays into the chemistry of cluster compounds.

A fascination with low-coordinate, low-valent and low-oxidation state compounds defines Power's career. However, this does not imply a monolithic approach and Power has worked in a wide range of areas as summarised hereafter.

Low Coordinate Species and Clusters

In 1981, Power took up a position at the University of California, Davis where he remains to this day. New appointees to Power's group are often told of his first impression of the Californian weather; "It was a hundred and ten when I got off the train... the biggest mistake I've ever made was not to turn around on the spot and leave". It is apparent from Power's successes that this is perhaps not the whole story. Work in collaboration with Lappert continued, with the X-ray crystallographic characterisation of the group 14 bisamides, $[M\{N(SiMe_3)_2\}_2]$ ($M = Ge, Sn$).⁵ This work is representative of much of Power's earlier work at Davis; the crystallographic characterisation of highly sensitive compounds, collaborating with Håkon Hope, and later Marilyn Olmstead, to develop practical techniques to address these fragile species, as well as in crystallographic analysis. Power began forays into novel ligand systems, such as bulky alkoxides, as in his paper entitled "Syntheses and X-ray crystal structures of lithium and chromium(II) complexes of the tri-*t*-butylmethoxide ligand".⁶ Subsequently, Power began working with the terphenyl ligands, $-C_6H_3-2,6-Ar_2$ ($Ar = 2,4,6-Me_3C_6H_2; 2,6-iPr_2C_6H_3$; hereafter Ar'), which have been the platform for many of his most stunning discoveries. Occasional work with into other ligand systems have provided a further range of striking compounds, such as the group 13 carbene analogue $[HC\{C(Me)N(2,6-iPr_2C_6H_3)\}_2]Ga$.⁷

Whilst Power has regularly returned to p-block compounds, he has worked with all blocks of the periodic table, and the terphenyls have been ably applied to transition metal chemistry yielding striking univalent Cr(I), Mn(I) and Fe(I) compounds, $Ar'M(\eta^6-C_6H_6)$,⁸ as well as two-coordinate heteroleptic Co(II) species $Ar'CoN(SiMe_3)_2$,⁹ amongst others. This latter species, through one of Power's multitude of fruitful collaborations, was shown to have unusual magnetic properties and a subsequent targeted approach focussing on axially anisotropic systems contributed to a new approach to single molecule magnetism.¹⁰ As well as describing a plethora of new compounds to the literature, Power has shown a yen for chasing down chemical mysteries from the past, work which yielded a recent focus on Ni(I) through his reinvestigation of the nickel bisamide $Ni\{N(SiMe_3)_2\}_2$ first reported by Bürger and Wannagat in the early 1960s.¹¹ Power has contributed to a range of useful reviews over the years, including the seminal text on such compounds, "Metal Amide Chemistry", with Lappert and others.

Beyond homoleptic species, the terphenyls have provided an excellent coligand for a variety of substituents on main group compounds. This has allowed the interrogation of divalent group 14 halides and hydrides, $Ar'MX$ ($M = Ge, Sn, Pb; X = H, Cl, Br$), the latter of which show fascinating structural isomerism.¹² These compounds have provided a source of much interesting reactivity, and Power has also used them as starting materials for clusters¹³ and multiply bonded species (*vide infra*). Power has also implicated tin(II) hydrides as catalytic intermediates in the isohypsic dehydrogenative coupling of amines and boranes, once again emphasising his willingness to address any challenge in the field.¹⁴

Multiple Bonds

Much work by Lappert on the group 14 alkyls $[M\{CH(SiMe_3)_2\}_2]$ ($M = Ge, Sn$) focussed on the rationalisation of their bonding, and attempts to address the existence (or lack thereof) of an $M=M$ double bond. A fascination with main group multiple bonding has permeated Power's work throughout the years, and yielded the compounds with which he is probably most closely associated. Initial work in this area interrogated the possibility of π -bonds in reduced diicosagen(4) radicals, such as in his paper "Comparison of B-B pi-bonding in singly reduced and neutral diborane(4) derivatives: Isolation and structure of $[Li(Et_2O)_2]\{MeO(mes)BB(mes)OMe\}$ ".¹⁵ In the hunt for multiple bonding

in group 14, Power then investigated reduction of the aforementioned heteroleptic terphenyl tetraphenyl halides, but the reaction of $\text{Ar}^{\text{r}}\text{GeCl}$ ($\text{Ar}^{\text{r}} = -\text{C}_6\text{H}_3-2,6-(2,4,6-\text{Me}_3\text{C}_6\text{H}_2)_2$) with potassium instead yielded instead radical and anionic clusters.¹⁶

Power's focus on multiply bonded species undiminished, the dipnictenes provided a rich seam of compounds such as in his report "Unsymmetric dipnictenes—synthesis and characterization of $\text{MesP}=\text{EC}_6\text{H}_3-2,6\text{-Trip}_2$ ($\text{E} = \text{As}$ or Sb ; $\text{Mes} = \text{C}_6\text{H}_2-2,4,6-\text{Me}_3$, $\text{Trip} = \text{C}_6\text{H}_2-2,4,6-\text{Pr}^i_3$)".¹⁷ It is at this point that one of Power's striking, and enduring characteristics is exemplified. Over the years, he has provided a range of useful, striking and often field-defining reviews, addressing and unifying broad swathes of organometallic chemistry as in his review entitled "Homonuclear multiple bonding in heavier main group elements".¹⁸

Power's attack on the heavier group 14 compounds was, however, not over and at this point the utility of the terphenyl system became apparent. Judicious, and readily accessible, alteration of the ligand coupled with Power's commitment to synthetic excellence allowed access to the heavier alkyne analogues $\text{Ar}^{\text{r}}\text{MMAr}^{\text{r}}$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$; $\text{Ar}^{\text{r}} = -\text{C}_6\text{H}_3-2,6-(2,6-\text{iPr}_2\text{C}_6\text{H}_3)_2$). Subsequently, group 13 analogues were similarly accessed with reports of $\text{Ar}^{\text{r}}\text{MMAr}^{\text{r}}$ ($\text{M} = \text{Ga}, \text{In}$; $\text{Ar}^{\text{r}} = -\text{C}_6\text{H}_3-2,6-(2,6-\text{iPr}_2\text{C}_6\text{H}_3)_2$), the gallium congener of which is the source of an oft heard comment in Power's lab "Green is good.". Power then reviewed this area¹⁹ and went on to modify the enduringly modular terphenyl system to analyse ligand effects on the metal-metal interaction in these species.²⁰ These compounds, landmarks in organometallic synthesis, have made it into text books and contributed much to change the field's perception of multiple bonding. Thus, Power's syntheses of beautiful compounds are not simply stamp collecting, but an opportunity to interrogate unique molecular systems. This fact is best displayed in his assessment of the reactivity of heavier main group multiple bonds.

Small Molecule Activation

While working in Power's lab, it was not unusual to hear the question "what would you do with 10 g of this compound?" Having access to multigram amounts of the heavier alkyne analogues, Power has done much to answer this question for such species, and in doing so contributed to a renaissance in main group chemistry which has done much to inspire the authors.

Power's investigations of the ditetraynes showed a reactivity towards activated alkenes²¹ and nitrosyl compounds²² amongst others. However, it is for their reactivity towards small molecules, otherwise considered inert to main group species under ambient conditions, that Power's heavier alkyne analogues are most well-known. In the paper "Addition of H_2 to distannynes under ambient conditions",²³ Power contributed to a recognition that certain main group compounds could be "transition metal mimetic", an understanding which has helped push back the frontiers of organometallic chemistry in the s- and p-blocks. The aforementioned multiply bonded group 13 compounds also showed striking reactivity, readily activating olefins.²⁴

The marked ability of terphenyl ligands to support multiple bonding is by no means isolated to the p-block. The synthesis of a Cr-Cr quintuple bond applying these ligands is one of Power's most well-known contributions, and this bond was shown to react with unsaturated nitrogen compounds.²⁵ Beyond the reactivity of multiple bonded species, Power has done much to assess the reactivity of homoleptic diaryls of both main group and transition metal species with small molecules, such as in his paper "Insertion reactions of a two-coordinate iron diaryl with dioxygen and carbon monoxide".²⁶

Dispersion

Sterically bulky ligands have not just provided Power with a collection of compounds which must be the envy of any synthetic organometallic chemist. It is apparent that the unique nature of these ligands have both directed Power's thinking and provided surprises demanding reinterrogation of results. Power's aforementioned willingness to chase down chemical mysteries has not been isolated to results of other workers but encompasses an eager willingness to reassess his compounds in the light of new findings. Power has recently begun to focus on the concept of C-H...H-C dispersion interactions in rationalising the structure and reactivity of main group and d-block compounds. It is thus fitting that this editorial closes with reference to a paper from Power which addresses a compound he first encountered during his PhD, and reflects his collaborative approach to science. In 2015, Power, in collaboration with Prof Shigeru Nagase, reassessed the question of M-M bonding in $[M\{CH(SiMe_3)_2\}_2]_2$ (M = Ge, Sn, Pb) and concluded "[a]lthough much effort has been expended in development of bonding models for the multiple bonds between heavier main group elements, it seems both probable and ironic that the dispersion force attraction forces exceed those of the multiple bonds in many instances and that a variety of more subtle interactions including packing effects are of key importance for the understanding of their bonding."²⁷

Final Thoughts

Phil's contributions to chemistry are thus expansive, dramatic and sometimes overlooked. He continues to be, and we are pretty sure he hates the term, an influencer in chemistry; bereft of the habit of talking up his work, it is instead for a plethora of truly ground-breaking, stunning experimental discoveries and seminal review articles and comments that he is recognised. Thus, we do not claim this is in any way a thorough assessment of Phil's work, but feel that these highlighted papers draw attention to an approach to chemistry which has been, without a doubt, defining. Nevertheless, two of us (RCF, DJL) have been fortunate enough to work with Phil and one (MSH) has been inspired by him. We hope that this collection, and related events around Phil's birthday are a suitable tribute. We thank the contributors to the collection for their hard work and willing, and we hope interested readers will join us in celebrating this anniversary of a living legend of organometallic chemistry. Finally we, and doubtlessly you, look forward to the ongoing contributions from Phil's lab to the ever increasingly exciting field of organometallic chemistry.

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