Weiss' Reagents: A synthetically useful class of iodine(III) coordination compounds

Robert Corbo and Jason L. Dutton*

Department of Chemistry and Physics, La Trobe Institute for Molecular Sciences

La Trobe University

Melbourne, Victoria, Australia

j.dutton@latrobe.edu.au

Abstract

The growing use of pyridine stabilized polycationic I(III) regents ($[PhI(Pyr)_2]^{2+}$) as versatile oxidizing agents is reviewed. Currently the number of examples describing the use of these oxidants is modest, however those that do exist are spread across a diverse range of topic areas. The highly oxidizing nature of the $[PhI(Pyr)_2]^{2+}$ polycations coupled with the potential for neutral ligand delivery to metal centers or *in situ* generation of the reactive $[PhI]^+$ electrophile gives access to a range of novel transformations across topic areas including organic, heavy main-group centered and organometallic chemistry.

Key words

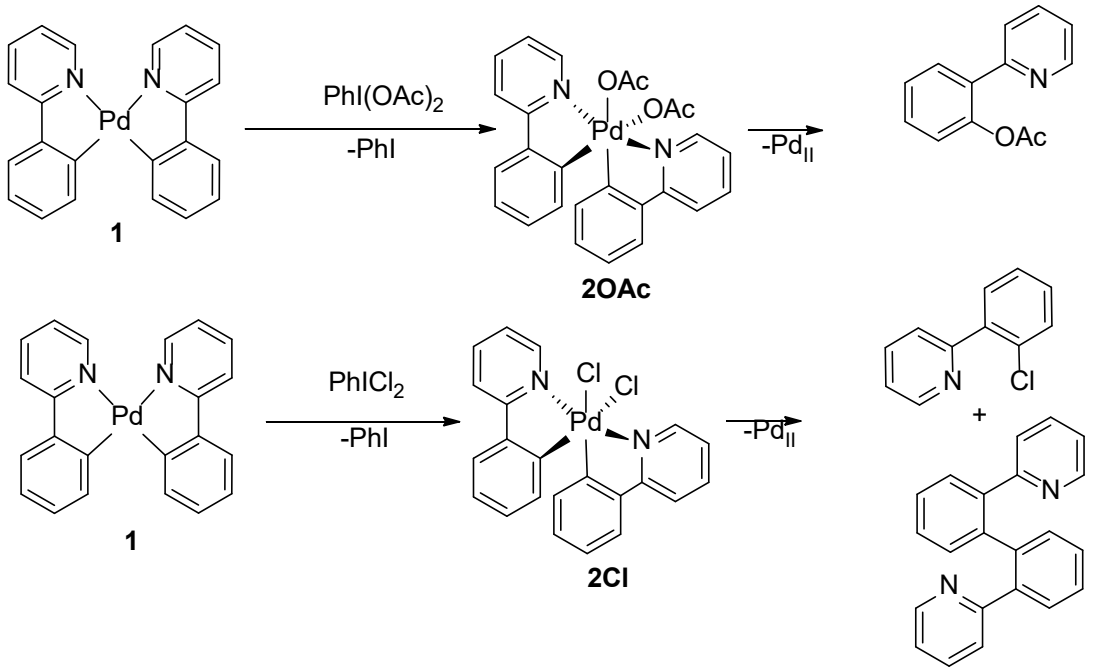
Iodine

Hypervalent

Oxidizing agents

Introduction

The first report of hypervalent iodine dates back well over 100 years with work by Willgerodt and co-workers describing the synthesis of $PhICl_2$ *via* the treatment of iodobenzene with chlorine gas.[1] Reagents of the iodine(III) family now represent a cohort of powerful oxidizing agents that can be typically weighed, reacted and stored safely making them well represented across many areas of synthetic chemistry. For example, $PhICl_2$ is now accessible without the cumbersome use of Cl_2,[2] providing a stoichiometric source of Cl_2 which is both a bench stable and weighable solid. Similarly, $PhI(OAc)_2$, also first reported by Willgerodt, offers an easy to handle replacement for the potentially explosive diacetyl peroxide $CH_3COO\text{-}OOCCH_3$. Of particular interest is the recent adoption of iodine(III) reagents as tools for accessing rare, and in some cases catalytically competent high valent platinum group metal complexes.[3] The synthetic value of reagents such as $PhICl_2$ in this area stems from the potential for concomitant oxidation and ligand delivery to a metal center. This is well illustrated by work described by Sanford demonstrating the efficacy of the I(III) reagents $PhICl_2$ and $PhI(OAc)_2$ in accessing a variety Pd(IV) complexes including **2Cl** and **2OAc** from the cyclometallated Pd(II) precursor **1** that may be isolated and crystallographically characterized, but remain thermally unstable and reactive towards productive reductive elimination processes (Scheme 1).[4-5] The reactivity of hypervalent iodine has been the subject of many reviews, most recently by Zhdankin and Wengryniuk.[6-7]

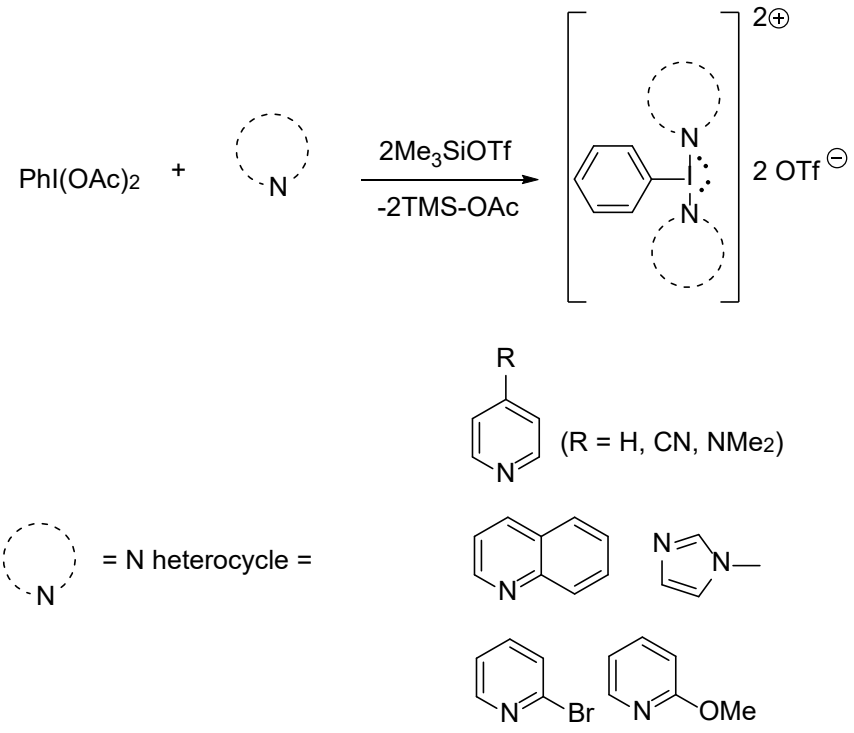


Scheme 1. Direct observation of C-C and C-heteroatom oxidative bond formation from a high oxidation state Pd center

A useful yet seemingly underexplored class of I(III) reagent are the bis(pyridinium)aryl I(III) dications, $[PhI(Pyr)_2]^{2+}$, namely, Weiss' Reagents. Thermochemical calculations demonstrate that these reagents are stronger oxidizing agents than the commonly employed and commercially available $PhI(OAc)_2$ reagent often used.[8] The synthetic value of these compounds in organometallic chemistry arises from the coupling of oxidation with facile ligand delivery to a metal center. This review will discuss the synthetic application of these dicationic iodine reagents from their inception to current applications and will highlight their increasing value across a diverse range of chemical landscapes.

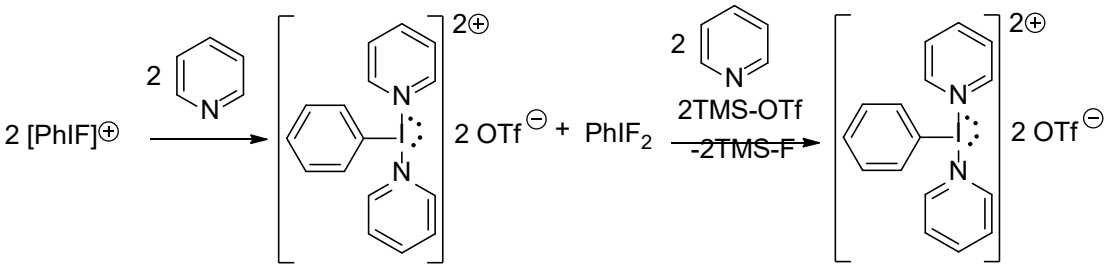
Synthesis and characterization

The pyridine ligated iodine(III) dications were first reported by Weiss and Seubert in 1994,[9] however structural verification of this class of compound did not come until crystallographic studies conducted by our group in 2012 revealed the expected T-shaped geometry about the I(III) center of $[PhI(Pyr)_2]^{2+}$ and $[PhI(4\text{-}DMAP)_2]^{2+}$(Scheme 2).[10] This synthetic approach has been expanded to also include ligand systems containing *ortho* substituted pyridine nucleophiles.[11] Zhdankin has explored monocationic hypervalent iodine derivatives furnished by heterocyclic nitrogen ligands as well as an iodine(V) dication which tolerates the bidentate chelating ligand 2,2'-bipy-ligand due to the altered geometry about the iodine(V) center.[12] Our group has reported the isolation of an 2,2'-bipy supported $[ICl_2]^+$ fragment which displayed similar geometric parameters.[12]



Scheme 2. Synthesis of $[PhI(Pyr)_2]^{2+}$ and reported derivatives.

The synthesis of $[PhI(Pyr)_2]^{2+}$is achieved through the treatment of $PhI(OAc)_2$ with two equivalents of TMS-OTf and then the addition of the desired pyridine based ligand to yield the final dication. Use of imidazole as the N-ligand was also demonstrated in the initial report. Until recently the reactive intermediate generated in this synthesis was believed to be $PhI(OTf)_2$, with a number of reports existing discussing its *in situ* generation and subsequent reactivity,[8, 13-14] however, NMR studies conducted by our group in 2015 were inconsistent with the generation of $PhI(OTf)_2$ and indicated that [PhI(OAc)][OTf] was the potential intermediate.[15] Structural confirmation came from crystallographic studies conducted by Shafir in 2016 and confirmed the intermediate to be the isolable monocationic species [PhI(OAc)][OTf], with the triflate weakly bound to iodine in the solid state.[16] The generation of $[PhI(Pyr)_2]^{2+}$ via the aforementioned synthetic approach is rapid and high yielding. This is aided by the highly soluble nature of the starting materials but insolubility of the iodine dications in CH_2Cl_2, which results in the immediate precipitation of the desired product upon addition of the selected ligand and allows for a simple CH_2Cl_2 wash as the only required purification step. Alternatively, the treatment of $[PhIF]^+$ with excess pyridine has been shown to result in the equimolar formation of $PhIF_2$ and $[PhI(Pyr)_2]^{2+}$.[17] The consumption of $PhIF_2$ can be achieved through the addition of TMS-OTf to yield $[PhI(Pyr)_2]^{2+}$ as the single major product (Scheme 3).

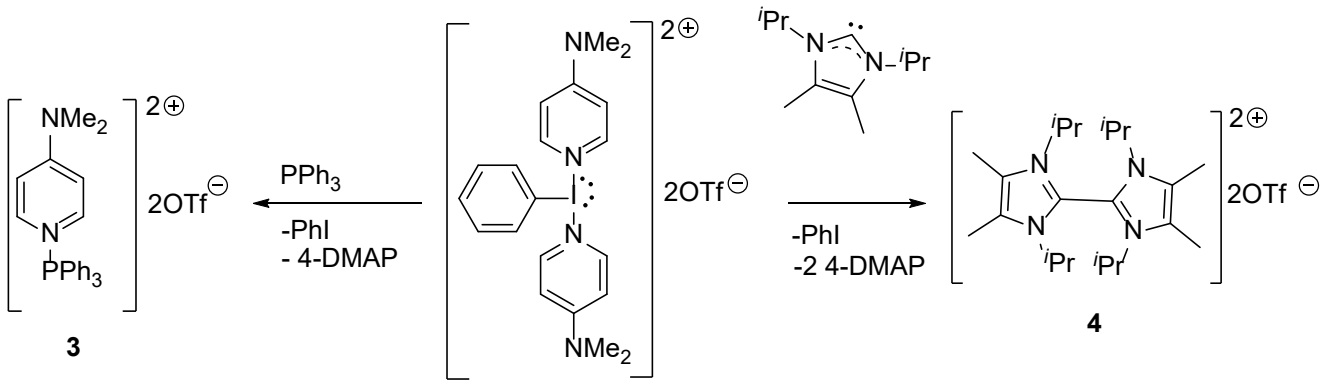


Scheme 3. Access to $[PhI(Pyr)_2]^{2+}$ *via* treatment of the fluoro(phenyl)iodonium monocation with TMS-OTf/pyridine.

The bonding for the N-I bonds along the N-I-N vector can be considered as a 3-center-4-electron bond, however we prefer to view the interaction as a coordinative bond. This is consistent with the synthesis of the complexes via direct ligation of iodine with the N-ligands. The pyridine ligands are also susceptible to classic ligand exchange reactions, with the addition of 4-DMAP to $[PhI(Pyr)_2]^{2+}$ resulting in replacement of the pyridines with 4-DMAP.[10] This was the first demonstration of a ligand exchange reaction at iodine involving neutral ligands. The partial charge on the iodine atom in $[PhI(Pyr)_2]^{2+}$ was calculated to be +1.14, consistent with the assignment of a formal charge of +2 at the iodine atom in the extreme "dative" model with purely coordinative bonds.

We envisioned that this coordination chemistry could be exploited to allow for the introduction of other neutral ligand systems. Attempts to generate NHC stabilized I(III) dications via ligands exchange reactions with Weiss' Reagent were unsuccessful. The addition of $^{i}Pr_2NHC(Me)_2$ to $[PhI(4\text{-}DMAP_2)]^{2+}$ resulted in oxidative homocoupling of the carbene to give dication **4**, and reduction of the I(III) center yielding PhI (Scheme 4). Spectral data obtained for the reaction of triphenyl phosphine with $[PhI(4\text{-}DMAP)_2]^{2+}$ indicated that the major product of the reaction was the 4-DMAP stabilized triphenylphospane ditriflate salt

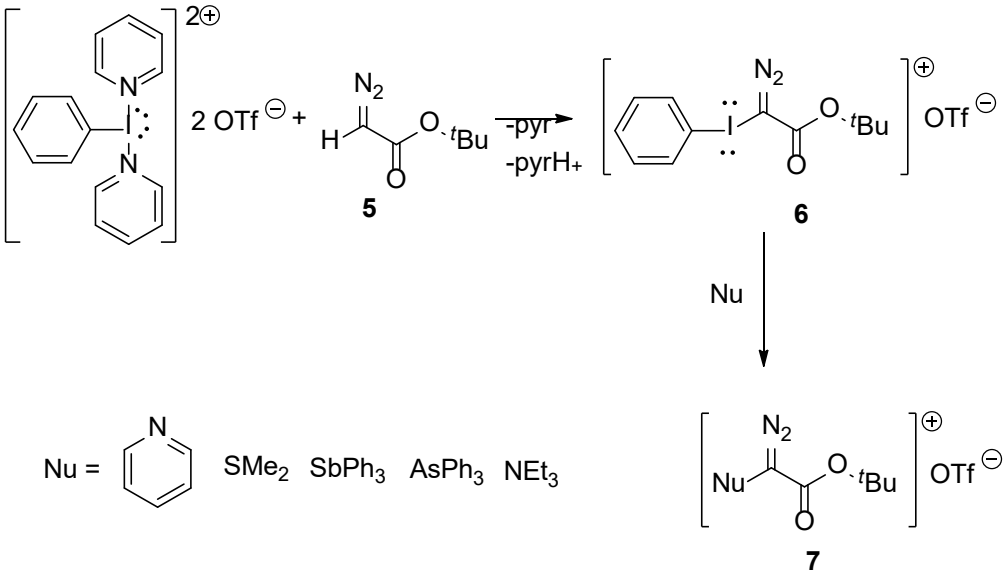
3,[18] which as is the case for the NHC example, arises from redox chemistry rather than the desired ligand exchange chemistry that was targeted.[18]



Scheme 4 NHC and phosphine mediated ligand exchange reactions involving 4-DMAP ligated Weiss' Reagent resulting in unproductive redox chemistry.

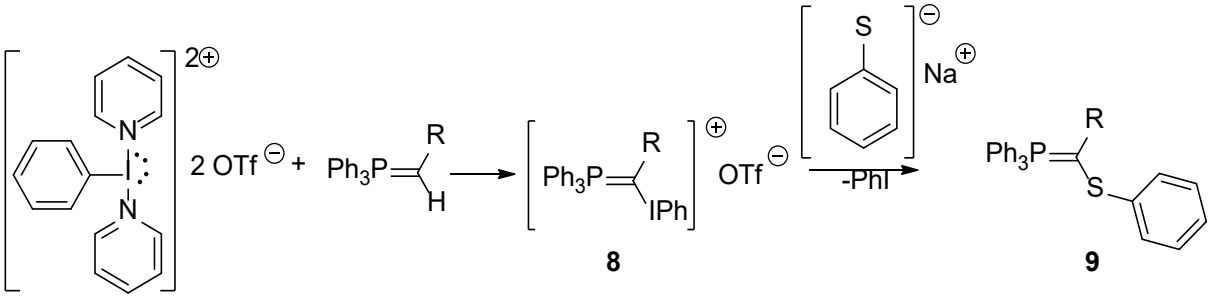
Organic reactions using Weiss' Reagents

Weiss and co-workers presented the first reported examples of reactions involving $[PhI(Pyr)_2]^{2+}$.[19] The treatment of tert-butyl diazoacetate (**5)** with $[PhI(Pyr)_2]^{2+}$ led to the formation of the diazo iodonium salt **6**, where the $[PhI]^+$ fragment behaves as an electrophilic unit. Exposure to selected nucleophiles allowed for the functionalization of the diazo α–C (Scheme 5) via displacement of PhI to form compounds **7**. The nucleofugal nature of iodine in compound **6** caused an umpolung of the expected reactivity at the α–C and resulted in nucleophilic substitution reactivity, which had not previously been observed in diazo compounds.



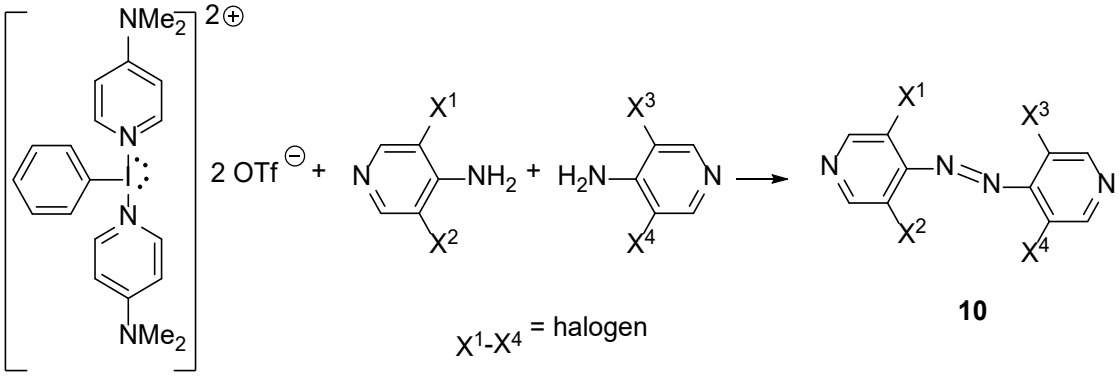
Scheme 5. Use of Weiss' Reagent to give first example of aryliodonium diazo compounds.

$[PhI(Pyr)_2]^{2+}$ was later employed by Zhadakin in the synthesis of mixed phosphoniun ylide derived phosphonium iodonium salts (Scheme 6).[20] Reactivity analogous to the diazo functionalization pathway reported by Weiss was observed. Exposure of the phosphonium iodonium cation **8** to the soft nucleophile thiophenolate resulted in the displacement of PhI and formation of thiophosphonium ylide **9**.



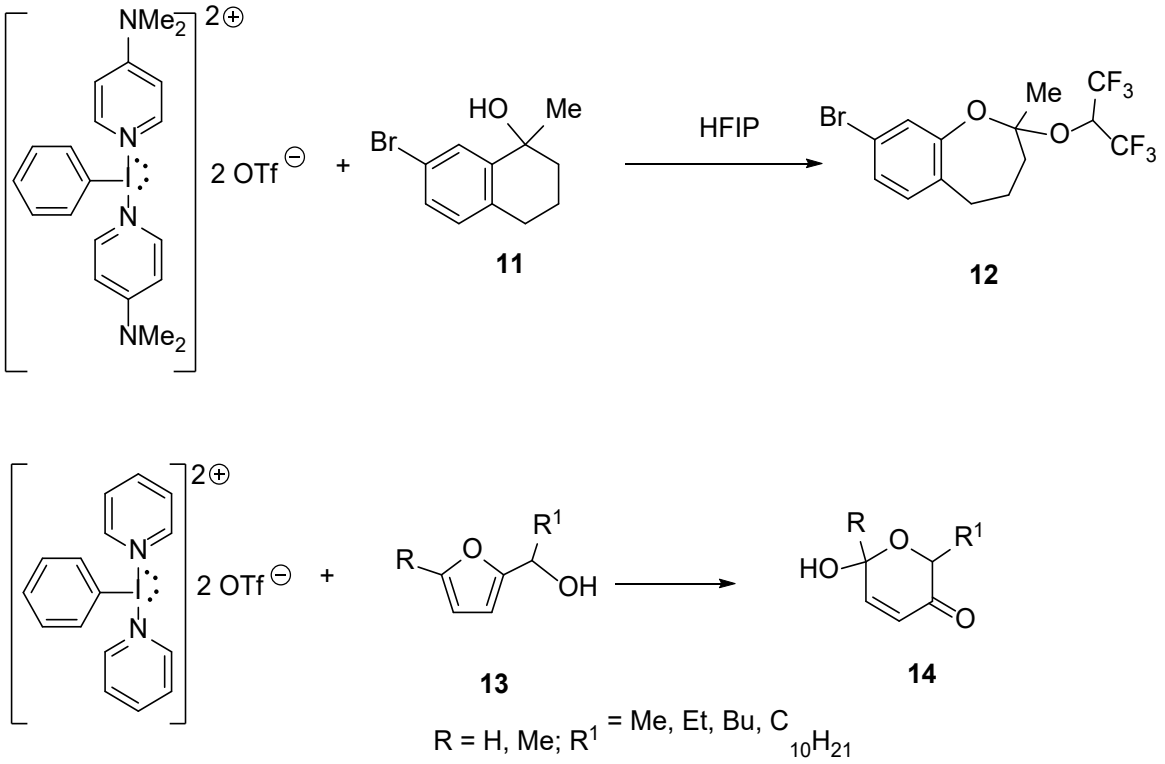
Scheme 6 Synthesis of mixed phosphonium iodonium salts *via* treatment of the corresponding phosphoniun ylide with $[PhI(Pyr)]^{2+}$.

The group of Huber identified azo-bridged bis(halopyridinium) compounds **10** as potential XB based halogen bond activators in 2012. These targets were accessed through the oxidative hetero and homo-coupling of anilines (Scheme 7) using the 4-DMAP ligated Weiss' Reagent.[21] In all examples use of the more common and less strongly oxidative coupling reagents NaOCl or $PhI(OAc)_2$ resulted in inadequate yields.



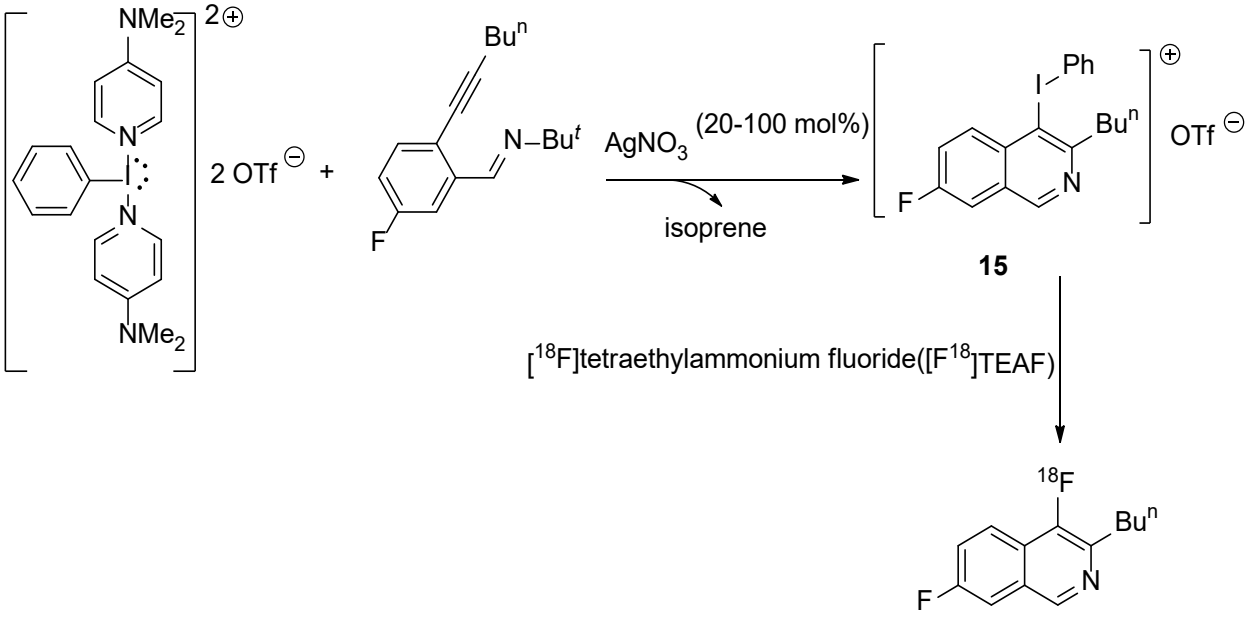
Scheme 7. 4-DMAP ligated iodine dication as competent oxidant for hetero and homo azo coupling reactions.

The 7 and 8 membered ring congeners of furans and pyrans are very common motifs within the structural architecture of natural products, however, are cumbersome to synthesize. To this end Wengryniuk employed $[PhI(Pyr)_2]^{2+}$ in the development of a protocol for the generation of medium-sized cyclic ethers via oxidative rearrangement of tertiary benzylic alcohols, i.e. **11 → 12** (Scheme 8).[11] Examples of ring expansions of furans (**13)** to yield 6 membered cyclic ethers (**14)** using Weiss' Reagent was also reported by Piancatelli shortly after Weiss' original paper.[22]



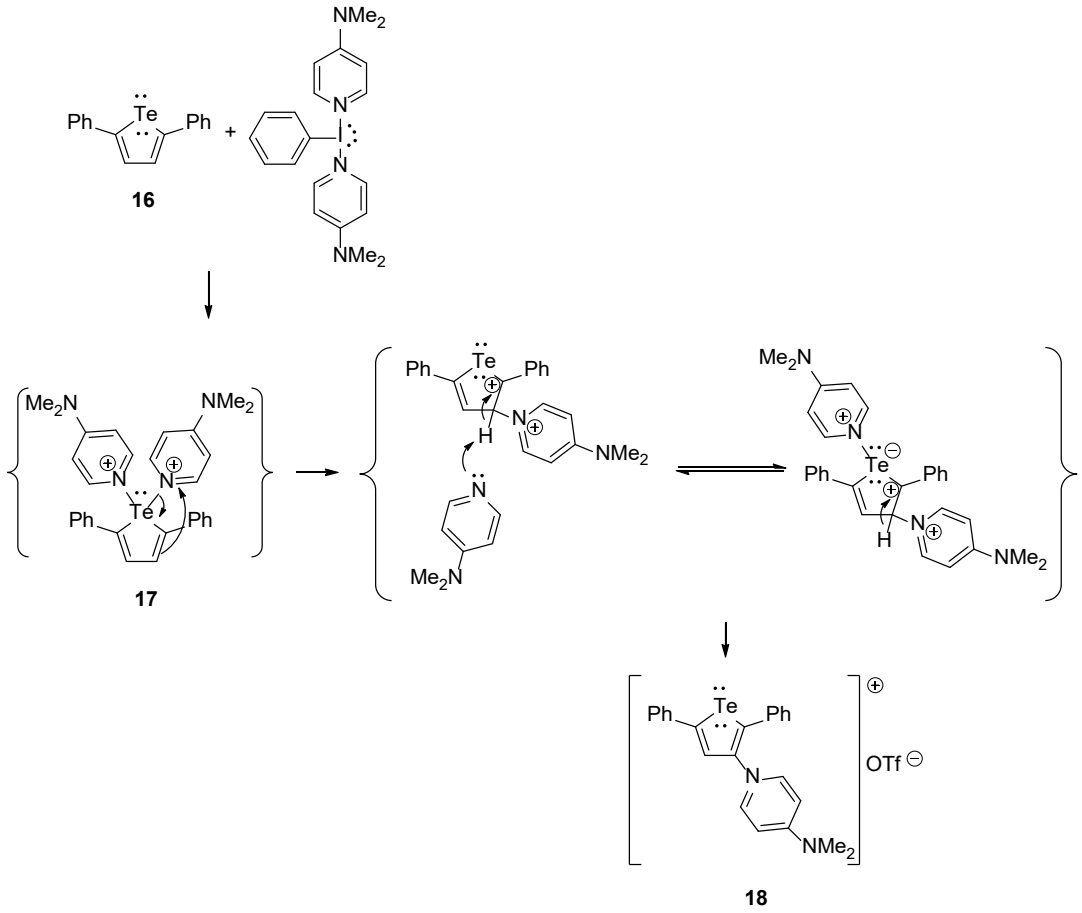
Scheme 8 Medium sized cyclic ether formation utilizing $[PhI(Pyr)_2]^{2+}$ for oxidative ring expansions

Work by Liu and Liang demonstrated the use of $[PhI(Pyr)_2]^{2+}$ in accessing labile I(III) precursors that were employed for ^{18}F radio-labeling (Scheme 9).[23] A host of [^{18}F]isoquinolines were shown to be readily accessible through the fluorination of phenyl(isoquinoline)iodonium salts (**15)**, which was achieved by exposure of the iodonium salt to the readily available [^{18}F]tetraethylammonium fluoride.



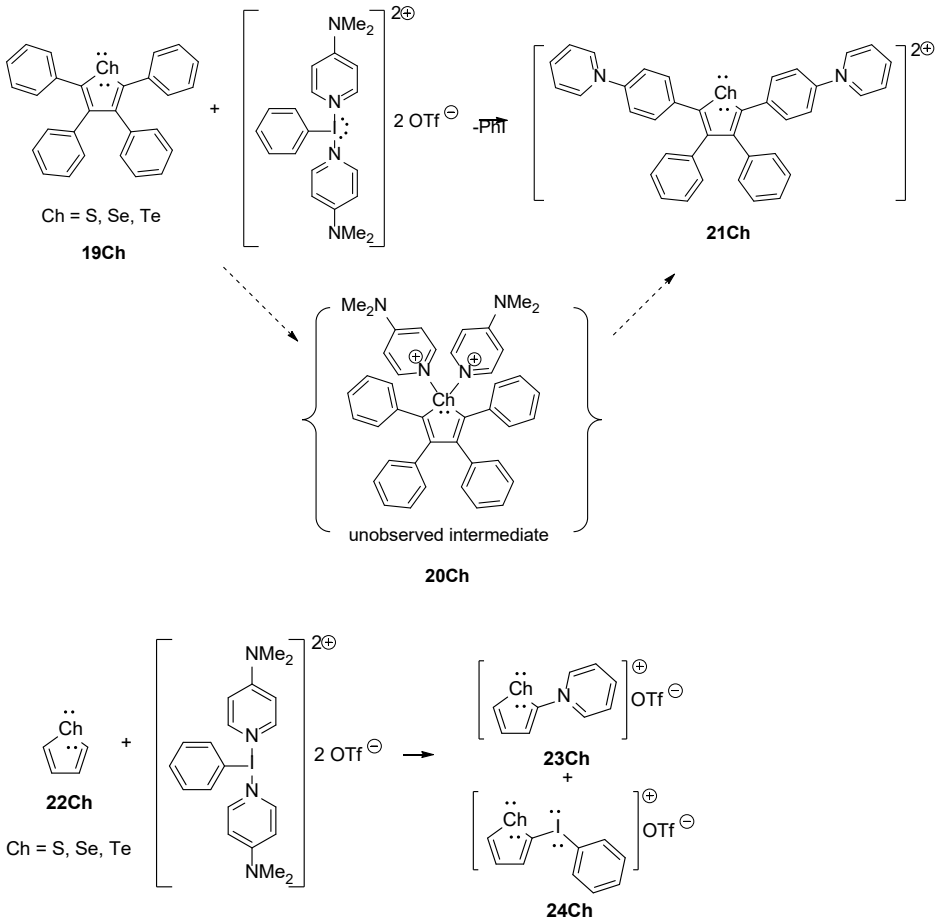
Scheme 9 Nucleophilic [^{18}F] fluorination of phenyl(isoquinoline)iodonium salts utilizing [^{18}F] TEAF as $^{18}F^-$source.

The introduction of heavier chalcogens into carbon polymers to enhance optical and electronic properties has been recently reported. Studies by Seferos and co-workers revealed that optical absorption properties of a group of small molecule tellurophenes could be tuned via redox reactivity at the tellurium center (Te(II) to Te(IV)). We identified tellurophene as an ideal candidate to test the utility of $[PhI(Pyr)_2]^{2+}$ toward main group oxidations which could possibly yield novel pyridine stalbilised dicationic Te(IV) complexes. Unexpectedly the oxidation of tellurophene **16** with $[PhI(4\text{-}DMAP)_2]^{2+}$ led to C-H activation and N-C bond forming reactivity, through a proposed Te(II)-Te(IV) pathway *via* intermediate **17** (Scheme 10).[15] This is in effect an electrophilic aromatic substitution reaction, where reduction of Te(IV) to Te(II) to achieve rearomatization results in the generation of an electrophilic N-pyridine atom, which goes on to be the substrate for substitution to yield triflate salt **18**.



Scheme 10 Proposed reaction pathway for the reaction of $[PhI(4\text{-}DMAP)_2]^{2+}$ with **16** yielding the substituted tellurophene **18**.

Follow up studies extended the scope of Weiss' Reagent to the oxidation of the lighter chalogens, however, attempts to generate Ch(IV) centers via oxidation of 2, 3, 4, 5-tetraphenylchalcogenophenes (**19Ch**) with $[PhI(4\text{-}DMAP)_2]^{2+}$ resulted in similar reactivity, however now at the 4-position of the *ortho* phenyl substituents yielding **21Ch** as the major product (Scheme 11).[24]

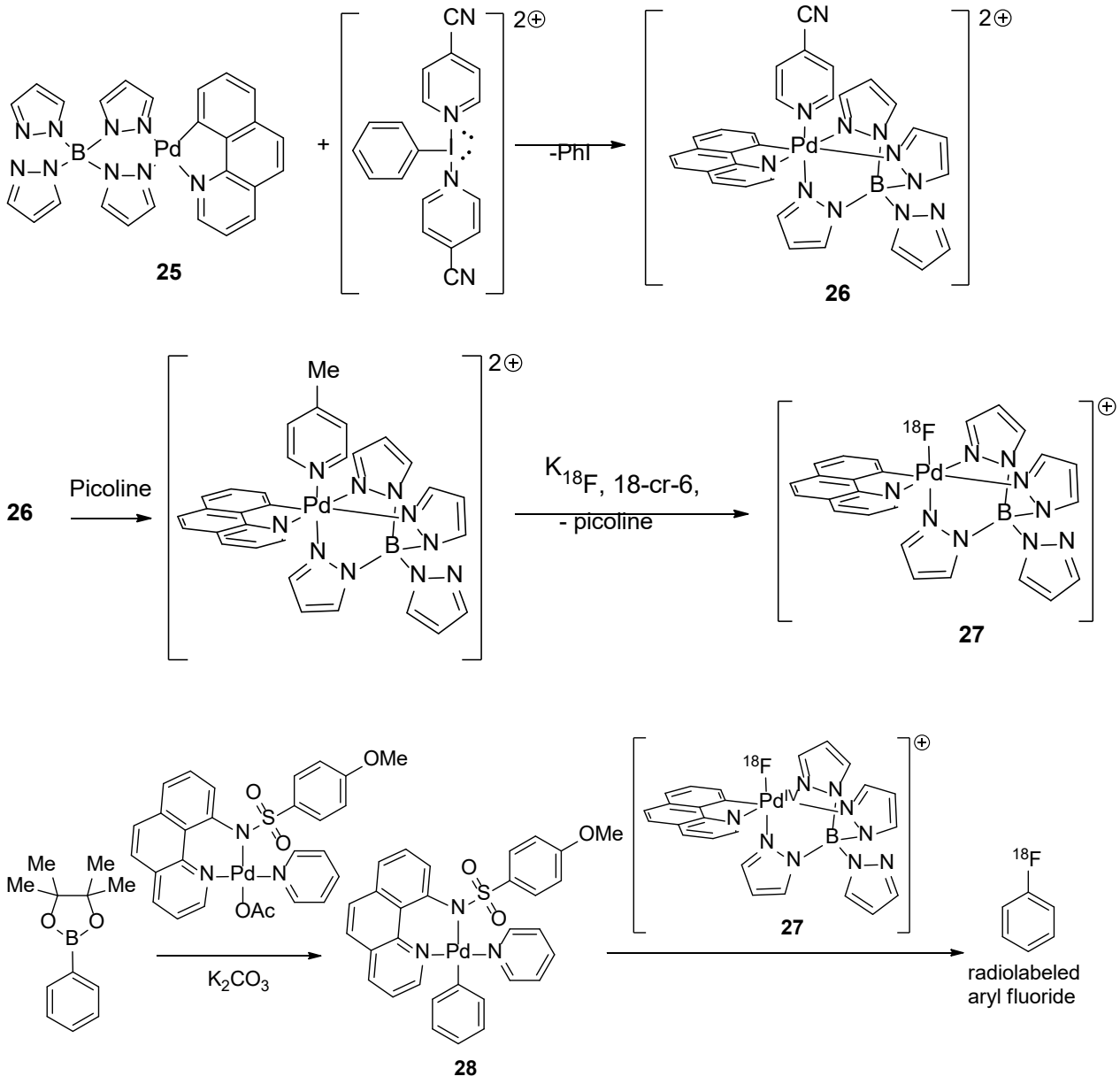


Scheme 11. Reactions of **19Ch** with $[PhI(Pyr)_2]^{2+}$ leading to electrophilic aromatic substitution of pyridine at the phenylene 4-position through a Ch(IV) intermediate **20Ch**.

Reaction of the parent thiophene (**22Te)** or selenophene (**22Se)** with $[PhI(Pyr)_2]^{2+}$ resulted in a competitive process with a mixture of **23** and **24** generated via electrophilic aromatic substitution with pyridine and –IPh as the substrates, respectively. Compound **24S** has previously been generated using Koser's reagent, [25] and could also be cleanly generated using [PhI(OAc)][OTf] as the oxidant. Compounds **23Se** and **24Se** represent novel derivatives of selenophene, again with **24Se** more cleanly synthesized using [PhI(OAc)][OTf].

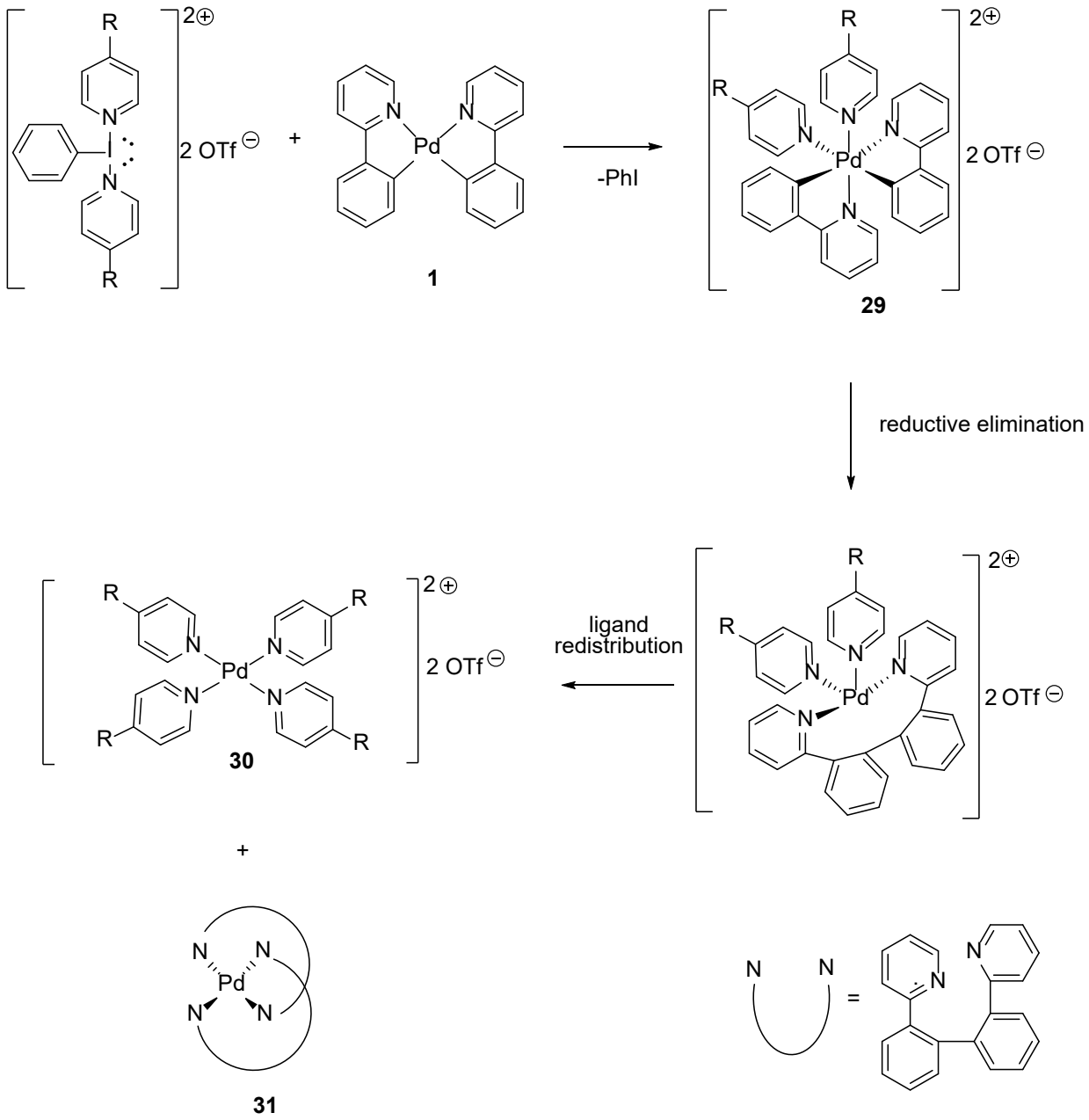
Inorganic/organometallic reaction involving Weiss' Reagents

Examples of the use of Weiss' Reagents for transition metal oxidation are still quite sparse. The first reported example was from Ritter and co-workers describing the synthesis of an isolable high valent Pd(IV) species via the oxidation of **25** with $[PhI(4\text{-}CNPyr)_2]^{2+}$ to give compound **26** (Scheme 12).[26-29] Through successive ligand exchange reactions F^- was then introduced into **26** to give access to the Pd(IV) fluoride **27**,which was subsequently utilized as an electrophilic source of fluorine for the generation a range of structurally diverse ^{18}F labelled PET imaging molecules. The fluorination of the desired organic substrate was achieved via the dual metallic Pd(II)/Pd(IV) system incorporating **27** and **28**. The selected organic substrate was introduced into the system via standard Pd(II)-boron chemistry to give **28**, with exposure to **27** yielding the desired radiolabelled aryl fluoride. One of the main motivation for conducting investigations into pyridine stabilized I(III) dicationic arises from this ability to couple delivery of neutral ligands and oxidation at that metal center allowing for the generation of highly charged metal salts with a handle for facile ligand displacement of the relatively labile pyridine ligands.



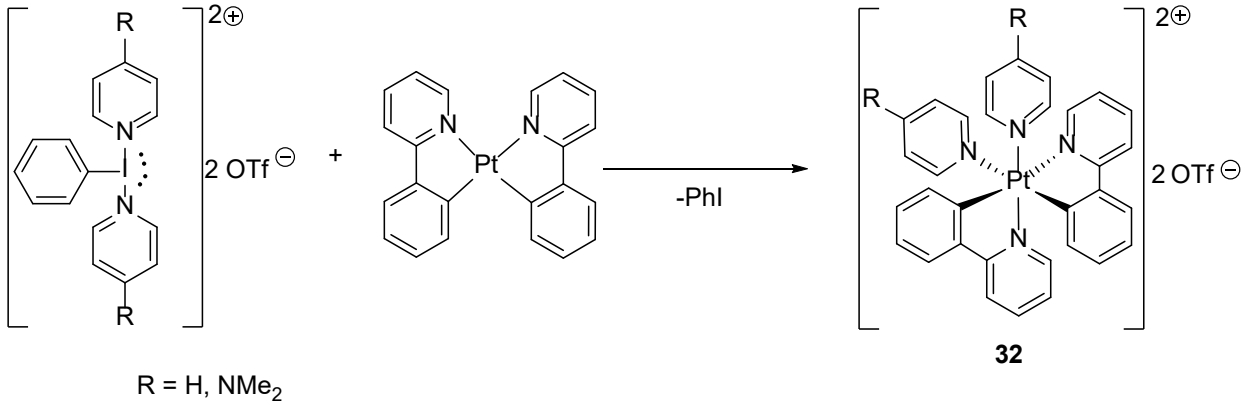
Scheme 12. Electrophilc late stage ^{18}F fluorinations via the high valent Pd(IV) fluoride compound **27**.

Our group investigated the use of the Weiss' Reagents for accessing a range of high valent Pd(IV) and Pt(IV) complexes.[30] The oxidation of **1** with $[PhI(4\text{-}DMAP)_2]^{2+}$ gave well defined Pd(II) complexes **30** and **31**, which were rationalised as forming *via* a Pd(IV)-Pd(II) reductive elimination pathway from compound **29** (Scheme 13).



Scheme 13 Reaction of $[PhI(4\text{-}DMAP)_2]^{2+}$ with the bis 2-phenylpyridine ligated **1** and proposed pathway for the formation of compounds **30** and compounds **31**.

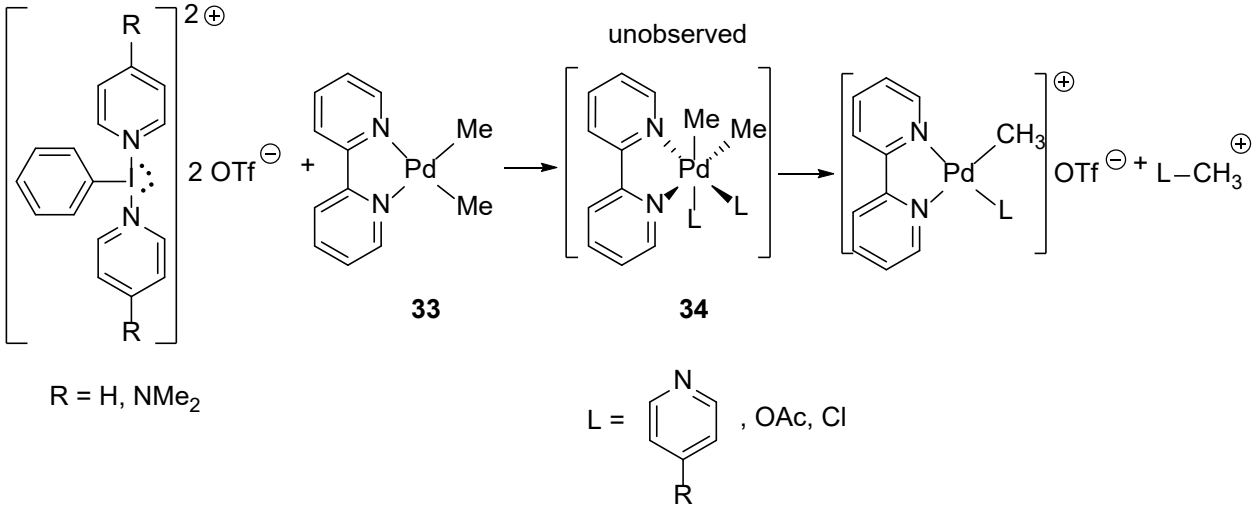
The oxidation of the Pt analogue of **1** using the 4-DMAP ligated Weiss' Reagent was shown to give to give isolable Pt(IV) dication **32** (Scheme 14), which displayed the added stability at the higher oxidation state afforded from descending the group 10 triad.



Scheme 14 Synthesis of Pt(IV) complex **32**.

Oxidations involving the reaction of Pd(II) complex **33** with $[PhI(4\text{-}DMAP)_2]^{2+}$ or $[PhI(Pyr)_2]^{2+}$ also gave no isolatable Pd(IV) species, however, the generation of the respective N-methyl pyridinium cations as the major product from both reactions supported a C-N bond forming reductive process occurring through high the valent Pd(IV) intermediate **34** (Scheme 15). Identical reactions were also conducted on **33** using either $PhICl_2$ or $PhI(OAc)_2$. In both cases methylation of the ligand (Cl or OAc) yielding either $ClCH_3$ or MeOAc as the major product from the reaction of **33** with $PhICl_2$ or $PhI(OAc)_2$, respectively. Ethane elimination was also identified as a minor competing pathway *via* ^{1}H NMR analysis, however computational analysis indicated ethane elimination as the thermodynamically favorable pathway. The formation of $[Me\text{-}Pyr]^+$ was calculated to be more favorable than MeCl or MeOAc. Similar studies conducted on the Pt(II) analogue of **33** gave a less well-defined product distribution most likely as a result of disproportionation.

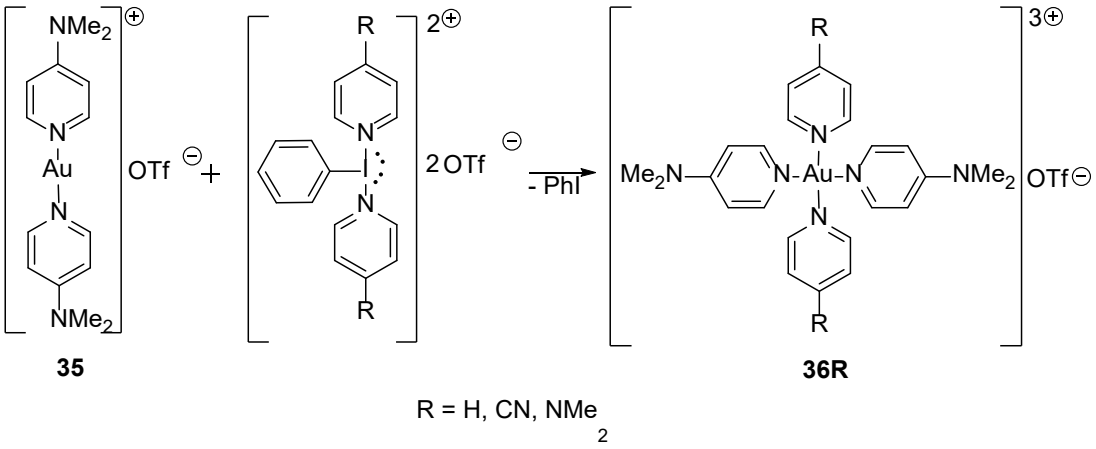
As previously discussed, the reaction of I(III) reagent $PhICl_2$ or $PhI(OAc)_2$ with **1** reported by Sanford gave isolable Pd(IV) complexes **2Cl** or **2OAc**, respectively, whereas the analogous reaction of $[PhI(4\text{-}DMAP)_2]^{2+}$ with **1** did not yield any observable Pd(IV) species This indicated that neutral pyridine ligands provide poor kinetic and thermodynamic stability at Pd(IV) centers.



Scheme 15 Oxidative products from the reaction of the pyridine and the 4-DMAP ligated Weiss' Reagent with Pt(II) compound **33**.

Recently, the Au(I)/Au(III) redox manifold has seen increasing use in catalysis,[31] however, the oxidative addition reactions commonly required in late transition metal catalysis[32] are typically inaccessible for Au(I)/Au(III) systems in the absence of forcing conditions. To circumvent this, exogenous oxidants including hypervalent iodine reagents such as $PhI(OAc)_2$ or $PhICl_2$ have been employed.[33-40] I(III) reagents have also been used to access a range of novel Au(III) coordination complexes.[41-46] We demonstrated the utility of the Weiss' Reagents as a halide-free oxidizing agents for the synthesis and characterization of tricationic Au(III) coordination complexes.[47] Initial investigations involved the oxidation of two

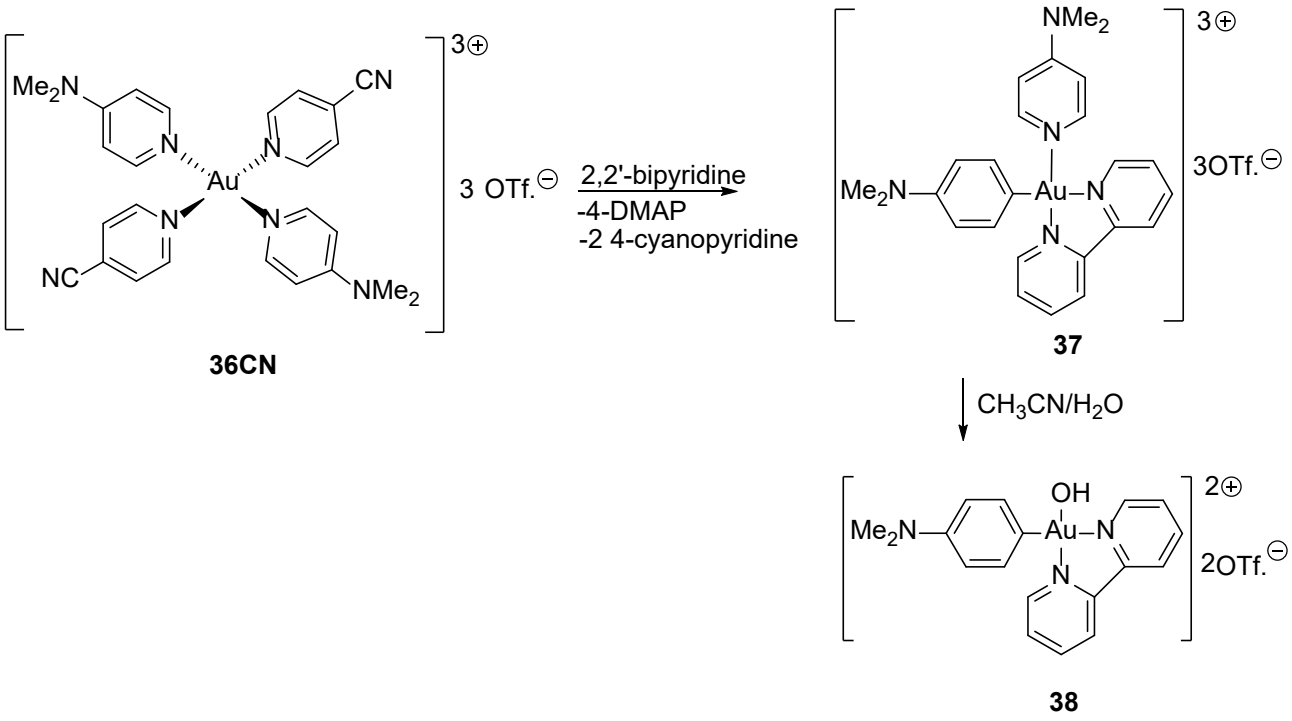
NHCAu(III)Cl based scaffolds with the $[PhI(4\text{-}DMAP)_2]^{2+}$ cation. These reactions gave a complex mixture of identifiable Au(III) compounds that in our hands were inseparable. The varied product distribution of these reactions was reasoned to arise from ligand scrambling at the Au(III) centers. Evidence of ligand/anion scrambling with other I(III)/Au redox couples has been reported.[38,48] To suppress any unwanted ligand redistribution reactions, the NHCAu(I)Cl scaffold was replaced with the homoleptic Au(I) cation **35**. In the reaction of **35** with $[PhI(L)_2]^{2+}$ (L = 4-DMAP, Pyr, 4-CNPyr), the homoleptic and pseudo-homoleptic tricationic Au(III) compounds **36R** were generated in high yield and purity (Scheme 16).



Scheme 16 First example of a tricationic Au(III) coordination complex supported by a monodentate ligand system.

The successful isolation and characterization of compounds **36R** represented the first example of tricationic Au(III) complexes supported by a neutral monodentate ligand system. In the example of **36CN**, the labile nature of the 4-cyanopyridine ligands allowed for the introduction of chelating ligand systems including 2,2'-bipyridine (**37**) through facile ligand exchange reactions. Initial investigations into the reactivity **37** revealed interesting reactivity toward water. Exposure of **37** to wet CH_3CN resulted in the formation of the rare Au(III)-OH

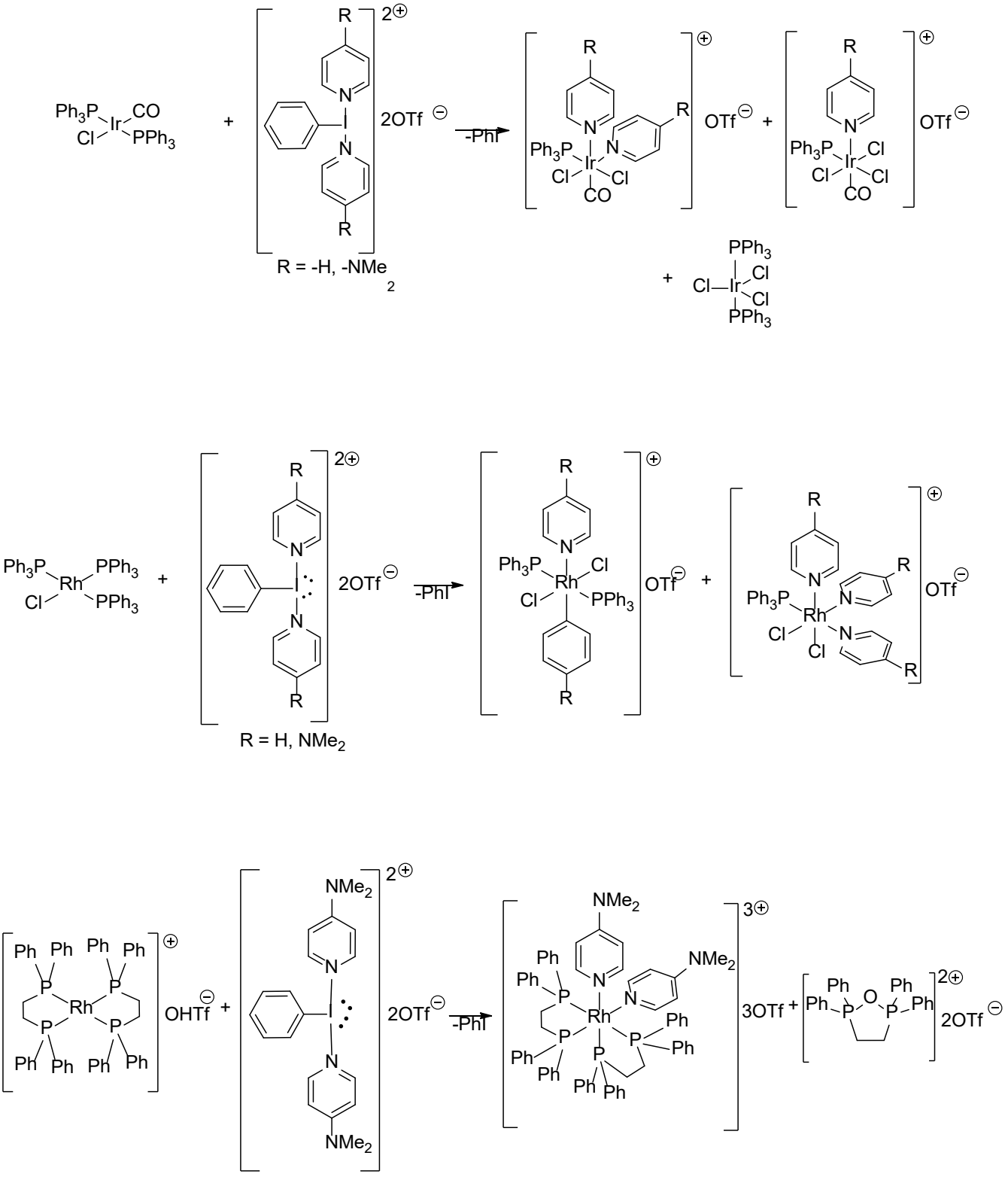
binding motif in dication **38** (Scheme 17). [49] The generation of **38** through simple aquo reactivity differs markedly from the generally employed synthetic approach for Au(III)-OH formation which relies on alkali metal or silver salt metathesis reactivity at a Au(III) chloride.[50-53]



Scheme 17 Ligand exchange reactivity at and facile formation of Au(III)-OH (**38**) *via* the exposure of **37** to water.

As was previously discussed, triphenylphosphine was shown to oxidize during attempted ligand exchange reactions with $[PhI(4\text{-}DMAP)_2]^{2+}$. Based on these results subsequent reactivity studies involving $[PhI(Pyr)_2]^{2+}$ in our lab have been confined to non-phosphine containing systems. Recently the reactions of a number of phosphine-containing Ir(I) and Rh(I) complexes with selected I(III) reagents including $[PhI(4\text{-}DMAP)_2]^{2+}$ were reported by us.[54] The outcomes for reactions involving 4-DMAP ligated Weiss' Reagent are shown in

Scheme 17. In all these examples complex product distributions arose from the occurrence of ligand and anion scrambling, which has also been reported for other organometallic systems employing I(III) oxidants, and seems to be dependent on the presence of chloride as either ligand or counter-ion.[38,48] No evidence of direct phosphine oxidation was observed in reactions involving complexes containing monodentate or chelating phosphine ligand architectures demonstrating the compatibility of metal bound phosphine ligands with Weiss' Reagent.



Scheme 18 Reactions of selected phosphine-containing Ir(I) and Rh(I) complexes with Weiss' Reagents.

Conclusion

There is now a growing number of examples demonstrating the use of pyridine ligated I(III) dications as diverse oxidizing agents. The ability of $[PhI(Pyr)_2]^{2+}$ to couple oxidation with neutral ligand delivery allows for the generation of a range of novel and synthetically interesting high oxidation state transition metal complexes. The generation of a high valent Pd(IV) complex *via* oxidations with $[PhI(4—CNPyr)_2]^{2+}$ allowed for the development of a late-stage ^{18}F fluorination protocol. The reaction of $[PhI(4\text{-}DMAP)_2]^{2+}$ with the homoleptic Au(I) cation $[Au(I)(4\text{-}DMAP)_2]^{+}$ gave rise to the first reported example of homoleptic Au(III) trications bound by a only by monodentate ligands. The formation of the electrophilic $[PhI]^{+}$ fragment is also important when describing the reaction patterns of $[PhI(Pyr)_2]^{2+}$. The formation of new C-I bonds within the reaction substrates of $[PhI(Pyr)_2]^{2+}$ allowed for the isolation of monocation iodonium salts as both major or minor products. In certain circumstances exposure of the isolated iodonium monocations resulted in nucleophilic substitution reactivity allowing for C-H functionalization.

Reference

1.Willgerodt, C., *Berichte der deutschen chemischen Gesellschaft* **1892,** *25* (2), 3494-3502.
2.Zhao, X.-F.; Zhang, C., *Synthesis* **2007,** *2007*, 551-557.
3.Hickman, A. J.; Sanford, M. S., *Nature* **2012,** *484*, 177-185.
4.Whitfield, S. R.; Sanford, M. S., *J Am Chem Soc* **2007,** *129*, 15142-15143.
5.Racowski, J. M.; Dick, A. R.; Sanford, M. S., *J Am Chem Soc* **2009,** *131*, 10974-10983.
6.Sousa e Silva, F.; Tierno, A.; Wengryniuk, S., *Molecules* **2017,** *22*, 780.
7.Yoshimura, A.; Zhdankin, V. V., *Chem Rev* **2016,** *116*, 3328-3435.
8.Pell, T. P.; Couchman, S. A.; Ibrahim, S.; Wilson, D. J. D.; Smith, B. J.; Barnard, P. J.; Dutton, J. L., *Inorg Chem* **2012,** *51*, 13034-13040.
9.Weiss, R.; Seubert, J., *Angew Chem Int Ed* **1994,** *33*, 891-893.
10.Georgiou, D. C.; Butler, P.; Browne, E. C.; Wilson, D. J. D.; Dutton, J. L., *Aust J Chem* **2013,** *66* , 1179-1188.
11.Kelley, B. T.; Walters, J. C.; Wengryniuk, S. E., *Org Lett* **2016,** *18*, 1896-1899.
12. a) Zhdankin, V. V.; Koposov, A. Y.; Yashin, N. V., *Tetrahedron Lett.* **2002,** *43*, 5735-5737, b) Shaw, A. J. M.; Corbo, R.; Wilson, D. J. D.; Dutton, J. L., *Dalton Trans* **2015,** *44*, 15083-15087.

13.Lin, S.; Li, M.; Dong, Z.; Liang, F.; Zhang, J., *Org Biomol Chem* **2014,** *12*, 1341-1350.
14.Kang, I.-J.; Wang, H.-M.; Lin, M.-L.; Chen, L.-C., *J Chin Chem Soc* **2002,** *49*, 1031-1034.
15.Aprile, A.; Iversen, K. J.; Wilson, D. J. D.; Dutton, J. L., *Inorg Chem* **2015,** *54*, 4934-4939.

16.Izquierdo, S.; Essafi, S.; del Rosal, I.; Vidossich, P.; Pleixats, R.; Vallribera, A.; Ujaque, G.; Lledós, A.; Shafir, A., *J Am Chem Soc* **2016,** *138*, 12747-12750.
17.Pirkuliyev, N. S.; Brel', V. K.; Zhdankin, V. V.; Zefirov, N. S., *Russ J Org Chem* **2002,** *38*, 1224-1225.
18. Weigand, J. J.; Burford, N.; Decken, A.; Schulz, A. Eur. J. Inorg. Chem. 2007, 4868−4872
19.Weiss, R.; Seubert, J.; Hampel, F., *Angew Chem* **1994,** *106*, 2038-2039.
20.Zhdankin, V. V.; Maydanovych, O.; Herschbach, J.; Bruno, J.; Matveeva, E. D.; Zefirov, N. S., *J Org Chem* **2003,** *68*, 1018-1023.
21.Kniep, F.; Walter, S. M.; Herdtweck, E.; Huber, S. M., *Chem Eur J* **2012,** *18*, 1306-1310.
22.De Mico, A.; Margarita, R.; Piancatelli, G., *Gazz Chim Ital* **1995,** *125*, 325.
23.Yuan, Z.; Cheng, R.; Chen, P.; Liu, G.; Liang, S. H., *Angew Chem Int Ed* **2016,** *55*, 11882-11886.
24.Egalahewa, S.; Albayer, M.; Aprile, A.; Dutton, J. L., *Inorg Chem* **2017,** *56*, 1282-1288.
25.Ito, M.; Ogawa, C.; Yamaoka, N.; Fujioka, H.; Dohi, T.; Kita, Y., *Molecules* **2010,** *15*, 1918.
26.Lee, E.; Kamlet, A. S.; Powers, D. C.; Neumann, C. N.; Boursalian, G. B.; Furuya, T.; Choi, D. C.; Hooker, J. M.; Ritter, T., *Science* **2011,** *334*, 639-642.
27.Brandt, J. R.; Lee, E.; Boursalian, G. B.; Ritter, T., *Chem Sci* **2014,** *5*, 169-179.
28.Kamlet, A. S.; Neumann, C. N.; Lee, E.; Carlin, S. M.; Moseley, C. K.; Stephenson, N.; Hooker, J. M.; Ritter, T., *PLOS ONE* **2013,** *8*, e59187.
29.Campbell, M. G.; Ritter, T., *Organic Process Research & Development* **2014,** *18*, 474-480.
30.Corbo, R.; Georgiou, D. C.; Wilson, D. J. D.; Dutton, J. L., *Inorg Chem* **2014,** *53*, 1690-1698.
31.Schmidbaur, H.; Schler, A., *Arab J. Sci. Eng.* **2012,** *37*, 1187-1225.
32.Labinger, J. A.; Bercaw, J. E., *Nature* **2002,** *417*, 507-514.
33.Brand, J. P.; Li, Y.; Waser, J., *Isr J Chem* **2013,** *53*, 901-910.
34.Brand, J. P.; Waser, J., *Angew Chem Int Ed* **2010,** *49*, 7304-7307.
35.Brand, J. P.; Charpentier, J.; Waser, J., *Angew Chem Int Ed* **2009,** *48*, 9346-9349.
36.Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A., *Science* **2012,** *337*, 544-548.
37.Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A., *J Am Chem Soc* **2014,** *136*, 254-264.
38.Hofer, M.; Nevado, C., *Tetrahedron* **2013,** *69*, 5751-5757.
39.Qiu, D.; Zheng, Z.; Mo, F.; Xiao, Q.; Tian, Y.; Zhang, Y.; Wang, J., *Org Lett* **2011,** *13*, 4988-4991.
40.Li, Z.; Ding, X.; He, C., *J Org Chem* **2006,** *71*, 5876-5880.
41.Orbisaglia, S.; Jacques, B.; Braunstein, P.; Hueber, D.; Pale, P.; Blanc, A.; Fremont, P., *Organometallics* **2013,** *32*, 4153-4164.
42.Jacques, B.; Hueber, D.; Hameury, S.; Braunstein, P.; Pale, P.; Blanc, A.; de Frémont, P., *Organometallics* **2014,** *33*, 2326-2335.
43.Blaya, M.; Bautista, D.; Gil-Rubio, J.; Vicente, J., *Organometallics* **2014,** *33*, 6358-6368.
44.Ghidiu, M. J.; Pistner, A. J.; Yap, G. P. A.; Lutterman, D. A.; Rosenthal, J., *Organometallics* **2013,** *32* , 5026-5029.
45.Huynh, H. V.; Guo, S.; Wu, W., *Organometallics* **2013,** *32*, 4591-4600.
46.Romanov, A. S.; Bochmann, M., *Organometallics* **2015,** *34*, 2439-2454.
47.Corbo, R.; Pell, T. P.; Stringer, B. D.; Hogan, C. F.; Wilson, D. J. D.; Barnard, P. J.; Dutton, J. L., *J Am Chem Soc* **2014,** *136*, 12415-12421.
48.Hofer, M.; Nevado, C., *Eur J Inorg Chem* **2012**, 1338-1341.
49.Corbo, R.; Ryan, G. F.; Haghighatbin, M. A.; Hogan, C. F.; Wilson, D. J. D.; Hulett, M. D.; Barnard, P. J.; Dutton, J. L., *Inorg Chem* **2016,** *55*, 2830-2839.
50.Cinellu, Maria A.; Minghetti, G.; Pinna, Maria V.; Stoccoro, S.; Zucca, A.; Manassero, M., *Eur J Inorg Chem* **2003**, 2304-2310.
51.Agostina Cinellu, M.; Minghetti, G.; Vittoria Pinna, M.; Stoccoro, S.; Zucca, A.; Manassero, M.; Sansoni, M., *J Chem Soc, Dalton Trans* **1998**, 1735-1742.
52.Cocco, F.; Cinellu, M. A.; Minghetti, G.; Zucca, A.; Stoccoro, S.; Maiore, L.; Manassero, M., *Organometallics* **2010,** *29*, 1064-1066.
53.Rosca, D.; Smith, D. A.; Bochmann, M., *Chem Commun* **2012,** *48*, 7247-7249.
54.Albayer, M.; Dutton, J. L., *Aust J Chem* **2017**, Early View. DOI 10.1071/CH17173