

Organometallic chemistry

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The literature from the organometallic arena appearing in 2012 is reviewed, and a selection of reports is assembled; the uses of organometallic compounds in synthesis and for electronic and energy applications are included.

Electroluminescence

Application to electroluminescence continues to be a very active field of research for organometallic materials. Indeed the heavy atom effect allows for efficient phosphorescence, enabling up to 100% internal efficiency in electroluminescent devices.

A particular area of interest is the search for improved blue emitters. Due to their ease of synthesis, derivatives of bis[2-(4,6-difluorophenyl)pyridinato- C^2,N]-picolinato)iridium(III) (FIrPic) are commonly studied, both to understand further the properties of such materials and for use as an emitting dopant in electroluminescent devices. A systematic study of the substituent effect of the ancillary ligand on the luminescence FIrPic was reported.¹ It was shown that substituents on a picolinate ancillary ligand of complexes **1**–**3**, have virtually no influence on the emission maxima whilst substituents on a quinoline-carboxylate show a significant influence (**4**: 532 nm; **5**: 566 nm; **6** and **7** are non-emissive). The results are explained by the difference in the emitting excited state, which is mainly determined by the ancillary ligand in the case of quinoline-carboxylate. Another systematic study looked at the variation of the halogen substituent on the main ligand of complexes **8**–**11**.² For the first time, in this study both *meta* and *para* Hammett constants have been taken into account to rationalise the change in emission maximum.

Another approach to modifying FIrPic is to graft additional substituents on the main ligand. In particular the position between the two fluorines is attractive to further blue-shift the emission maximum by using strong acceptor substituents. Complex **12** emits at 463 nm compared with FIrPic at 470 nm and complex **13** has a maximum emission at 459 nm, but the trifluoromethyl ketone groups lead to non radiative low-lying excited states, which quench significantly the emission.³ Similarly, complex **14** has an additional sulfonyl substituent and **15** a phosphoryl

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substituent between the two fluorines of FirPic; the emission maxima are 459 and 460 nm, respectively, with good emission quantum yields (PLQY) around 50%.⁴ Interestingly, complex **15** was used to prepare a white OLED (organic light emitting diode) delivering a maximum current efficiency of 25 cd A⁻¹, and a maximum external quantum efficiency (EQE) of 15%.⁴ Complex **16** retains the global *trans*-geometry of FirPic, but the use of 2,3'-bipyridine as the main ligand, combined with the bulky *tert*-butyl groups and pyridine–pyrazole ancillary ligand, leads to deep-blue emission at 440 nm and reduced aggregation. These features are particularly suitable for electroluminescence and deep-blue electroluminescence is observed with CIE coordinates (0.159, 0.185) (Fig. 1).⁵

Besides particular efforts on blue emitters, other colours still attract significant research aimed at improving further the efficiency of the relevant materials.

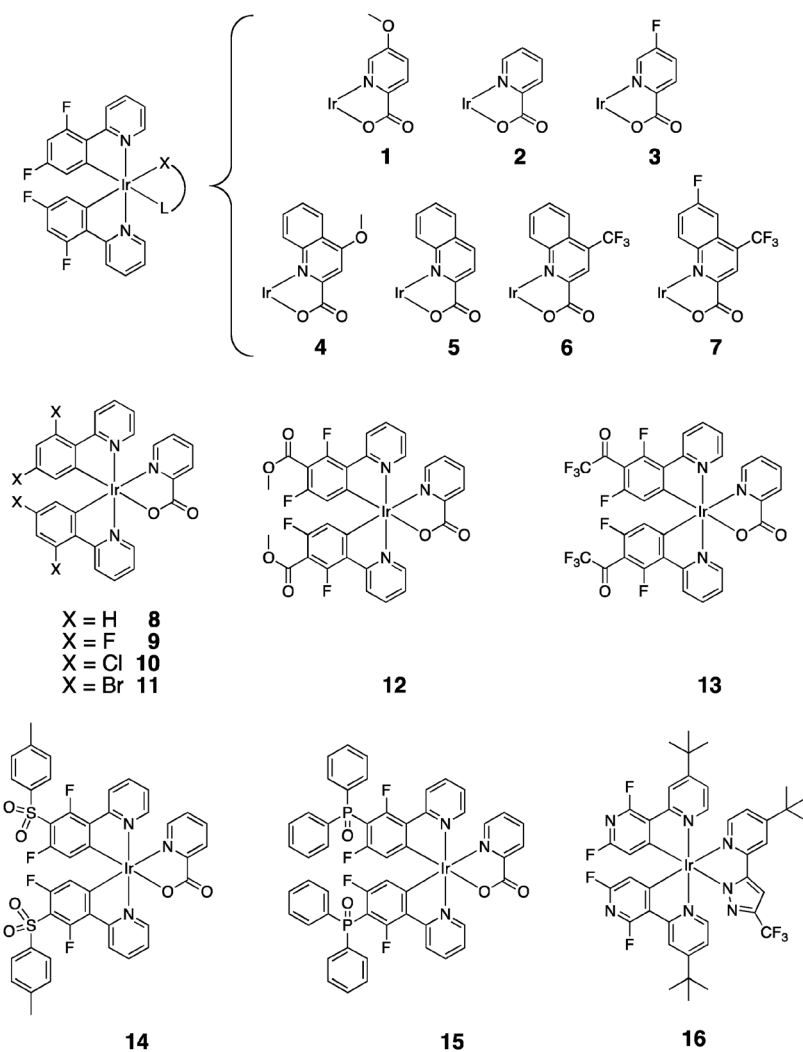


Fig. 1 IrPic-like complexes **1**–**15** and complex **16**.

The series of complexes based on **17**, where R^1 and R^2 are various aromatic or aliphatic substituents, uses a substituted guanidinate ancillary ligand.⁶ The resulting complexes emit in the green to orange region of the visible spectrum and have current efficiencies above 100 cd A^{-1} . Two series of complexes **18** and **19** contain a carbazole as orthometallated unit,⁷ and it was shown that complexes of series **18** are blue shifted compared with those of series **19**. Furthermore, simple devices could be made of only a single spin-coated layer, and despite the simplicity of the architecture, efficiencies typical of multilayer architectures were obtained.⁷ Complexes with ligands based on the benzothiazole unit are particularly suitable for orange emission,^{8,9} and complex **20**, along with its tris-cyclometallated analogues **21–24**, contains a naphthalenylphenylamino unit as a hole transporting group. Solution processed devices with CIE coordinates (0.60, 0.40) were obtained using **20**.⁸ Charged complexes **25** and **26** have been used as dopants in a PVK:PBD matrix to prepare devices with an emission maximum above 700 nm (Fig. 2).¹⁰

Besides the standard bis-cyclometallated iridium complexes, other types of materials are being explored for OLEDs. Bryce and coworkers have prepared chloro-bridged and isocyanato-bridged iridium dimers such as **27** and have shown that they are surprisingly good emitters with PLQY values ranging from 20 to about 40%; they are useful for preparing orange emitting solution processed devices.¹¹ A neutral complex with mixed ligands based on a terdentate bis-benzothiazole,

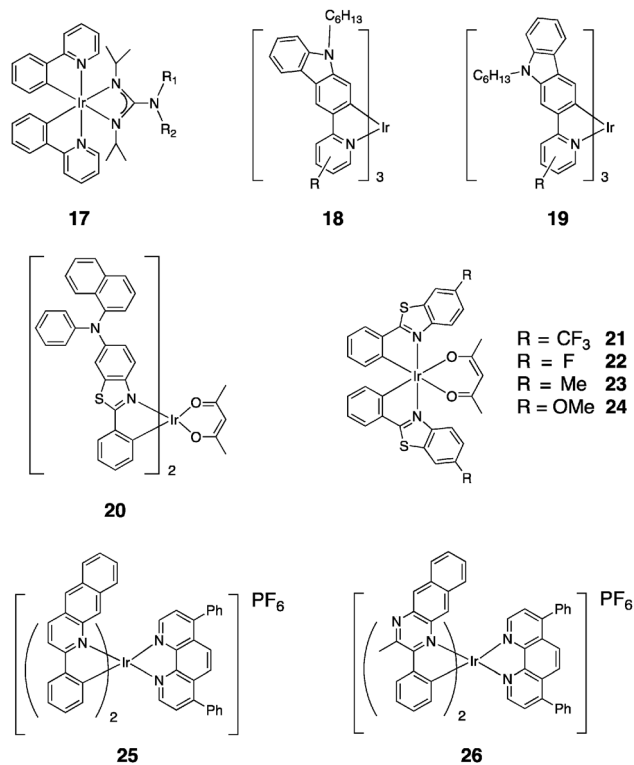


Fig. 2 Complexes 17–26.

a bidentate phenyl-pyridine and a monodentate chloride, complex **28**, was reported to have a PLQY of 89% in dichloromethane solution and to be suitable for orange OLEDs with an EQE > 10%.¹² Williams and co-worker also reported a series of complexes based on the same terdentate/bidentate/monodentate ligand architecture, using a bis-pyridinephenyl as the terdentate ligand, complexes **29–31**.¹³ Using a combination of acceptor substituents, they could tune the emission from greenish-blue to red with PLQY values of up to 71% in solution and 95% in PMMA film. Use of square-planar cyclometallated platinum complexes has been shown to offer an interesting alternative to use of octahedral iridium complexes for OLEDs. A platinum complex **32** based on a C[^]N[^]C terdentate ligand¹⁴ and another **33** based on a dimethylboron substituted N[^]C[^]N terdentate ligand¹⁵ were reported to show emission in the orange and bluish-green regions of the visible spectrum, respectively (Fig. 3).

Light-emitting electrochemical cells (LECs) are a promising low-cost alternative to OLEDs. Due to significant progress in performance in recent years, this technology is now attracting considerable interest and aspects were well reviewed in 2012.¹⁶ The tris-heteroleptic complex **34**¹⁷ was prepared,¹⁸ and was used as a green emitter in LECs resulting in the best performing device for this part of the visible spectrum with luminance > 1000 cd m², EQE of 3%, and lifetime of 55 hours.¹⁷ Generally charged bis-cyclometallated iridium(III) complexes for LECs are based on a neutral N[^]N ancillary ligand such as bipyridine or phenanthroline, but this approach limits the potential for tuning the emission towards the blue. Non-chromophoric pyridine-carbene ligands have been used to overcome this bottleneck, with complex **35** emitting greenish-blue and **36** emitting below

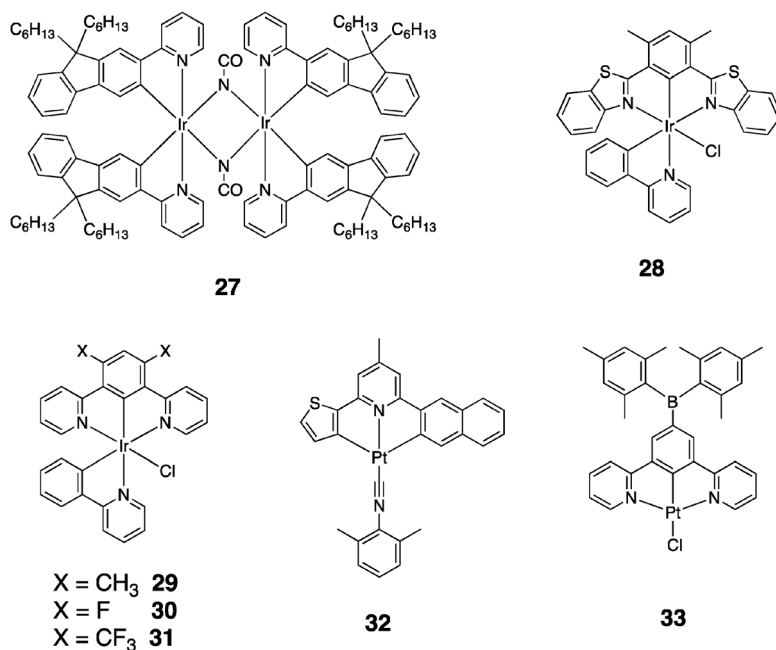


Fig. 3 Complexes **27–33**.

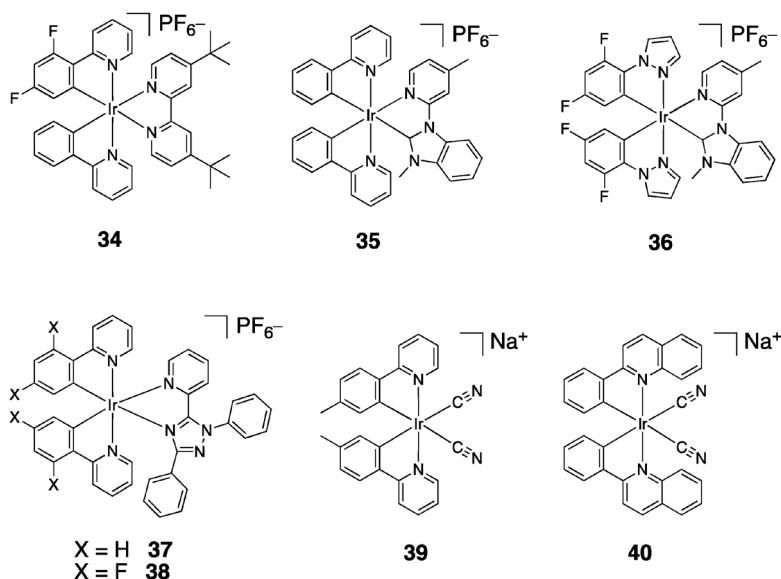


Fig. 4 Charged complexes 34–40.

400 nm at low temperature.¹⁹ Whilst displaying low PLQY in solution, this family of complexes has been found to be suitable for LECs.¹⁹ Following on previous reports of intramolecular π -stacking as a mean to improve stability of LECs, Liao and coworkers reported complexes **37** and **38** having a pyridine–pyrazole bidentate ligand with a pendant phenyl involved in intramolecular π -stacking.²⁰ Finally, the use as emissive material in LECs of anionic emitters **39** and **40** has been reported.²¹ Unfortunately, due to the lack of bulky substituents to prevent self-quenching and the difficulty of injecting electrons into the LUMO, performances are low (Fig. 4).

Sensing, bioimaging, and drugs

Transition metal complexes for sensing have been reviewed.²² Interestingly, hybrid materials based on upconversion nanophosphors modified by a cyclometallated iridium complex have been used to detect cyanide anions in water.²³ Complex **41** has been reported as a lab-on-a-molecule for sensing simultaneously cyanide and fluoride in aqueous solution.²⁴ The principle is based on a two-channel detection: first phosphorescence to sense cyanide, which displaces the ancillary ligand, and second electrochemiluminescence, which allows the detection of fluoride. The green emitter **42** becomes an orange emitter upon chromium(III) binding to the bis(2-(2-(methylthio)ethylthio)ethyl)amino receptor.²⁵ Following this, an intramolecular oxidative cleavage of the receptor slowly converts the orange emitter to a new green emitter. This unique sequence of events allows for the selective and accurate sensing of chromium(III) ion in the presence of other metal ions.²⁵ Complex **43** is made of a fluorescent part non-sensitive to the presence of oxygen and a phosphorescent part sensitive to the presence of oxygen; this enables the ratiometric sensing of oxygen.²⁶

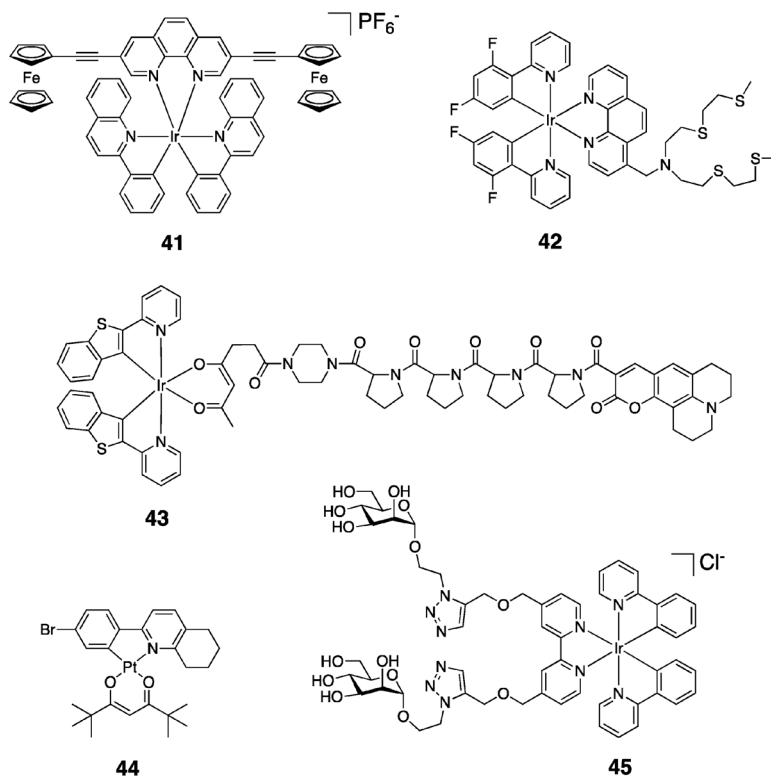


Fig. 5 Complexes 41–45.

Complexes 12 and 13, mentioned earlier, have also been used in combination with a nanostructured solid support to achieve highly sensitive oxygen sensing.³ Complexes similar to 44 have been investigated and are reported to have emissions surprisingly insensitive to the presence of oxygen; as for 44 itself the lifetime of its excited state displays significant temperature dependence around room-temperature.²⁷ The complex 45 bearing mannose groups has been used to sense concanavalin A (Fig. 5).²⁸

Organometallic complexes are also used for bioimaging and as drugs.²⁹ In particular, highly phosphorescent materials are particularly suitable for bioimaging and the field has been thoroughly reviewed in 2012.³⁰ Some specific examples of interest are given below. Complex 46 is a d–f heteronuclear complex having a phosphorescent cyclometallated iridium complex onto which is grafted a magnetic resonance imaging (MRI) active gadolinium complex and as such it can act as a dual-mode bioimaging probe for luminescence imaging and MRI.³¹ The monocyclometallated cationic platinum complex 47 has shown some activity towards the inhibition of TNF- α stimulated NF- κ B-dependent gene transcription and therefore is a potential anti-cancer agent.³² Complex 48 (both iridium and rhodium versions) contains a steroidal conjugate and has displayed increased activity relative to cisplatin towards T47D breast cancer cells.³³ Finally complex 49 has been used to prepare mesoporous silica nanoparticles with the ability to sense cysteine and homocysteine in biological media (Fig. 6).³⁴

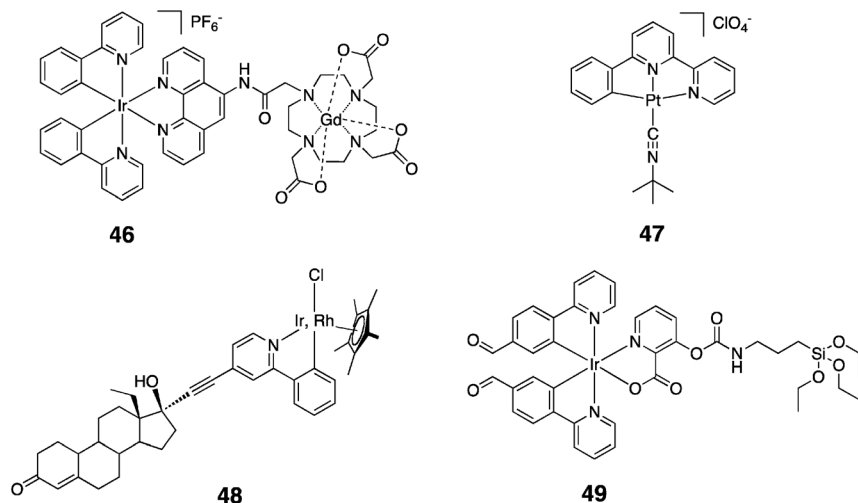
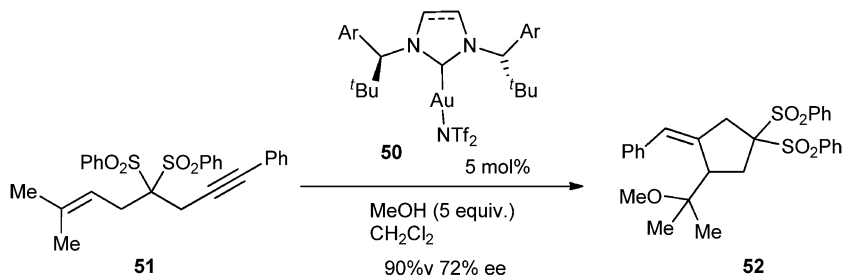


Fig. 6 Complexes 46–49.

Synthesis

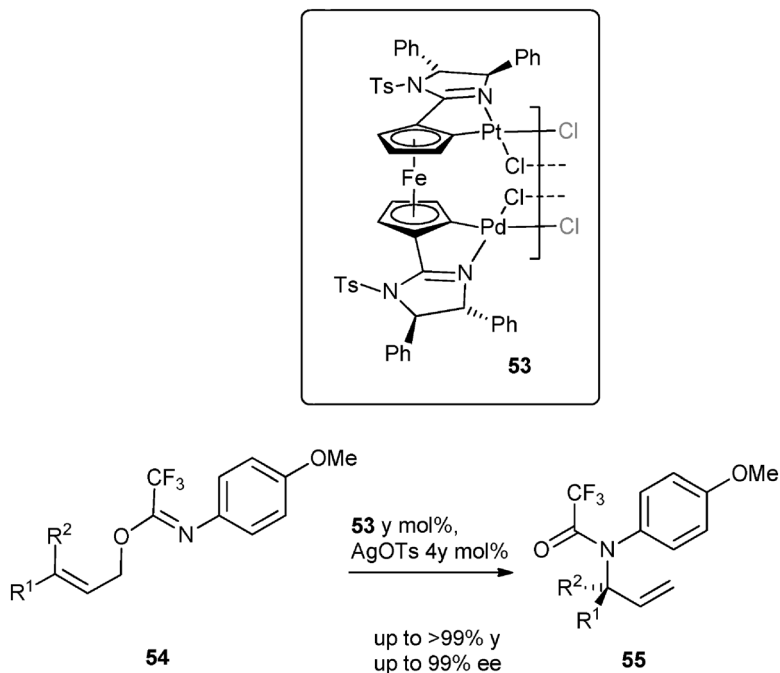
Gold carbenes continue to play an important role in synthetic chemistry; particularly noteworthy are asymmetric examples for the generation of challenging substrates. Kundig and co-workers were able to use chiral gold(I) NHC complexes to form enantioenriched carbocycles in good yield and ee.³⁵ By using 5 mol% of *in situ* formed gold NHC triflimide in the presence of methanol and dichloromethane the cyclisation of substrate **51** to product **52** was achieved in upto 72% ee (Scheme 1).



Scheme 1 Chiral gold(I) NHC catalysed carbocyclisation of **51** to **52**.

Hashmi *et al.* have explored gold NHC complex mediated reactions of bis-terminal alkynes and demonstrated the importance of intermediates bearing two gold acetylide units.³⁶ In their work they were able to convert 1,2-diethynylbenzenes and benzene into 1- or 2-phenylnaphthalenes under the control of various gold NHC complexes.

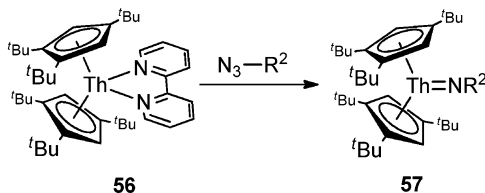
Metallocene scaffolds are a mainstay of applied organometallic chemistry and 2012 saw some exciting contributions to the area. A particularly intriguing finding was that a bis metallocyclic derivative of ferrocene showed heterobimetallic cooperativity. Peters and co-workers showed how a ferrocene bearing two C–N metallocyclic units (top and bottom Cp fragment derivatives) gave superior results in



Scheme 2 Conversion of **54** to **55** by bismetallo-cyclic ferrocene derived catalyst **53**.

asymmetric aza-Claisen rearrangements.³⁷ Scheme 2 shows the heterometallo-cyclic catalyst **53** which, after halide abstraction with a silver salt, is capable of synergistically binding and activating the nitrogen (*via* cationic palladium) and the alkene (*via* platinum) of **54** to give isomeric product **55** in excellent yields and selectivities.

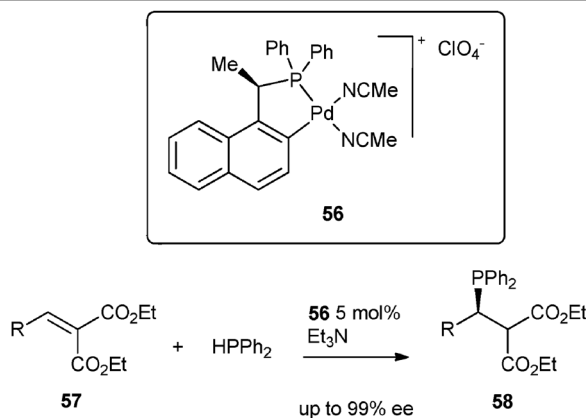
In the area of metallocene chemistry a new type of complex has been reported. A thorium metallocycle bearing a bis-pyridyl ligand was reported by Walter and co-workers, and its reactivity was investigated.³⁸ Among the interesting reactions reported is the conversion of thorium bis-pyridyl metallocene **56** to imido complex **57** upon reaction with organo azides. Importantly in their study they identified the importance of the redox properties of ligands (like bis-pyridyl) in the chemistry of these actinide compounds (Scheme 3).



Scheme 3 Conversion of **56** into **57**.

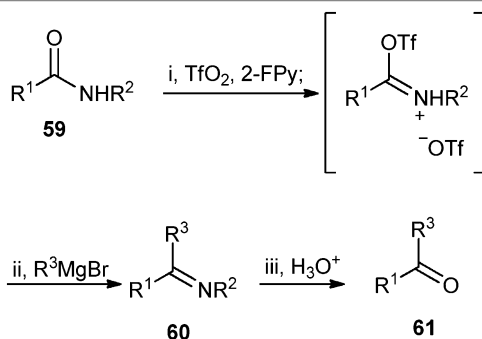
Chiral phosphines are important ligands in asymmetric synthesis, and Xu *et al.* have been able to use a chiral C,P-metallocycle to catalyse the selective introduction of a diphenylphosphino unit to a Michael acceptor.³⁹ The hydrophosphination of **57** proceeded in the presence of 5 mol% of catalyst **56** at -80°C in the presence of

triethylamine to give chiral phosphines **58** in up to 99% ee, demonstrating the potential for palladium catalysed asymmetric, overall, P-H addition to activated substrates (Scheme 4).



Scheme 4 Asymmetric introduction of diphenyl phosphine to **57** by catalyst **56** to give product **58**.

Organometallic reagents are important building blocks in organic chemistry and in 2012 Charette and co-workers were able to demonstrate chemoselective addition of organometallic reagents, such as Grignard reagents, to amides.⁴⁰ In their report they detailed the reaction of an amide (**59**) with triflic anhydride in the presence of 2-FPy to form an activated intermediate, which upon treatment with Grignard reagents forms ketimines **60**. Following either basic or acidic treatment, ketimines (**60**) or ketones (**61**), respectively, were isolated (Scheme 5).



Scheme 5 Selective formation of ketimines **60** and ketones **61**.

The various advances in organometallic chemistry, both in terms of synthesis of organometallic species or applications of organometallic reagents in synthesis, continue to make it a fascinating area of fundamental chemical research.

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