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Synthesis and reactivity of half-sandwich (η5-C5Me5)Ir(III) complexes of a cyclometallated aryl phosphine ligand†‡

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Reaction of the Ir(III) dimer [(η5-C5Me5)IrCl2]2 with PMeXyl2 (Xyl = 2,6-C6H3Me2), in the presence of the poorly coordinating base 2,2,6,6-tetramethyl piperidine, gives a chloride complex 1-Cl, resulting from hydrogen chloride elimination involving one of the phosphine benzylic hydrogen atoms and concomitant cyclometallation . Related compounds containing other halide or pseudohalide ligands, 1-Br, 1-Cl, 1-SCN, can be made, the latter featuring S-coordination of the ambidentate thiocyanate to the soft Ir(III) Lewis acid centre, as suggested by IR data and demonstrated by X-ray crystallography . Hydride 2-H, and alkyl derivatives 3 (Me) and 4 (CH2SiMe3) can also be prepared from 1-Cl and appropriate hydride and alkylating reagents. An interesting H/D exchange chemistry that occurs in the presence of CD3OD has been disclosed for 1-Cl, 1-Br and 2-H. For the halide derivatives, deuterium incorporation takes place into the methylene and methyl sites of their cyclometallated ligand, whereas for 2-H only the hydride and methylene (Ir–CH2) protons participate in the exchange, which is strikingly accelerated by catalytic amounts of acids.

Introduction

Cyclometallated iridium complexes are attractive synthetic targets due to their remarkable chemical reactivity, their use in catalysis and their applications in a wide range of areas of materials science.1,2 An important group of complexes of this kind consists of half-sandwich (η5-C5Me5)Ir units bound to a cyclometallated ligand. Often the latter consists of a donor heteroatom (for instance, O, N or P; see structure A in Scheme 1) and a carbon atom that forms a sigma Ir–C bond as a consequence of a metal-mediated intramolecular C–H activation reaction (for example an ortho-metallation). Neutral compounds of this type or their cationic derivatives (structure B) are expected to exhibit unusual reactivity in processes that imply the activation of H–H, H–C and other H–element bonds (e.g. B, N, Si, etc.).

With the precedent of the remarkable reactivity toward C–H activation discovered by the group of Bergman3 for the Ir(III) cation [(η5-C5Me5)Ir(Me)(PMe3)(ClCH2Cl)]+ (isolated as the BArF− salt; BArF = B(3,5-C6H3(CF3)2)4), we have recently started to develop related complexes in which the phosphine and alkyl functionalities are the constituents of a cyclometallated ligand.4 To avoid side reactions like β-H elimination, while at the same time achieving formation of a five-membered metallacycle, aryl phosphines metallated at a benzylic position (structure C in Scheme 1) have been chosen. Herein we report the synthesis and characterization of compounds of type C (Scheme 1) derived from the phosphine PMeXyl2 (Xyl = 2,6-Me2C6H3), in which iridium is also bonded to a halide or pseudohalide unit. Corresponding alkyl and hydride derivatives are also reported. A preliminary communication describing part of this work has already appeared.5

Results and discussion

Halide and pseudohalide complexes

As already reported,5 reaction of the Ir(III) dimer [{(η5-C5Me5)IrCl2}2] with one equivalent of PMe(Xyl)2 in the presence of the weakly coordinating base 2,2,6,6-tetramethylpiperidine (TMPP in Scheme 2a) yields the cyclometallated compound 1-Cl, in the form of two diastereomers in a ca. 7[thin space (1/6-em)]:[thin space (1/6-em)]3 ratio. Metathesis reactions of 1-Cl with LiBr, MgI2 or NH4SCN afford corresponding complexes 1-X, as shown in Scheme 2b. Under the stated experimental conditions, 1-Br and 1-I are produced as single stereomers, whereas 1-SCN forms two isomers in an approximately 6[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture. In each case, the major (or exclusive) reaction product is proposed to be the sterically more favourable isomer, namely that minimizing steric interactions by the adoption of a syn distribution of the X and methyl phosphine groups . This has been demonstrated by X-ray studies carried out for complexes 1-Cl and 1-SCN, and by NOE experiments performed with the related methyl complex 3 (vide infra). While for 1-Cl mild heating of the stereomers mixture (CH2Cl2/MeOH, 40 °C) causes conversion into its major component, interconversion between the two isomers of 1-SCN is less facile. As discussed below, complex 1-Cl undergoes facile chloride dissociation under these conditions (see structure D in Scheme 4) facilitating this exchange.

Compounds 1 are orange or yellow crystalline solids that exhibit good solubility properties in common organic solvents . Although they have been prepared and manipulated under an inert atmosphere, they display moderate stability toward oxygen and moisture, particularly in the form of crystalline samples. NMR data are in accord with the proposed formulation. For all compounds the η5-C5Me5 ligand yields a doublet in the 1H NMR spectrum due to weak coupling between the C5Me5 protons and the phosphorus nucleus (δ 1.3–1.6 ppm, 4JHP of ca. 2 Hz). Resonances due to the diastereotopic Ir–CH2 protons are characteristic and can be considered as diagnostic of the metallation reaction. They appear as two multiplets that can be readily identified as the AB portions of an ABX spin system (X = 31P), where only one of the two 1H nuclei features observable coupling to 31P. Data for each of these complexes can be found in the Experimental section that includes also NMR features for the minor stereomers of 1-Cl and 1-SCN. These proton signals are associated with a 13C{1H} resonance in the range of

17–20 ppm, which exhibits negligible coupling to 31P. The 31P{1H} resonances of complexes 1 cluster in a narrow chemical shift range (7–11 ppm).

The thiocyanate compound 1-SCN has been prepared with the aim of ascertaining whether iridium coordination of the ligand occurs through the nitrogen or the sulfur atom. N- or S-bonding of the thiocyanate anion can be rationalized in terms of the hardness or softness of the metal Lewis acid centre.6 Since the iridium Lewis acid present in these complexes may be viewed as soft,7 S-coordination would be electronically favoured.8 However, N-coordination might be preferred on steric grounds in view of the bulkiness of the C5Me5 and cyclometallated PMeXyl2 ligands.7 Infrared spectroscopy has often been used as diagnostic for S- or N-thiocyanate binding. Even if the following criteria do not have general application, the CN stretching frequency (around 2100 cm−1) occurs at higher wavenumbers for S-thiocyanates than for N-bonded complexes,9 whereas for the C–S stretching frequency (ca. 800 cm−1) the opposite is observed.9 For 1-SCN these bands are registered at 2100 cm−1 and 795 cm−1, suggesting coordination through the sulfur atom. This has been demonstrated by X-ray crystallography .

Fig. 1 collects ORTEP diagrams for complexes 1-Cl and 1-SCN. Crystallographic data for these and other complexes described in this work are provided in the Experimental section. The molecular structure of the complexes confirms that cyclometallation of the xylyl-substituted phosphine has occurred at one of the benzylic carbon atoms, giving rise to a five-membered iridacycle. This unit is characterized by Ir–C and Ir–P bonds with lengths of ca. 2.12 and 2.25 Å, respectively. Bond angles between the P, C and X (Cl or S) atoms that complete the three-legged piano stool structure are close to 90°, in particular the P1 –Ir1–X angles (ca. 89.6°). The X-ray analysis confirms also the proposed syn arrangement of the X ligand and the phosphine methyl group that leaves the larger, non-metallated phosphine xylyl substituent on the opposite region of space.

Cyclometallated iridium complexes with hydride and alkyl ligands

Compound 1-Cl is also a good starting material for the synthesis of complexes that contain Ir–H and Ir–C σ bonds. Iridium hydride 2-H is best prepared (Scheme 3) by reaction of tetrahydrofuran (THF) solutions of 1-Cl and LiAlH4, at 45 °C for 2 h. In an alternative and also high-yield procedure, THF solutions of 1-Cl can be treated with cold pentane solutions (−40 °C) of LiBut and stirred at room temperature for a period of 4 h. The crude hydride forms as a pale yellow powder that converts into a colourless crystalline material after crystallization from pentane. For the deuterated isotopologue, 2-D, LiAlD4 or NaOCD3 may be utilized as a deuteride source. The hydride forms in an approximate 20[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of diasteromers.

A medium-to-weak intensity infrared absorption at 2090 cm−1 that shifts to 1470 cm−1 in 2-D is indicative of the presence of an Ir–H (and Ir–D) functionality. This is further demonstrated by the observation for 2-H of a characteristic 1H NMR signal with δ −17.24 (2JHP = 35.2 Hz) that is absent in the spectrum of 2-D. EXSY NMR studies performed at 0 °C give no indication for exchange between the Ir–H and Ir–CH2 sites of 2-H. However, H/D exchange takes place when solutions of 2-D, or of [D11]-2-H (the latter deuterated at the methylene and methyl sites of the two xylyl groups), are heated at 90 °C in C6D6. This may occur by a series of C–H reductive

couplings of the Ir–CH2 and Ir–H moieties of 2-H, and oxidative additions of the C–H bonds of the xylyl methyl substituents in a putative Ir(I) intermediate, [(η5-C5Me5)Ir(PMeXyl2)]. Since heating a solution of 2-H in C6D6 at 200 °C in a pressure vessel for 48 h results in no deuteration of the metallated ligand, intermolecular benzene C–D activation must be either unproductive or much slower than intramolecular oxidative C–H cleavage.

As summarized in Scheme 3, the methyl derivative 3 is best prepared by reaction of 1-Cl with ZnMe2 or Mg(Me)Br. The stronger methylating reagent, LiMe, also yields 3 but accompanied by a product with three Ir–C σ bonds, as a consequence of metallation of the P-bound methyl group .5 The latter compound will be described elsewhere. Alkylation of 1-Cl can be readily extended to other alkyl groups that lack β-H atoms. This is shown in Scheme 3 for the synthesis of the Ir–CH2SiMe3 complex 4.

The NMR data recorded for the C5Me5 and cyclometallated phosphine ligands of 3 and 4 are similar to those already discussed for 1 and 2. They are collected in the Experimental section and need no further explanation. The alkyl groups of 3 and 4 produce high-field 1H NMR signals that are observed for the former compound at 0.35 ppm (d, 3JHP = 5.2 Hz). In the latter, the Ir–CH2SiMe3 protons are diastereotopic and appear as multiplets in the chemical shift range of 0.30–0.19 ppm. As expected, the 13C{1H} resonances found for these Ir–C units are strongly shielded and appear at −22.9 (complex 3) and −29.6 (4) ppm.

The molecular structures of 2-H and 3 have been confirmed by X-ray studies (Fig. 2). The Ir1–C17 bonds in the two complexes are identical within experimental error (ca. 2.11 Å) and are also identical to corresponding bonds in 1-Cl and 1-SCN. For the methyl complex 3, the two Ir–C bonds, i.e. Ir1–C17 and Ir1–C28, have practically the same length. For the latter compound, the solid-state structure corroborates the syn distribution of the Ir–Me and P–Me groups deduced in solution from NOE studies.

Hydrogen/deuterium exchange reactions

As already indicated, the cyclometallated complexes described in this work have been prepared with the aim of ascertaining their role in the activation of E–H bonds (E stands for H, C or other main-group element like N or Si) and their utility as precursors for the synthesis of related, neutral or cationic, iridium complexes, which may be useful for the same purpose. Compounds labelled with the hydrogen isotopes are widely employed as internal standards for mass spectrometric studies, as well as in the investigation of the interaction of small molecules with receptors, enzymes and other biomolecules.10 The importance of deuterium labelling of organic molecules11 has prompted a number of studies in this field by different research groups .12–15 Heating compounds 1 in a 1[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of CH2Cl2[thin space (1/6-em)]:[thin space (1/6-em)]CD3OD at 45 °C in a closed reaction vessel for ca. 24 h results in clean incorporation of deuterium into all sp3-hybridized C–H bonds of the phosphine xylyl substituents only for 1-Cl and 1-Br. In contrast to a somewhat related derivative containing a cyclometallated N-heterocyclic carbene ligand reported by Peris and co-workers,13b the iodide complex 1-I does not undergo H/D exchange under similar conditions. The thiocyanate complex 1-SCN also fails to promote H/D scrambling, which might be due to the less polar and more covalent character of the Ir–I and Ir–S bonds in the two complexes. For 1-Cl and 1-Br the deuteration is facile and occurs with a half-live, t1/2

= 490 min at 45 °C for 1-Cl, using the above 1[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of solvents .

In parallel experiments, the deuteration of 1-Cl has been observed to slow down by a factor of ten when the CH2Cl2/CD3OD solvent mixture is saturated with LiCl.12a,14b Moreover, the H/D exchange is significantly accelerated when the concentration of CD3OD in the solvent mixture is increased (see Experimental section). Accordingly, participation of a cationic species resulting from momentary dissociation of chloride (structure D in Scheme 4) in the H/D exchange appears to be a reasonable proposal. Subsequent incorporation of deuterium onto all benzylic positions of 1-Cl (or 1-Br) requires, in all probability, cleavage of the Ir–CH2 bond to the cyclometallated carbon. Hence, D may undergo deuteration of this bond giving an agostic structure such as E in Scheme 4, which would afterwards experience C–H (or C–D) activation at all benzylic sites. Whether this C–H activation occurs by an internal electrophilic substitution or a related mechanism14,16 is unclear at this stage. Evidence for a similar H/D exchange involving D2 as the deuterium source has been obtained recently for a closely related rhodium compound.15b

Recent work from Goldberg, Brookhart and their co-workers17 has revealed that an Ir(I)–CH3 complex stabilized by the pincer ligand PONOP17 experiences facile deuterium incorporation in the methyl group in the presence of the acidic deuterated solvents CD3OD and D2O. For this proton -assisted C–D/H activation a mechanism implying generation of an Ir(III) methyl hydride (or deuteride) intermediate that features reductive coupling and oxidative cleavage reactivity was proposed, with participation of an Ir(I) σ–methane complex intermediate.17 In contrast with these observations the Ir(III) compound 3 does not participate in H/D exchange under the conditions given above for 1-X, and is recovered unaltered after being heated in CH2Cl2[thin space (1/6-em)]:[thin space (1/6-em)]CD3OD (1[thin space (1/6-em)]:[thin space (1/6-em)]1) at 60 °C for 24 h. It thus seems likely that methanol is unable to protonate 3 and generate the cationic Ir(V) methyl hydride intermediate that could promote H/D scrambling in this complex.

At variance with the lack of reactivity of 3, hydride 2-H experiences facile D incorporation, albeit exclusively in the Ir–H and Ir–CH2 bonds. A CD3OD concentration of only 10% in the CH2Cl2[thin space (1/6-em)]:[thin space (1/6-em)]CD3OD solvent mixture utilized suffices to promote the scrambling at 20 °C, with t1/2 = 130 min. 1H NMR monitoring of the exchange reveals no detectable differences in the rates of deuteration of the chemically distinct hydride and alkyl functionalities. Addition of 5% of p-toluenesulfonic acid uncovers a remarkable catalytic effect, as deuteration occurs with t1/2 ≤ 3 min. Larger acid amounts (≥20%) produce fully deuterated [D11]-2-D, as a consequence of additional incorporation of deuterium in the benzylic positions of the phosphine ligand. Most likely, this results from cleavage by the acid of the Ir–CH2 bond, to give an agostic species similar to E in Scheme 4. Addition of a base (NaOCD3 or NaOD) completely inhibits the H/D scrambling. In fact this observation explains that generation of 2-D from 1-Cl and LiAlD4 (Scheme 3) occurs selectively with more than 95% deuterium incorporation at the hydride position (and not into the methylene sites, despite addition of H2O to quench the excess of the deuteride reagent). In much the same manner, the alternative synthesis of 2-D in Scheme 3 uses NaOCD3 to selectively label with deuterium the hydride position.

The remarkable selectivity of the acid-catalysed H/D scrambling in 2-H suggests the participation as a key intermediate of a cationic iridium alkylidene, resulting from an α-H elimination, or a H-abstraction reaction. Despite our efforts, a clear mechanistic picture has not yet evolved. However, work in progress with complexes of related PR2Xyl ligands may shine light on this intriguing rearrangement . This advises deferring a definitive mechanistic proposal until sufficient information is gathered.

Conclusions

In summary, readily prepared cyclometallated complex 1-Cl has proved to be an excellent synthetic precursor for the synthesis of related halide (or pseudohalide), hydride and alkyl derivatives. Compounds 1-Cl and 1-Br feature H/D scrambling in the presence of CD3OD affecting all benzylic sites whereas for the hydride 2-H an unusual acid-catalysed reaction permits D incorporation exclusively into the Ir–H and Ir–CH2 units.

Experimental section

General

All operations were performed under an argon atmosphere using Standard Schlenk techniques, employing dry solvents and glassware. Microanalyses were performed by the Microanalytical Service of the Instituto de Investigaciones Químicas (Sevilla, Spain). Infrared spectra were recorded on a Bruker Vector 22 spectrometer . The NMR instruments were Bruker DRX-500, DRX-400 and DRX-300 spectrometers . Spectra were referenced to external SiMe4 (δ 0 ppm) using the residual proton solvent peaks as internal standards (1H NMR experiments), or the characteristic resonances of the solvent nuclei (13C NMR experiments), while 31P was referenced to external H3PO4. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. The crystal structures were determined in a Bruker-Nonius, X8Kappa diffractometer . Dimer [(η5-C5Me5)IrCl2]2 was prepared as described in the literature.18 In the 1H NMR spectra all aromatic couplings are of ca. 7.5 Hz. 1H NMR simulations were performed employing the P.H.M. Budzelaar gNMR V4.01 package, Cherwell Scientific Publishing, Oxford, U.K.

[(η5-C5Me5)I[upper bond 1 start]r(Cl){PMe(2,6-C[upper bond 1 end]H2(Me)C6H3)(2,6-Me2C6H3)}] (1-Cl)

[(η5-C5Me5)IrCl2]2 (1.53 g, ca. 1.92 mmol) was dissolved in dry CH2Cl2 (40 mL) in a Schlenk flask with a stir bar. The dark solution was cooled to 0 °C and PXyl2Me (1.00 g, 3.89 mmol) dissolved in CH2Cl2 (10 mL) was added, followed by the addition of 2,2,6,6-tetramethyl piperidine (660 μL, 3.89 mmol). The reaction mixture was allowed to warm to room temperature and additionally stirred for 2 h. The solvent was removed in vacuo and the product extracted with toluene in air. The solution was evaporated to dryness providing a bright yellow powder, which was washed with pentane to yield compound 1-Cl as a mixture of two isomers (ca. 7[thin space (1/6-em)]:[thin space (1/6-em)]3 ratio; 2.16 g, 3.50 mmol, 90%). Heating this mixture to 40 °C in CH2Cl2/MeOH (1[thin space (1/6-em)]:[thin space (1/6-em)]1) for 2 h provides exclusively the major stereomer for which characterization data are given below. Crystallization from CH2Cl2/pentane provides analytically pure samples of the desired

product. Fig. 3 includes labelling for the assignment of NMR data. 1H NMR (500 MHz, C6D6, 25 °C) δ: 7.54 (d, 1 H, Ha), 7.04 (td, 1 H, 5JHP = 1.6 Hz, Hb), 6.89 (td, 1 H, 3JHP = 1.0 Hz, He), 6.84, 6.62 (dd, 1 H each, 4JHP = 2.3 Hz, Hd, Hf), 6.69 (dd, 1 H, 4JHP = 2.7 Hz, Hc), 4.15 (dd, 1 H, 2JHH = 14.5, 3JHP = 3.8 Hz, IrCHH), 3.87 (d, 1 H, 2JHH = 14.5 Hz, IrCHH), 2.35, 1.47 (s, 3 H each, Meβ, Meγ), 2.28 (d, 3 H, 2JHP = 10.4 Hz, PMe), 1.78 (s, 3 H, Meα), 1.32 (d, 15 H, 4JHP = 1.9 Hz, C5Me5). 13C{1H} NMR (125 MHz, C6D6, 25 °C) δ: 158.3 (d, 2JCP = 32 Hz, C1), 140.8 (d, 1JCP = 61 Hz, C2), 141.5, 139.9 (d, 2JCP = 8 Hz, C4, C6), 139.2 (C3), 131.7 (d, 1JCP = 44 Hz, C5), 129.4, 129.3 (CHd, CHf), 129.8 (CHb), 128.9 (CHe), 128.0 (CHa), 127.1 (d, 3JCP = 6 Hz, CHc), 91.7 (d, 2JCP = 2 Hz, C5Me5), 25.0, 22.7 (d, 3JCP = 4 Hz, 8 Hz, Meβ, Meγ), 20.8 (Meα), 20.3 (IrCH2), 18.0 (d, 1JCP = 40 Hz, PMe), 7.8 (C5Me5). 31P{1H} NMR (200 MHz, C6D6, 25 °C) δ: 11.3. Anal. calcd. for C27H35ClIrP: C, 52.46; H, 5.71. Found: C, 52.0; H, 6.1%.

The minor diastereomer of compound 1-Cl is characterized by 1H NMR multiplets with δ 4.70 and 3.59 ppm, due to the IrCH2 protons and by a doublet at 1.47 ppm associated with the C5Me5 ligand. In the 31P{1H} NMR spectrum a singlet is recorded with δ 7.8 ppm.

Synthesis of complexes 1-Br, 1-I and 1-SCN

A mixture of 1-Cl (100 mg, 0.16 mmol), with a ca. ten- or twenty-fold excess of LiBr, MgI2 or NH4SCN, was suspended in THF (10 mL) under argon, and heated at 60–70 °C for 12 h (for 1-Br the reaction mixture was refluxed for three days). The solvent was then evaporated under reduced pressure and the resulting residue extracted with CH2Cl2 (1-Br) or with toluene (3 × 10 mL for 1-I and 1-SCN). Filtration of the solution and removal of the solvent under vacuum yielded the desired complexes in the form of orange (1-Br: 98 mg, 0.15 mmol, 92% yield) or yellow powders (1-I: 91 mg, 0.13 mmol, 80%; 1-SCN: 85 mg, 0.13 mmol, 83%). Crystalline, analytically pure samples of the compounds were obtained by crystallization from CH2Cl2/pentane solvent mixtures. The thiocyanate complex forms as a ca. 85[thin space (1/6-em)]:[thin space (1/6-em)]15 mixture of stereomers. Analytical and spectroscopic data for these compounds are given below.

1-Br

1H NMR (400 MHz, CDCl3, 25 °C) δ: 7.32 (d, 1 H, Ha), 7.12, 6.86 (m, 2 H and 1 H, Hd, He, Hf), 7.04 (td, 1 H, 5JHP = 1.8 Hz, Hb), 6.75 (dd, 1 H, 4JHP = 3.0 Hz, Hc), 3.82 (dd, 1 H, 2JHH = 14.9 Hz, 3JHP = 3.9 Hz, IrCHH), 3.74 (d, 1 H, 2JHH = 14.9 Hz, IrCHH), 2.61, 1.45 (s, 3 H each, Meβ, Meγ), 2.42 (d, 3 H, 2JHP = 10.2 Hz, PMe), 1.96 (s, 3 H, Meα), 1.49 (d, 15 H, 4JHP = 1.7 Hz, C5Me5). 13C{1H} NMR (100 MHz, CDCl3, 25 °C) δ: 157.9 (d, 2JCP = 31 Hz, C1), 141.4, 139.9 (d, 2JCP = 8 Hz, C4, C6), 140.1 (d, 1JCP = 62 Hz, C2), 139.3 (C3), 131.4 (d, 1JCP = 45 Hz, C5), 129.9, 129.5 (d, J = 8 Hz, CHd, CHf), 129.6 (CHb), 129.1 (CHe), 127.4 (d, 3JCP = 14 Hz, CHa), 127.1 (d, 3JCP = 7 Hz, CHc), 92.1 (d, 2JCP = 3 Hz, C5Me5), 25.5, 22.7 (d, 3JCP = 5 Hz, 7 Hz, Meβ, Meγ), 21.3 (d, 1JCP = 41 Hz, PMe), 20.5 (Meα), 18.6 (IrCH2), 8.2 (C5Me5). 31P{1H} NMR (160 MHz, CDCl3, 25 °C) δ: 7.9. Anal. calcd. for C27H35BrIrP: C, 48.94; H, 5.32. Found: C, 48.7; H, 5.3%.

1-I

1H NMR (400 MHz, CD2Cl2, 25 °C) δ: 7.30 (d, 1 H, Ha), 7.18, 6.91 (m, 2 H and 1 H, Hd, He, Hf), 7.10 (td, 1 H, 5JHP = 1.8 Hz, Hb), 6.83 (dd, 1 H, 4JHP = 2.9 Hz, Hc), 4.04 (dd, 1 H, 2JHH = 14.8 Hz,

3JHP = 4.7 Hz, IrCHH), 3.76 (d, 1 H, 2JHH = 14.8 Hz, IrCHH), 2.70 (d, 3 H, 2JHP = 10.0 Hz, PMe), 2.60, 1.44 (s, 3 H each, Meβ, Meγ), 1.98 (s, 3 H, Meα), 1.60 (d, 15 H, 4JHP = 1.7 Hz, C5Me5). 13C{1H} NMR (100 MHz, CD2Cl2, 25 °C) δ: 159.1 (d, 2JCP = 30 Hz, C1), 141.6, 140.5 (C4, C6), 141.3 (1JCP = 60 Hz, C2), 140.2 (C3), 132.1 (d, 1JCP = 44 Hz, C5), 130.4, 129.9 (d, 3JCP = 8 Hz, CHd, CHf), 129.8 (CHe), 129.5 (CHb), 127.70 (d, 4JCP = 7 Hz, CHc), 127.3 (d, 4JCP = 14 Hz, CHa), 93.0 (C5Me5), 28.2 (d, 1JCP = 43 Hz, PMe), 26.1, 22.9 (d, 3JCP = 5, 7 Hz, Meβ, Meγ), 20.8 (Meα), 14.8 (IrCH2), 8.9 (C5Me5). 31P{1H} NMR (160 MHz, CD2Cl2, 25 °C) δ: 3.2. Anal. calcd. for C27H35IIrP: C, 45.70; H, 4.97. Found: C, 45.5; H, 4.6%.

1-SCN

IR (Nujol): major diastereomer: ν(CN) 2100, ν(CS) 795 cm−1; minor diastereomer: ν(CS) 2123 cm−1. 1H NMR (400 MHz, CD2Cl2, 25 °C) δ: 7.35 (d, 1 H, Ha), 7.20 (m, 2 H, Hd/f, He), 7.13 (t, 1 H, Hb), 6.93 (m, 1 H, Hd/f), 6.86 (dd, 1 H, 4JCP = 7.2, 2.9 Hz, Hc), 3.55 (d, 1 H, 2JHH = 15.2 Hz, IrCHH), 2.87 (dd, 1 H, 2JHH = 15.2 Hz, 3JHP = 4.1 Hz, IrCHH), 2.59, 1.47 (s, 3 H each, Meβ, Meγ), 2.30 (d, 3 H, 1JCP = 9.8 Hz, PMe), 2.01 (s, 3 H, Meα), 1.52 (d, 15 H, 4JHP = 1.7 Hz, C5Me5). 13C{1H} NMR (100 MHz, CD2Cl2, 25 °C) δ: 157.3 (d, 2JCP = 30 Hz, C1), 141.8, 140.8 (d, 2JCP = 8 Hz, C4, C6), 140.2 (d, 2JCP = 2 Hz, C3), 140.1 (d, 1JCP = 60 Hz, C2), 130.6 (d, 1JCP = 46 Hz, C5), 130.4, 130.0 (d, 3JCP = 8 Hz, CHd, CHf), 130.3, 129.9 (d, 4JCP = 2 Hz, CHb, CHe), 128.1 (d, 3JCP = 7 Hz, CHc), 127.5 (d, 3JCP = 14 Hz, CHa), 121.2 (d, 3JCP = 4 Hz, SCN), 94.4 (d, 2JCP = 3 Hz, C5Me5), 25.5, 22.9 (d, 3JCP = 6 Hz, 8 Hz, Meβ, Meγ), 20.7 (Meα), 18.5 (d, 1JCP = 41 Hz, PMe), 17.0 (IrCH2), 7.8 (C5Me5). 31P{1H} NMR (160 MHz, CD2Cl2, 25 °C) δ: 7.70. Anal. calcd. for C28H35IrNPS: C, 52.48; H, 5.50; N, 2.19; S, 5.00. Found: C, 52.5; H, 5.6; N, 2.2; S, 4.8%.

The minor isomer of compound 1-SCN is characterized by 1H NMR multiplets with δ 3.49 and 3.36 ppm, due to the IrCH2 protons and by a doublet at 2.20 ppm associated with the PMe methyl group . The signal corresponding to the C5Me5 ligand overlaps with that of the major diastereomer. In the 31P{1H} NMR spectrum a singlet is recorded with δ 12.7 ppm.

[(η^5-C$_5$Me$_5$)Ir(H){PMe(2,6-CH$_2$(Me)C$_6$H$_3$)(2,6-Me$_2$C$_6$H$_3$)}] (2-H**)**

Compound 1-Cl (100 mg, 0.16 mmol) was dissolved in THF (5 mL) under an argon atmosphere. A solution of LiAlH4 in THF (1 M, 0.49 mL) was added via a syringe. The reaction was heated at 45 °C for 2 h and then quenched with H2O (20 µL). The solvent was removed under vacuum and the residue extracted with pentane, then evaporated to dryness to provide the product as a pale yellow powder (88 mg, 0.151 mmol, 93%). For further purification , recrystallization from pentane yielded colourless crystals (69 mg, 0.12 mmol) in 73% yield. The same procedure was followed using LiAlD4 (1 M) in THF for the preparation of the deuterated material 2-D with a similar yield. A second procedure for the preparation of compound 2-H was developed. A solution of 1-Cl (40 mg, 0.065 mmol) in THF (2 mL) was cooled to −40 °C and a solution of LitBu in pentane (1.7 M, 50 µL) was added dropwise. The reaction mixture was allowed to warm gradually to room temperature and stirred for 4 h. The solvent was removed in vacuo and the product extracted with pentane, then evaporated to dryness to provide the hydride as a yellow powder in 85% crude yield (32 mg, 0.06 mmol). IR (Nujol): ν(Ir–H) 2090 cm−1. 1H NMR (400 MHz, C6D6, 25 °C) δ: 7.54 (d, 1 H, Ha), 7.04 (dt, 1 H, 5JHP = 1.6 Hz, Hb), 6.91, 6.70 (m, 2 H each, Hc, Hd He, Hf), 3.98 (d, 1 H, 2JHH = 14.9 Hz, IrCHH), 3.20 (d, 1 H, 2JHH = 14.9, IrCHH), 2.41, 1.60 (s, 3 H each, Meβ, Meγ), 2.21 (d, 3 H, 2JHP = 10.8 Hz, PMe), 1.92 (s, 3 H, Meα), 1.69

(d, 15 H, 4JHP = 1.5 Hz, C5Me5), −17.24 (d, 1 H, 2JHP = 35.2 Hz, Ir-H). 13C{1H} NMR (100 MHz, C6D6, 25 °C) δ: 160.1 (d, 2JCP = 31 Hz, C1), 143.9 (d, 1JCP = 60 Hz, C2), 141.8, 139.1 (d, 2JCP = 8 Hz, C4, C6), 139.3 (C3), 133.0 (d, 1JCP = 40 Hz, C5), 129.9, 129.7 (d, 3JCP = 7 Hz, CHd, CHf), 129.5 (CHb), 128.6 (CHe), 127.6 (d, 3JCP = 14 Hz, CHa), 127.1 (d, 3JCP = 6 Hz, CHc), 91.9 (d, 2JCP = 3 Hz, C5Me5), 31.0 (d, 1JCP = 44 Hz, PMe), 25.1, 20.9 (d, 3JCP = 4 Hz, Meβ, Meγ), 21.9 (d, 3JCP = 9 Hz, Meα), 8.7 (C5Me5), 4.3 (IrCH2). 31P{1H} NMR (160 MHz, C6D6, 25 °C) δ: 8.3. Anal. calcd. for C27H36IrP: C, 55.55; H, 6.22. Found: C, 56.0; H, 6.7%.

Only very small amounts of a minor isomer are present in solutions of compound 2-H. This is characterized by a hydride signal with δ −17.57 ppm in the 1H NMR spectrum and by a 31P{1H} resonance at 7.70 ppm.

[(η^5-C$_5$Me$_5$)Ir(Me){PMe(2,6-C$_6$H$_2$(Me)C$_6$H$_3$)(2,6-Me$_2$C$_6$H$_3$)}] (3)

A solution of 1-Cl (100 mg, 0.16 mmol) in CH2Cl2 (4 mL) was cooled to 0 °C and a solution of ZnMe2 in toluene (2 M, 120 µL) was added dropwise. The yellow solution rapidly cleared up to become nearly colourless. The mixture was stirred at 20 °C for 1 h, quenched with H2O (10 µL) and the solvent removed in vacuo to provide crude compound 3 as a pale yellow solid. The product was extracted with pentane, concentrated and cooled to −25 °C. Yellow crystals of complex 3 were isolated in 63% yield (62 mg, 0.10 mmol). 1H NMR (400 MHz, C6D6, 25 °C) δ: 7.56 (d, 1 H, Ha), 7.04 (td, 1 H, 5JHP = 1.8 Hz, Hb), 6.91, 6.70 (m, 2 H each, Hc, Hd He, Hf), 3.50 (d, 1 H, 2JHH = 15.0 Hz, IrCHH), 2.89 (dd, 1 H, 2JHH = 15.0, 3JHP = 3.2 Hz, IrCHH), 2.32, 1.58 (s, 3 H each, Meβ, Meγ), 1.91 (s, 3 H, Meα), 1.83 (d, 3 H, 2JHP = 9.4 Hz, PMe), 1.43 (d, 15 H, 4JHP = 1.5 Hz, C5Me5), 0.35 (d, 3 H, 3JHP = 5.2 Hz, Ir-Me). 13C{1H} NMR (100 MHz, C6D6, 25 °C) δ: 159.2 (d, 2JCP = 31 Hz, C1), 142.4 (d, 1JCP = 57 Hz, C2), 141.8, 139.2 (d, 2JCP = 8 Hz, C4, C6), 139.6 (C3), 133.6 (d, 1JCP = 42 Hz, C5), 129.9, 129.8 (d, 3JCP = 7 Hz, CHd, CHf), 129.5 (CHb), 128.6 (CHe), 128.5 (d, 3JCP = 6 Hz, CHa), 127.3 (d, 3JCP = 6 Hz, CHc), 91.7 (d, 2JCP = 4 Hz, C5Me5), 25.3, 22.3 (d, 3JCP = 7 Hz, Meβ, Meγ), 21.0 (d, 3JCP = 9 Hz, Meα), 16.9 (IrCH2), 16.4 (d, 1JCP = 38 Hz, PMe), 8.2 (C5Me5), −22.9 (d, 2JCP = 8 Hz, Ir-Me). 31P{1H} NMR (160 MHz, C6D6, 25 °C) δ: 8.4. Anal. calcd. for C28H38IrP: C, 56.26; H, 6.41. Found: C, 56.2; H, 6.6%.

[(η^5-C$_5$Me$_5$)Ir(CH$_2$SiM$_3$){PMe(2,6-C$_6$H$_2$(Me)C$_6$H$_3$)(2,6-Me$_2$C$_6$H$_3$)}] (4)

Compound 1-Cl (100 mg, 0.16 mmol) was placed in a Schlenk flask and dissolved in THF (10 mL) under argon. A solution of LiCH2SiMe3 (1.78 mL, 0.1 M in pentane) was added at 0 °C and the mixture was allowed to warm slowly to room temperature, and then stirred for two hours. The solvent was evaporated under vacuum and the residue extracted with pentane and filtered under argon through a pad of silica. The bright yellow filtrate was evaporated to dryness to yield the product as a fine yellow powder (69 mg, 0.10 mmol, 64%). 1H NMR (400 MHz, C6D6, 25 °C) δ: 7.50 (d, 1 H, Ha), 7.00 (td, 1 H, 5JHP = 1.7 Hz, Hb), 6.90 (m, 2 H, Hd/f, He), 6.66 (m, 2 H, Hc, Hd/f), 3.47 (m, 2 H, IrCH2), 2.34, 1.47 (s, 3 H each, Meβ, Meγ), 1.95 (d, 3 H, 2JHP = 9.4 Hz, PMe), 1.91 (s, 3 H, Meα), 1.37 (d, 15 H, 4JHP = 1.7 Hz, C5Me5), 0.30–0.19 (m, 2 H, IrCH2Si, AB part of ABX system (X = 31P), 0.18 (s, 9 H, SiMe3). The multiplet signal at 0.30–0.19 ppm, which may be described as the AB part of an ABX system (X = 31P), has been simulated using gnmr software. The peak distribution within this region is in agreement with δA = 0.28 and δB = 0.23 ppm, and coupling constants 2JAB = 13.0, 3JAX = 8.9 and 3JBX = 3.5 Hz. 13C NMR (100 MHz, C6D6, 25 °C) δ: 159.7 (d, 2JCP = 32 Hz, C1), 143.1 (d, 1JCP = 59 Hz, C2), 141.5, 140.0 (d,

2JCP = 8 Hz, C4, C6), 139.4 (C3), 134.0 (d, 1JCP = 44 Hz, C5), 129.9, 129.6 (d, 3JCP = 8 Hz, CHd, CHf), 129.5, 128.7 (CHb, CHe), 128.1 (CHa, overlapped with C6D6), 127.4 (d, 3JCP = 6 Hz, CHc), 92.6 (d, 2JCP = 4 Hz, C5Me5), 26.1, 23.0 (d, 3JCP = 7 Hz, Meβ, Meγ), 21.1 (Meα), 17.9 (d, 1JCP = 39 Hz, PMe), 12.2 (IrCH2), 8.4 (C5Me5), 4.2 (SiMe3), −29.6 (d, 2JCP = 7 Hz, IrCH2Si). 31P{1H} NMR (160 MHz, C6D6, 25 °C) δ: 6.41. Anal. calcd. for C31H46IrPSi: C, 55.57; H, 6.92. Found: C, 55.6; H, 6.7%.

Hydrogen/deuterium exchange reactions

H/D exchange of complexes 1. Following by 1H NMR spectroscopy the reaction of compounds 1 with a 1[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of CD2Cl2 and CD3OD, under argon, a progressive decline in the intensity of the resonances due to the methylene and methyl protons of the metallated ligand, and a concomitant increase of the CD3OH signal was apparent. In a typical experiment, a solution of 1 (0.01 mmol) in 0.5 mL of a 1[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of CD2Cl2[thin space (1/6-em)]:[thin space (1/6-em)]CD3OD was heated in an oil bath at 45 °C (bath temperature). From these experiments a t1/2 value of 490 min was determined for 1-Cl. After ca. 24 h the deuteration was essentially complete. The velocity of deuteration was proved to be dependent upon the concentration of CD3OD, as shown in Table 1.

The rate of deuteration of 1-Br under the same conditions is similar to that observed for 1-Cl, whereas no exchange was observed either for 1-I or for 1-SCN, even by heating at 80 °C.

H/D exchange of complex 2-H. Deuteration experiments with 2-H were performed as described above for 1 although in this case a ca. 10[thin space (1/6-em)]:[thin space (1/6-em)]1 mixture of CD2Cl2[thin space (1/6-em)]:[thin space (1/6-em)]CD3OD was utilized. Deuteration occurred at room temperature with a half-life of t1/2 = 130 min. For comparative purposes t1/2 for the H/D exchange in 1-Cl measured also at 25 °C is ca. 10 days.

X-Ray crystallography

Data collections for compounds 1-Cl, 1-SCN, 2-H and 3 were performed on a Bruker-Nonius X8Apex II CCD diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Intensity data were collected at 173 K. Empirical absorption corrections were applied using the SADABS program.19 All structures were solved by direct methods and refined by full-matrix least squares fitting on F2 by SHELXS-97.20 All non-hydrogen atoms were refined anisotropically. The Ir-bound hydrogen atom H1Ir, in compound 2-H, was located on a difference Fourier map and refined without restraints. All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. Crystal data for 1-Cl: C27H35ClIrP, M = 618.17, monoclinic, a = 8.2431(7) Å, b = 8.5307(7) Å, c = 17.2481(14) Å, α = 90.00°, β = 91.802(2)°, γ = 90.00°, V = 1212.28(17) Å3, T = 173(2) K, space group P21, Z = 2, μ = 5.695 mm−1, 22[thin space (1/6-em)]032 reflections measured, 5845 independent reflections (Rint = 0.0555). The final R1 values were 0.0435 (I > 2σ(I)). The final wR(F2) values were 0.0934 (I > 2σ(I)). The final R1 values were 0.0586 (all data). The final wR(F2) values were 0.0988 (all data). The goodness of fit on F2 was 1.051. The Flack parameter was 0.065(12). Crystal data for 1-SCN: C28H35IrNPS, M = 640.80, monoclinic, a = 18.1597(9) Å, b = 8.2917(4) Å, c = 16.8404(7) Å, α = 90.00°, β = 95.1430(10)°, γ = 90.00°, V = 2525.5(2) Å3, T = 173(2) K,

space group P21/c, Z = 4, μ = 5.449 mm−1, 53[thin space (1/6-em)]297 reflections measured, 7644 independent reflections (Rint = 0.0277). The final R1 values were 0.0372 (I > 2σ(I)). The final wR(F2) values were 0.0988 (I > 2σ(I)). The final R1 values were 0.0397 (all data). The final wR(F2) values were 0.1001 (all data). The goodness of fit on F2 was 1.093. Crystal data for 2-H: C27H36IrP, M = 583.73, monoclinic, a = 17.9598(5) Å, b = 8.2824(2) Å, c = 17.0958(5) Å, α = 90.00°, β = 111.7080(10)°, γ = 90.00°, V = 2362.66(11) Å3, T = 173(2) K, space group P21/c, Z = 4, μ = 5.730 mm−1, 38[thin space (1/6-em)]266 reflections measured, 7141 independent reflections (Rint = 0.0369). The final R1 values were 0.0231 (I > 2σ(I)). The final wR(F2) values were 0.0519 (I > 2σ(I)). The final R1 values were 0.0326 (all data). The final wR(F2) values were 0.0547 (all data). The goodness of fit on F2 was 1.046. Crystal data for 3: C28H38IrP, M = 597.75, monoclinic, a = 8.459(4) Å, b = 8.524(4) Å, c = 17.285(8) Å, α = 90.00°, β = 93.025(18)°, γ = 90.00°, V = 1244.5(10) Å3, T = 173(2) K, space group P21, Z = 2, μ = 5.441 mm−1, 25[thin space (1/6-em)]407 reflections measured, 7543 independent reflections (Rint = 0.0690). The final R1 values were 0.0333 (I > 2σ(I)). The final wR(F2) values were 0.0498 (I > 2σ(I)). The final R1 values were 0.0585 (all data). The final wR(F2) values were 0.0542 (all data). The goodness of fit on F2 was 0.870. Because of an intermediate value of the Flack parameter compound 3 was refined as a racemic twin using the TWIN and BASF instructions; the final value of the BASF parameter was 0.130(7).

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Footnotes

† This paper is dedicated with much appreciation to Professor Didier Astruc, on the occasion of his 65th birthday, in recognition of his fundamental contributions to Inorganic and Organometallic Chemistry.

‡ CIF files for compounds 1-Cl, 1-SCN, 2-H and 3. CCDC reference numbers 817784–817787. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20244h

Figure and scheme captions

Scheme 1

Scheme 2. Synthesis of halide and thiocyanate complexes 1-X.

Scheme 3. Synthesis of hydride and alkyl complexes 2–4.

Scheme 4. Deuteration of 1-Cl and 1-Br with CD3OD

Figure 1. ORTEP diagrams for complexes 1-Cl and 1-SCN

Figure 2. ORTEP diagrams of complexes 2-H and 3 (50% probability thermal ellipsoids; H atoms have been omitted for clarity).

Figure 3. Compound 1-Cl labelled for the assignment of 1H and 13C-NMR signals. The same labelling criteria are used for all complexes.

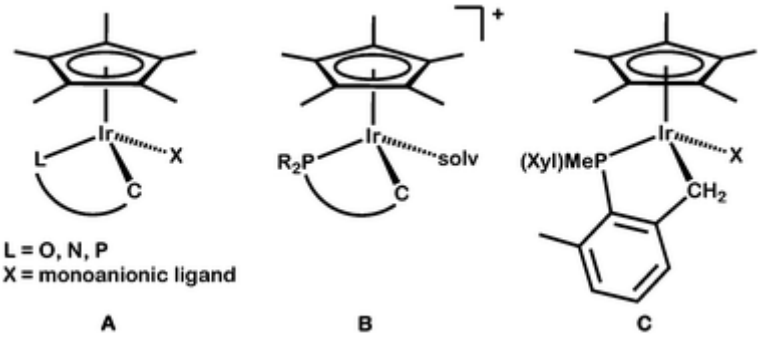
Table 1

Table 1 Dependence of the rate of deuteration of **1-Cl** with CD_3OD concentration[a]

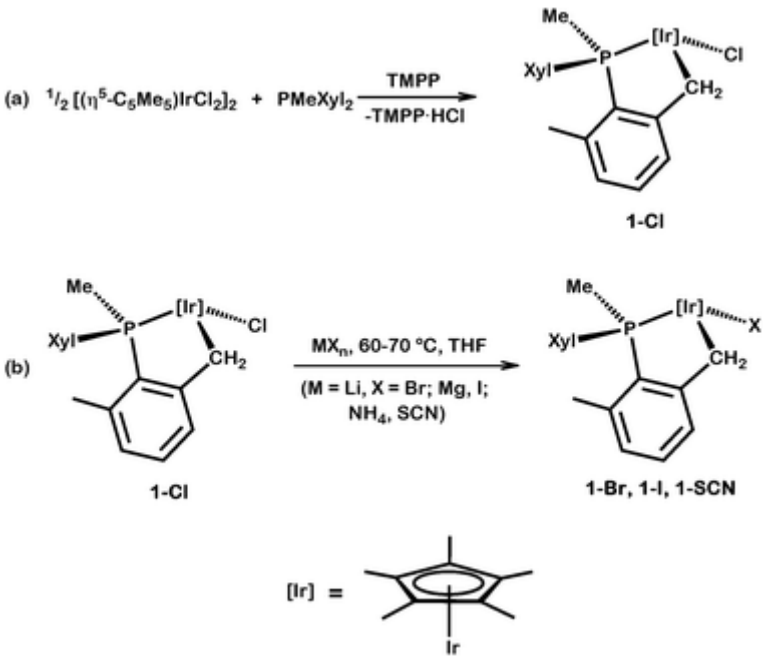
CD_3OD (%)	**$t_{1/2}$/min**
25	900
40	560
50	490
60	240
75	180

a Deuteration reactions carried out in an NMR tube at 45 °C with 0.5 mL of a deuterated solvent at variable ratios of CD_2Cl_2 : CD_3OD.

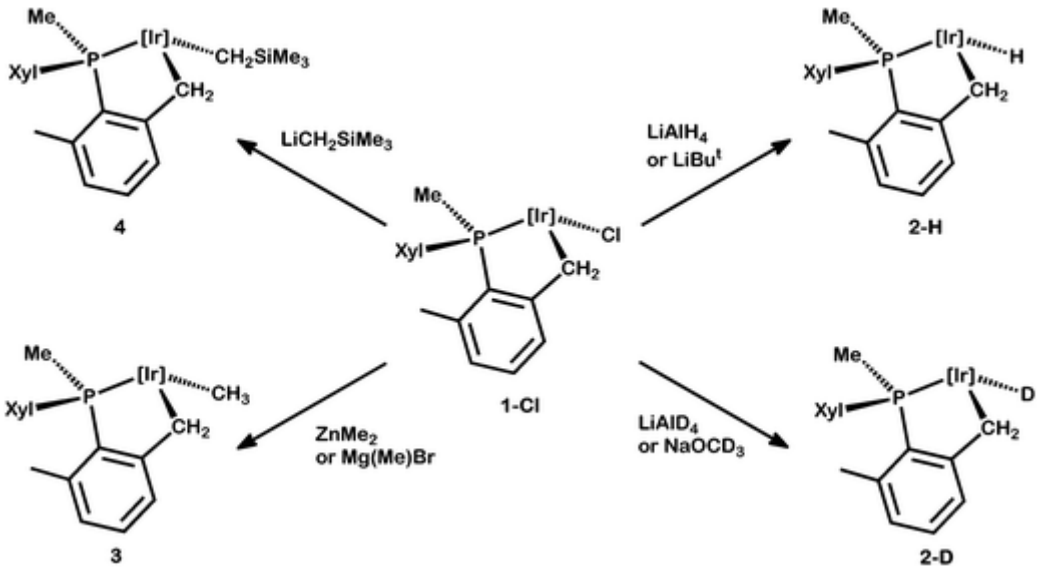
Scheme 1


Ir
L
X
C
L = O, N, P
X = monoanionic ligand
A
Ir
R2P
solv
C
+
B
Ir
(Xyl)MeP
X
CH2
C

Scheme 2


(a) $^1/_2$ [(η^5-C_5Me_5)$IrCl_2$]$_2$ + $PMeXyl_2$
TMPP
-TMPP·HCl
Me
[Ir]
Cl
Xyl
P
CH_2
1-Cl
(b)
MX_n, 60-70 °C, THF
(M = Li, X = Br; Mg, I;
NH_4, SCN)
1-Cl
1-Br, 1-I, 1-SCN
[Ir] =
Ir

Scheme 3


Me
[Ir]
CH2SiMe3
Xyl
P
CH2
4
LiCH2SiMe3
Me
[Ir]
Cl
Xyl
P
CH2
1-Cl
LiAlH4
or LiBut
Me
[Ir]
H
Xyl
P
CH2
2-H
Me
[Ir]
CH3
Xyl
P
CH2
3
ZnMe2
or Mg(Me)Br
LiAlD4
or NaOCD3
Me
[Ir]
D
Xyl
P
CH2
2-D

Scheme 4

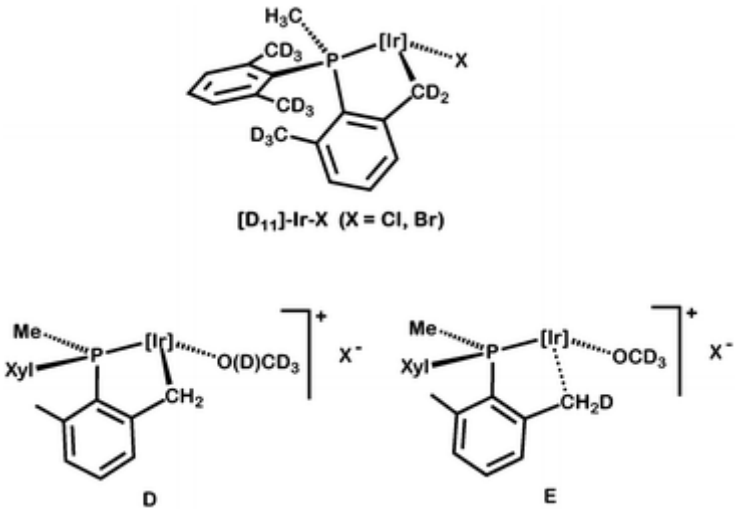

H3C
CD3
P
[Ir]
X
CD2
CD3
D3C
[D11]-Ir-X (X = Cl, Br)
Me
Xyl
P
[Ir]
O(D)CD3
X-
CH2
D
Me
Xyl
P
[Ir]
OCD3
X-
CH2D
E

Figure 1

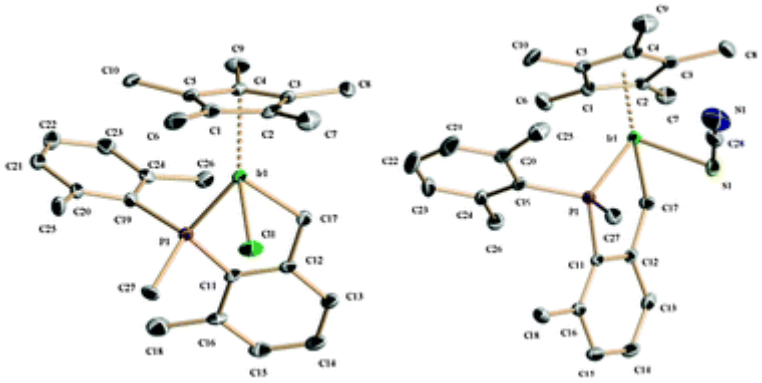


Figure 2

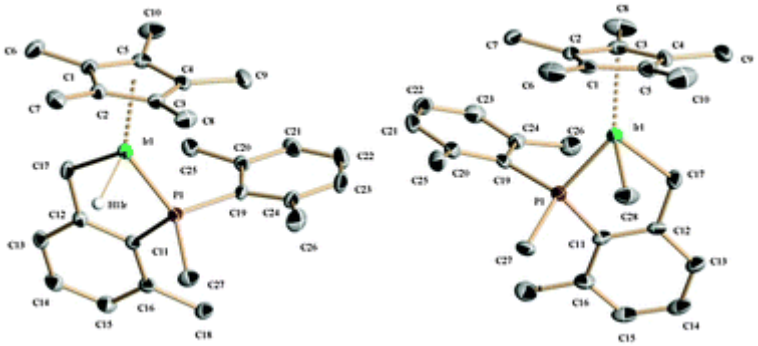


Figure 3