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Optimised Syntheses of the Half-Sandwich Complexes FeCl(dppe)Cp*, FeCl(dppe)Cp, RuCl(dppe)Cp*, and RuCl(dppe)Cp

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Thanks to their synthetic versatility, the half-sandwich metal chlorides MCl(dppe)(η^5-C_5R_5) [M = Fe, Ru; dppe = 1,2-bis (diphenylphosphino)ethane, R = H (cyclopentadiene, Cp), CH_3 (pentamethylcyclopentadiene, Cp*)] are staple starting materials in many organometallic laboratories. Here we present an overview of the synthetic methods currently available for FeCl(dppe)Cp*, FeCl(dppe)Cp, RuCl(dppe)Cp*, and RuCl(dppe)Cp, and describe in detail updated and optimised multigram syntheses of all four compounds.

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Introduction

Half-sandwich complexes are known for all of the d-block metals and most of those in the f-block.[1,2] These systems, typified by complexes of the cyclopentadienyl ligand (Cp), η^5-C_5H_5, and derivatives but also including a wide array of cyclic hydrocarbons, have been fundamental to the development of organometallic chemistry. Through decades of inspiring work, half-sandwich compounds now find application in an immense range of catalytic transformations, including olefin polymerisation[3–6] and asymmetric processes which take advantage of chirality introduced through either substitution of a chiral auxiliary at the periphery of the cyclic hydrocarbon, use of chiral supporting ligands, or otherwise engineering asymmetry in the supporting ligand environment.[7–12] The capacity to control shape, solubility, and supporting ligands of half-sandwich compounds has led to further developments in the use of half-sandwich compounds in biological and biomedical contexts,[13,14] including applications as enzyme inhibitors and metal-based drugs.[15,16]

The synthetic versatility of the generic half-sandwich platform has seen these systems routinely applied as frameworks upon which to support and further develop the chemistry of ligands such as carbenes[17] and vinylidenes,[18] silyls and silyenes,[19] the polyyndiyl and cumulene forms of linear C_n fragments supported by ML_2(η^5-C_5R_5), and related fragments.[20,21] The ligand substitution chemistry that has been developed on various half-sandwich complexes has led to their use as building blocks in supramolecular architectures[22–25] and surface-supported nanoarchitectures,[26,27] and as frameworks for the investigation of non-linear optical properties.[28–33] The synthetic versatility is augmented by well defined one-electron redox processes[34,35] which opens a range of further possibilities for use of these systems as platforms through which to generate and study mixed-valence complexes and electron-transfer phenomena.[36–40] The ability to systematically vary the nature of the metal and the steric and electronic properties of the half-sandwich fragment has allowed detailed investigation of the electronic and spectroscopic properties of such complexes. In this context, the compounds FeCl(dppe)Cp*, $RuCl(PPh_3)_2Cp$, RuCl(dppe)Cp*, MoBr(dppe)(η^7-C_7H_7), and $ReCl(NO)(PPh_3)Cp^*$ (dppe = 1,2-bis(diphenylphosphino)ethane, Cp* = pentamethylcyclopentadiene, η^5-$C_5(CH_3)_5$), which are considerably more electron-rich than similar half-sandwich carbonyl complexes such as $MCl(CO)_2Cp$, $MCl(CO)_2Cp^*$ (M = Fe, Ru), $MoBr(CO)_2$(η^7-C_7H_7), $MCl(CO)_3Cp$, $MCl(CO)_3Cp^*$ (M = Mo, W), have proven to be especially useful.

However, despite the demonstrable utility of both FeCl(dppe)Cp* and RuCl(dppe)Cp* as valuable starting materials, the closely related cyclopentadienyl derivatives FeCl(dppe)Cp[41] and RuCl(dppe)Cp,[42] which offer intermediate electron donor capacity and smaller steric bulk at the metal centre than the Cp* derivatives, have been less thoroughly exploited.[43–47] In part the restricted use of these compounds might be attributed to the limitations in synthetic routes to them. Here we summarise the known synthetic routes to the family of complexes MCl(dppe)(η^5-C_5R_5) (M = Fe, Ru; R = H (Cp), CH_3 (Cp*)), and describe in detail multigram scale procedures which afford these compounds in two-pot processes from commercial $FeCl_2{\cdot}4H_2O$ or $RuCl_3{\cdot}xH_2O$.

Results and Discussion

*FeCl(dppe)Cp**

The iron complex FeCl(dppe)Cp* was first prepared in the late 1980s by Lapinte and co-workers.[48] In this early report colloidal potassium (generated using high intensity ultrasound) was treated with a mixture of pentamethylcyclopentadiene and $[FeCl_2(dppe)]_n$ in a toluene/tetrahydrofuran mixture and allowed to react under ultrasonic irradiation for 30 min at −10°C. An otherwise identical reaction conducted at 50°C yielded the corresponding iron hydride FeH(dppe)Cp*. An alternative procedure involving reaction of lithium pentamethylcyclopentadienide with $[FeCl_2(dppe)]_n$ in tetrahydrofuran under reflux (1 h) or at room temperature (overnight) affording FeCl(dppe)Cp* in 85 % isolated yield was later described.[49] Similar reactions provide a general entry point to $FeCl(PMe_3)_2(\eta^5\text{-}C_5R_5)$ ($C_5R_5 = C_5H_5$ (Cp), $C_5H_4(CH_3)$ (Cp'), $C_5(CH_3)_5$ (Cp*)) complexes.[50]

Most recently, Liddle and colleagues have explored the synthetic chemistry associated with the preparation of a wide range of half-sandwich $FeCl(dppe)(\eta^5\text{-}C_5R_5)$ compounds ($C_5R_5 = C_5H_5$ (Cp), $C_5(CH_3)_5$ (Cp*), $C_5H_4SiMe_3$, $C_5H_3(SiMe_3)_2$, and $C_5H_3(^tBu)_2$).[51] In this case FeCl(dppe)Cp* was synthesised (73 %) by a 1 : 1 reaction of potassium pentamethylcyclopentadienide with $[FeCl_2(dppe)]_n$ in toluene (−78°C → r.t., 18 h), although only generalised reaction conditions were given for the series of half-sandwich complexes reported. The reaction temperature was noted as being important for achieving the reported yields, with formation of ferrocenes and free 1,2-bis(diphenylphosphino)ethane from ligand scrambling processes being problematic in reactions conducted at room temperature, but being largely eliminated in reactions carried out initially at −78°C.

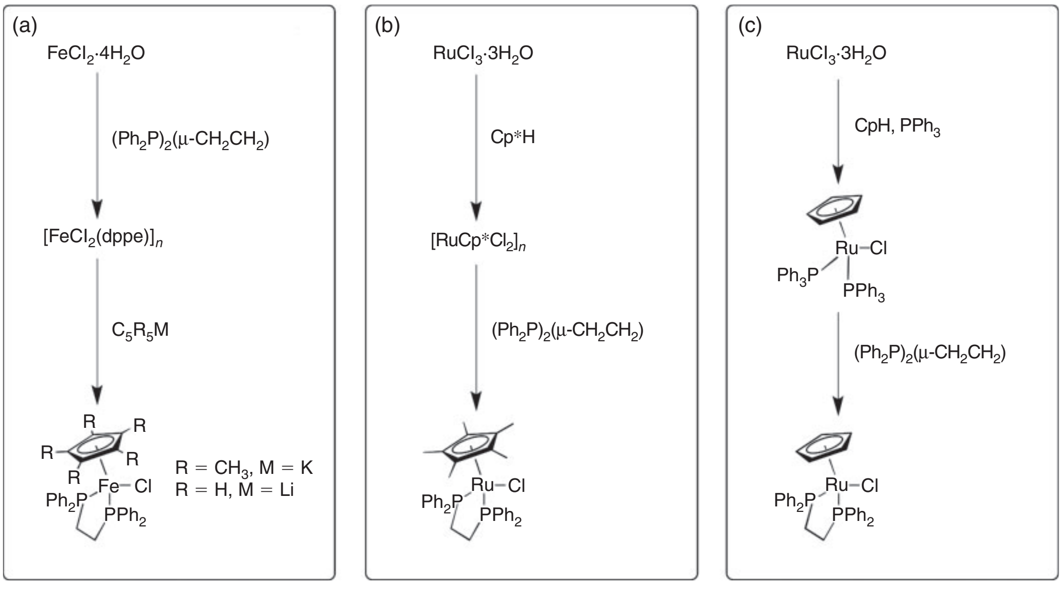
A more convenient laboratory preparation of FeCl(dppe)Cp* would avoid the use of ultrasonic irradiation, and the isolation and manipulation of air sensitive lithium[52] or pyrophoric potassium[53] pentamethylcyclopentadienides, while taking advantage of the ready availability of $[FeCl_2(dppe)]_n$. Although $[FeCl_2(dppe)_2]_n$ is commonly prepared from reaction of anhydrous $FeCl_2$ with 1,2-bis(diphenylphosphino)ethane[41,51] it has been recently shown that $[FeCl_2(dppe)]_n$ can be conveniently synthesised in high yield (~80 %) by treatment of $FeCl_2{\cdot}4H_2O$ with 1,2-bis(diphenylphosphino)ethane in acetone/chloroform mixtures[44,54] thereby avoiding the tedious preparation, or considerably greater cost, of anhydrous $FeCl_2$ (As of March 2016, $FeCl_2{\cdot}4H_2O$ costs ~A\$65 per mole and $FeCl_2$ ~A\$390 per mole, prices from Sigma Aldrich.) Recently, a single crystal X-ray diffraction study identified $[FeCl_2(dppe)]_n$ as a coordination polymer, rather than the often presumed molecular species, $FeCl_2(dppe)$.[54]

Here, the following method is proposed (Scheme 1a). Potassium pentamethylcyclopentadienide is produced in situ by reaction of pentamethylcyclopentadiene with potassium metal in refluxing toluene,[53] and precipitates from the reaction as a fine white powder. The potassium pentamethylcyclopentadienide so produced is not isolated, but rather the reaction mixture is allowed to cool, diluted with a further portion of toluene, and treated with thoroughly dried $[FeCl_2(dppe)]_n$.[44,54] Following overnight reaction at room temperature, the workup involves a simple filtration, removal of solvent, and crystallisation (dichloromethane/*n*-pentane) of the residue. The target complex is obtained in high yield (78 %, relative to K) in a 7.7 mmol reaction as the dichloromethane solvate. Conducting the addition of $[FeCl_2(dppe)]_n$ initially at −78°C did not improve the yield.

FeCl(dppe)Cp

The synthesis of FeCl(dppe)Cp was first reported in 1969 from the reaction of $FeCl(CO)_2Cp$[55,56] with 1,2-bis(diphenylphosphino)ethane in benzene under UV irradiation, and isolated in 45 % yield.[57] Several years later Mays and Sears developed an alternative synthesis of FeCl(dppe)Cp from $[FeCl_2(dppe)]_n$ and thallium cyclopentadienide in a reaction conducted in benzene. Workup involved chromatographic purification to remove ferrocene, which is the main by-product of the reaction.[41]

The arene(cyclopentadienyl) iron complex $[FeCp(\eta^6\text{-}C_6H_5CH_3)]PF_6$ can be obtained by ligand exchange reactions of ferrocene with toluene[58] and reduced to the highly reactive 19-electron radical $FeCp(\eta^6\text{-}C_6H_5CH_3)$ by Na:Hg amalgam.[59] During the course of an exploration of a wide range of reactions in which the toluene ligand is displaced from $FeCp(\eta^6\text{-}C_6H_5CH_3)$ it was found that reaction with 1,2-bis(diphenylphosphino)ethane gave either FeH(dppe)Cp (56 %, from reactions in THF) or FeCl (dppe)Cp (30 %, from reactions in CH_2Cl_2), although limited synthetic details were given. In a similar study detailing



Scheme 1. Syntheses of (a) FeCl(dppe)Cp* and FeCl(dppe)Cp, (b) RuCl(dppe)Cp*, and (c) RuCl(dppe)Cp.

investigations of the scope and the mechanism of the reactions of [CpFe(COD)][Li(TMEDA)] (COD = 1,5-cyclooctadiene, TMEDA = tetramethylethylenediamine) with benzyl halogens,[60] FeCl(dppe)Cp was observed in ~2 % conversion following reaction with $C_6H_5CH_2Cl$ in the presence of 1,2-bis (diphenylphosphino)ethane, the major product being identified as $Fe(CH_2C_6H_5)(dppe)Cp$.

More recently, several groups have reported syntheses of FeCl(dppe)Cp using methods closely related to that originally described by Mays and Sears,[41] and involve treatment of $[FeCl_2(dppe)]_n$ with a metal cyclopentadienide (M = Li[43,51] or Tl[44]) in an aromatic solvent. Two points are worth highlighting from these more modern investigations: as detailed in the discussion of FeCl(dppe)Cp* one report notes that conduction of the reaction initially at −78°C suppresses the formation of ferrocene derivatives;[51] the use of a sub-stoichiometric amount of thallium cyclopentadienide also limits the formation of ferrocene, with the excess $[FeCl_2(dppe)_2]_n$ being readily removed by filtration together with thallium chloride from the reaction mixture during workup.[44]

In elegant recent studies, the groups of Bouwman[61] and Whiteley[62] have shown the thermal conversion of $FeI(CO)_2Cp$ to FeI(dppe)Cp in yields of 74 % (0.2 mmol scale) to 48 % (8.2 mmol scale), and taking advantage of the strong Fe–I bond which hinders the formation of the cationic mono-carbonyl substitution product [Fe(CO)(dppe)Cp]I. While this approach is not suitable for the synthesis of the chloride complex FeCl(dppe) Cp, which is the focus of this discussion, FeI(dppe)Cp displays essentially identical reactivity to FeCl(dppe)Cp and thus is a viable alternative entry into such half-sandwich systems.

Our efforts towards producing FeCl(dppe)Cp in a convenient laboratory setting have considered approaches from [FeCl (dppe)]$_n$ and metal cyclopentadienide sources. The use of thallium cyclopentadienide in the manner originally described by Mays and Sears[41] and later optimised[44] is highly effective, but the use of toxic thallium reagents is less than desirable. Efforts to arrive at a synthetic method that takes advantage of an in situ synthesis of an alkali metal cyclopentadienide (M = Li, Na, K) resulted in a maximum yield of 37 % from M = Li. Although isolating alkali metal organometallics is less convenient than an in situ approach, lithium cyclopentadienide can be handled without issue in a glovebox, is considerably less sensitive to atmospheric exposure than the corresponding pyrophoric sodium[63] and potassium[64] compounds, and naturally avoids the toxicity issues associated with thallium compounds. We therefore consider that on balance the route proposed by Liddle and co-workers[51] provides the best entry into the chemistry of FeCl(dppe)Cp. Solid samples of lithium cyclopentadienide[65] and $[FeCl_2(dppe)]_n$ are prepared and isolated, the solids are mixed in a Schlenk flask under nitrogen (a glovebox greatly simplifies this procedure) and the flask cooled to −78°C (dry ice/acetone). Dry toluene is added dropwise to the reaction flask, which is then left to warm slowly to room temperature. Workup consists of a simple filtration and crystallisation, and affords the desired compound in 72 % yield from a 7.6 mmol scale reaction (Scheme 1a).

*RuCl(dppe)Cp**

The complex RuCl(dppe)Cp* was reported essentially simultaneously by two independent research groups using different approaches. Treichel et al. described a ligand exchange reaction from 1,2-bis(diphenylphosphino)ethane and $RuCl(PPh_3)_2Cp^*$, the initial ruthenium complex being prepared in a one pot reaction from $RuCl_3{\cdot}xH_2O$, triphenylphosphine, and pentamethylcyclopentadiene,[66] in a manner entirely analogous to the synthesis of $RuCl(PPh_3)_2Cp$.[67] In contrast the group of Suzuki and Moro-oka reacted oligomeric $[RuCl_2Cp^*]_n$, obtained from direct reaction of $RuCl_3{\cdot}xH_2O$ and pentamethylcyclopentadiene in refluxing methanol[68] or ethanol,[69] with 1,2-bis(diphenylphosphino)ethane in ethanol (room temperature) to give the target compound RuCl (dppe)Cp* in 41 % yield.[69]

The product obtained from the reaction of $RuCl_3{\cdot}xH_2O$ with pentamethylcyclopentadiene in alcohol solvents is often described as either a dimer $[RuCl_2Cp^*]_2$, or the oligomeric (or polymeric) form $[RuCl_2Cp^*]_n$. In the course of their investigations, the Suzuki and Moro-oka group noted the synthesis of this key reagent $[RuCl_2Cp^*]_x$ ($x = 2$ or n) was sensitive to the nature of the solvent used in the preparation;[69] similar observations on the composition of this material and the formation of decamethylruthenocene as a by-product having also been made by Tilley et al.[68] Later, Koelle and Kossakowski explored and optimised the synthesis of $[RuCl_2Cp^*]_2$, noting that the use of methanol and a 2.5 fold excess of pentamethylcyclopentadiene gave better yields of the less soluble oligomeric species $[RuCl_2Cp^*]_n$, while the use of ethanol led to greater proportions of the more soluble dimer $[RuCl_2Cp^*]_2$ with decamethylruthenocene as a by-product in up to 30 % yield. The dimeric $[RuCl_2Cp^*]_2$ obtained using ethanol as the solvent was described as redder in colour, more soluble and leading to cleaner subsequent reactions. Reduction of the dimer with cobaltocene gave the mixed valence dimer $[(Cp^*Ru)_2(\mu\text{-}Cl)_3]$. Both RuCl(dppe)Cp* and $RuCl(PPh_3)_2Cp^*$ were synthesised by reaction of the mixed valence compound with the appropriate phosphine, the yield indicative of reaction of only the 'Ru^{II}' portion of the dimer.[70]

Aside from a mention of the formation of RuCl(dppe)Cp* in a study of the enthalpies of displacement of COD from RuCl (COD)Cp* with a variety of bidentate phosphines and arsines,[71] which is not an attractive synthetic procedure both step- and yield-wise, subsequent reports[72–74] have focussed on small scale variations on the ligand exchange synthesis originally described by Treichel and co-workers.[66]

Seeking to develop a simplified, optimised, high yielding, multigram procedure we reinvestigated the Tilley, Grubbs, and Bercaw, and Suzuki and Moro-oka based procedures. Reaction of ~2.8 equivalents of pentamethylcyclopentadiene with $RuCl_3{\cdot}xH_2O$ in methanol yielded the intermediate oligomeric ruthenium species $[RuCl_2Cp^*]_n$ as an insoluble brown powder, which was freed of decamethylruthenocene by washing with hexanes. Subsequent reaction of $[RuCl_2Cp^*]_n$ with 1,2-bis (diphenylphosphino)ethane under reflux in ethanol (Scheme 1b) allowed the isolation of RuCl(dppe)Cp* in 87 % yield (relative to $RuCl_3{\cdot}xH_2O$, 12.1 mmol scale) by crystallisation directly from the reaction mixture. Thus the target half-sandwich complex can be synthesised in a two pot, two step reaction sequence directly from $RuCl_3{\cdot}xH_2O$ avoiding any intermediate purification or chromatography.

RuCl(dppe)Cp

Three separate groups reported the synthesis of RuCl(dppe)Cp nearly simultaneously in late 1979 and early 1980,[42,75,76] by thermally driven phosphine exchange of 1,2-bis(diphenylphosphino)ethane with $RuCl(PPh_3)_2Cp$ in refluxing benzene or toluene in yields of ~80 %.[42] Over the following years several researchers have explored this ligand exchange synthesis with slight variations on the early procedures.[43,45,46,66,77–80] An important point highlighted in two of these studies is that the side products $RuCl_2(dppe)_2$ and $[RuClCp]_2(\eta^2$-μ_2-dppe$)_2$ can be isolated when the ligand exchange reaction is carried out using 2[80]–10 mol-%[45] excess of 1,2-bis(diphenylphosphino)ethane. The original Bruce report also notes formation of an initial yellow precipitate which was discarded before the desired product was isolated by crystallisation,[42] suggesting that one or both of the side products described by later researchers was also formed in this early work. Interestingly, phosphine exchange reactions of $RuCl(PPh_3)_2Cp$ with one equivalent of 1,2-bis(diphenylphosphino)methane (dppm) under conditions of high concentration (0.1 M) in benzene leads to the mono-substituted product $RuCl(PPh_3)(\kappa^1$-dppm)Cp (dppm = 1,1-bis(diphenylphosphino)methane).[81] Presumably, competition with the liberated triphenylphosphine prevents the ligand exchange equilibria from shifting to the four membered chelate ring. In more dilute solution (0.005 M), the competition with external triphenylphosphine is less significant and RuCl(dppm)Cp is obtained.[42,81] In contrast, the greater stability of the five-membered chelate in RuCl(dppe)Cp leads to ready formation of this species from $RuCl(PPh_3)_2Cp$ and 1,2-bis(diphenylphosphino)ethane under a range of concentrations.[42,43,45,46,66,75–80] As described below, the 1 : 1 reaction of $RuCl(PPh_3)_2Cp$ and 1,2-bis(diphenylphosphino)ethane in refluxing toluene yields only the desired complex RuCl(dppe)Cp (94 % isolated yield, 5.5 mmol scale) even from relatively concentrated solutions.

Routes requiring milder conditions for the final step in the synthesis of RuCl(dppe)Cp exist; typically these involve displacement of a more labile, unsaturated organic ligand from a cyclopentadienyl ruthenium precursor. However, while the final step in these syntheses is indeed mild, the production of the labile precursors is decidedly non-trivial. The methods discussed include thermal decomposition of the η^3-allyl ruthenium complex $RuCl(Me)(\eta^3$-$C_3H_5)Cp$ in the presence of 1,2-bis(diphenylphosphino)ethane. The precursor $RuCl(Me)(\eta^3$-$C_3H_5)Cp$ is produced by substitution of the corresponding dichloride $RuCl_2(\eta^3$-$C_3H_5)Cp$ with methyl lithium.[82] In turn, $RuCl_2(\eta^3$-$C_3H_5)Cp$ is obtained from oxidative addition of allyl chloride with $RuCl(CO)_2Cp$, carried out in decane at 140°C[82] Further reports describe substitution of the cyclooctadiene ligand of RuCl(COD)Cp by 1,2-bis(diphenylphosphino)ethane, although the synthesis of RuCl(COD)Cp involves the use of thallium cyclopentadienide and carbon tetrachloride,[83,84] and reaction of $[RuCp(C_{10}H_{10})]^+$ with a halide source, typically a tetrabutylammonium halide, and 1,2-bis(diphenylphosphino)ethane.[85] However, the synthesis of this precursor $[RuCp(C_{10}H_{10})]^+$, among other difficulties, requires ruthenocene (involving a challenging synthesis itself)[86] as a starting material and includes a 50 h reflux.[87]

The most regularly used route to RuCl(dppe)Cp, based on the procedures for ligand exchange from $RuCl(PPh_3)_2Cp$ developed by Bruce and co-workers,[42] Davies and Scott, [75] and Treichel and Komar,[76] is recognisably robust. However, we felt there may be a possibility of improving on the established thermal phosphine exchange reaction of $RuCl(PPh_3)_2Cp$ and 1,2-bis(diphenylphosphino)ethane and so explored the prospect of reducing the number of steps and reagents required to make the target complex. Thus, 1,2-bis(diphenylphosphino)ethane was dissolved in an ethanol/tetrahydrofuran mixture at reflux, and a mixture of freshly cracked cyclopentadiene and $RuCl_3{\cdot}xH_2O$ was added in a steady stream. This method was intended to mimic that used in the synthesis of $RuCl(PPh_3)_2Cp$[67] and $RuCl(PPh_3)_2Cp^*$,[66] however the desired product was not obtained. Instead, pure *trans*-$RuCl_2(dppe)_2$ was isolated and identified by ^1H and ^{31}P NMR spectroscopy of the precipitate formed in this reaction. This is consistent with the early syntheses of *trans*-$RuCl_2(dppe)_2$[88] and the observations of side products in the established phosphine exchange synthesis of RuCl(dppe)Cp.[45,89] A revised synthesis of this material is described below.

In our hands, RuCl(dppe)Cp was best obtained following reaction of $RuCl(PPh_3)_2Cp$[67] with 1,2-bis(diphenylphosphino)ethane in a 1 : 1 ratio under reflux in toluene (94 % yield, 5.5 mmol scale, Scheme 1c). Workup consists of reduction of the solution volume and addition of hexanes to precipitate the product, which is recovered by a simple filtration. This procedure is essentially very similar to the wealth of previous reports,[42,43,45,46,66,75–80] however taking care to employ the correct stoichiometric ratio of ruthenium to phosphine allows the product to be obtained in high yield and purity directly from the reaction mixture.

trans-*$RuCl_2(dppe)_2$*

As noted above, attempts to synthesise RuCl(dppe)Cp directly from $RuCl_3{\cdot}xH_2O$, cyclopentadiene and 1,2-bis(diphenylphosphino)ethane resulted in the isolation of pure *trans*-$RuCl_2(dppe)_2$. These findings are consistent with the early organometallic literature where the synthesis of *trans*-$RuCl_2(dppe)_2$ is described under very similar conditions.[88] Accordingly a targeted synthesis of *trans*-$RuCl_2(dppe)_2$ was developed by addition of an ethanol solution of $RuCl_3{\cdot}xH_2O$ to a solution of 1,2-bis(diphenylphosphino)ethane in a refluxing tetrahydrofuran/ethanol mixture. This results in almost immediate formation of a yellow crystalline precipitate, the reaction being complete within 10 min. Following cooling of the reaction solution, *trans*-$RuCl_2(dppe)_2$ can be isolated in 88 % yield via simple filtration.

Conclusion

Robust, large scale, high yield syntheses for the widely used family of half-sandwich complexes $MCl(dppe)(\eta^5$-$C_5R_5)$ (M = Fe, Ru; R = H (Cp), CH_3 (Cp*)) obtained in two-pot processes from commercial $FeCl_2{\cdot}4H_2O$ or $RuCl_3{\cdot}xH_2O$ have been described in detail. These methods represent, in our hands, the most convenient entry to the chemistry of these versatile reagents and minimise the use of highly toxic (TlCp) or isolation of highly pyrophoric (KCp*) compounds. The ready availability of these MCl(dppe)Cp derivatives should see growth in the interest in these compounds within the myriad of applications of half-sandwich compounds and add further opportunities to explore the electronic and steric effects of the ligand sphere in the chemistry of ML_2Cp'-derived complexes.

Experimental

General Conditions

All reactions were carried out under an atmosphere of dry argon (FeCl(dppe)Cp*) or nitrogen (all other reactions) using standard Schlenk techniques. Toluene and hexanes were dried by passage over an alumina column, other solvents were standard reagent grade and used as received. No special precautions were taken to exclude air or moisture during workup except where otherwise indicated. Commercial pentamethylcyclopentadiene was distilled before use, cyclopentadiene was freshly cracked from dicyclopentadiene,[90] and $RuCl(PPh_3)_2Cp$[67] and lithium cyclopentadienide[65] were synthesised according to literature procedures. All other reagents were commercially available and used as received. As the water content of $RuCl_3$ varies and is difficult to accurately determine, all calculations were performed assuming that the molecular formula is $RuCl_3{\cdot}3H_2O$. NMR spectra were recorded at 25°C on a Bruker Avance III HD 600 (^{1}H 600.1 MHz, ^{13}C 150.9 MHz, ^{31}P 242.9 MHz) or a Varian Inova 300 (^{1}H 300.2 MHz, ^{31}P 121.5 MHz) spectrometer using $CDCl_3$ or C_6D_6 as the solvent. Chemical shifts were determined relative to internal residual solvent signals (^{1}H, ^{13}C)[91] or external 85 % H_3PO_4 (^{31}P 0.0 ppm).

Synthesis of [FeCl$_2$(dppe)]$_n$

Acetone (480 mL) was deoxygenated by sparging with nitrogen, and $FeCl_2{\cdot}4H_2O$ (10.0 g, 50.5 mmol) was added giving a green suspension. Separately, 1,2-bis(diphenylphosphino)ethane (20.2 g, 50.8 mmol) was dissolved in chloroform (120 mL) and the solution also deoxygenated by sparging. The 1,2-bis(diphenylphosphino)ethane solution was then transferred into the stirred $FeCl_2{\cdot}4H_2O$ mixture via cannula; during the addition a white precipitate began to form almost immediately. This reaction mixture was subsequently heated to reflux for 3 h after which a copious white precipitate had formed. The precipitate was collected by filtration, washed with diethyl ether (3 × 100 mL) and dried, first in air and then in a vacuum desiccator for a minimum of 16 h, to afford $[FeCl_2(dppe)]_n$ in 98 % yield as a free flowing cream powder (26.2 g, 49.9 mmol).[†]

Synthesis of [FeCl(dppe)Cp] · CH$_2$Cl$_2$*

Warning: Potassium pentamethylcyclopentadienide is a highly reactive material, spontaneously combustible in air.[53] *The procedures described below are designed to avoid the isolation of this compound and any exposure of this material to the atmosphere must be avoided.*

A mixture of potassium (300 mg, 7.67 mmol), pentamethylcyclopentadiene (1.15 g, 8.44 mmol), and toluene (15 mL) was heated to reflux until a fine white precipitate had formed and pieces of potassium metal were no longer visible (~3 h). Following cooling of the reaction mixture to ambient temperature, toluene (35 mL) was added followed by $[FeCl_2(dppe)]_n$ (4.31 g, 8.21 mmol) and the resulting dark mixture was stirred for 16 h. Subsequently, the reaction mixture was filtered through Celite and the filter cake was washed with toluene until the washings were colourless (~60 mL). The combined filtrant and washings were then concentrated to dryness, and the residue was dissolved in the minimum volume of dichloromethane (~15 mL) and layered with *n*-pentane (~60 mL). This mixture was left undisturbed overnight to afford large black crystals and a fine brown powder, the crystals were recovered by decanting the liquors and fine particles, and washing with *n*-pentane to afford $[FeCl(dppe)Cp^*]{\cdot}CH_2Cl_2$ as black crystals in 78 % yield (3.74 g, 5.99 mmol). δ_H (300.2 MHz, C_6D_6) 1.34 (br s, 15H, $C_5(CH_3)_5$), 1.83 (br s, 2H, dppe), 2.41 (br s, 2H, dppe), 4.27 (s, 2H, CH_2Cl_2), 7.03–7.27 (m, 16H, C_6H_5), 8.01 (br s, 4H, C_6H_5). δ_P (121.5 MHz, C_6D_6) 92.4. Found: C 62.29, H 5.82. Anal. Calc. for $C_{36}H_{39}P_2ClFe{\cdot}CH_2Cl_2$: C 62.60, H 5.88 %.

The signals in the NMR spectra of $[FeCl(dppe)Cp^*]{\cdot}CH_2Cl_2$ are broad. This effect is minimised by the use of C_6D_6 as the NMR solvent. Spectra recorded in CD_2Cl_2 are broader, but the key signals are still identifiable although naturally the solvent of crystallisation (CH_2Cl_2) is not. Spectra recorded in $CDCl_3$ give rise to very broad signals, providing little meaningful information. Introduction of a reducing agent, cobaltocene, did not alter the signal resolution and so these effects are presumably due to some spin crossover to the high-spin d_6 Fe^{II} form.

Synthesis of Lithium Cyclopentadienide[65]

Warning: Although no difficulties have been encountered in the preparation or handling of lithium cyclopentadienide, which is considerably less reactive than the Na or K analogues, organolithiums should be regarded as air-sensitive, flammable, and potentially pyrophoric materials. All manipulations of this compound should be conducted under a rigorously anaerobic environment, by a competent worker.

Cyclopentadiene (5.06 g, 76.6 mmol) was dissolved in hexanes (120 mL), the solution was cooled to 0°C (ice/salt cooling bath) and *n*-butyl lithium (30.6 mL, 2.5 M, 76.6 mmol of *n*-BuLi) was added dropwise over a 10 min period. The reaction mixture quickly developed a thick white suspension, which was stirred for 18 h and allowed to warm slowly to ambient temperature. The product was isolated by filtration under Schlenk conditions, washed with dry hexanes (3 × 50 mL), and vacuum dried affording lithium cyclopentadienide as a white powder in 78 % yield (4.29 g, 59.6 mmol) which was transferred to a nitrogen filled glovebox for subsequent manipulation. δ_H (600.1 MHz, $(CD_3)_2SO$) 5.33. δ_C (150.9 MHz, $(CD_3)_2SO$) 103.0. The ^{13}C NMR data are in agreement with the literature.[92]

Synthesis of FeCl(dppe)Cp

Lithium cyclopentadienide (549 mg, 7.62 mmol) and $[FeCl_2(dppe)]_n$ (4.00 g, 7.62 mmol) were combined in a Schlenk flask within a glove box, before being transferred to an efficient Schlenk line to conduct the remainder of the experiment. The flask containing the solid reagents was cooled to −78°C (dry ice/acetone cooling bath), and toluene (50 mL) was added dropwise over 10 min to the stirred mixture. Upon completion of solvent addition the cooling bath was left in place and the reaction mixture, an off-white suspension, was allowed to stir and slowly warm to room temperature over a period of 16 h. After this time the deep blue-black mixture was filtered through Celite and washed through with dichloromethane (200 mL). The combined washings were concentrated to dryness and the black residue dissolved in the minimum volume of dichloromethane (~10 mL) and layered with *n*-pentane (~50 mL). This mixture was left undisturbed overnight yielding blue-black crystals which were recovered by decanting the liquors and washing with *n*-pentane to afford FeCl(dppe)Cp as blue-black crystals in 72 % yield (3.05 g, 5.49 mmol). δ_H (600.1 MHz, C_6D_6) 2.02 (m, 2H, dppe), 2.34 (m, 2H, dppe), 4.17 (s, 5H, C_5H_5), 6.93 (m, 4H, C_6H_5), 6.99 (m, 2H, C_6H_5), 7.10 (m, 4H, C_6H_5), 7.17 (m, partly obscured by C_6D_5H signal, 2H, C_6H_5), 7.24 (m, 4H, C_6H_5), 8.13 (m, 4H, C_6H_5). δ_P (242.9 MHz, C_6D_6) 97.8. Found: C 67.23, H 5.32. Anal. Calc. for $C_{31}H_{29}P_2ClFe$: C 67.11, H 5.27 %.

*Synthesis of RuCl(dppe)Cp**

Pentamethylcyclopentadiene (4.0 mL) was added to a suspension of $RuCl_3{\cdot}3H_2O$ (3.16 g, 12.1 mmol) in methanol (50 mL) and the mixture was heated to reflux for 6 h. Subsequent cooling, first to ambient temperature and then to 0°C, gave a black solid in a black solution. The solid was isolated by filtration and washed with

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[†] Failure to deoxygenate the solvents in this procedure will lead to brown colouration of the product, presumably due to the formation of Fe^{III} oxide species. Such samples can be further utilised, although will result in lower yields of the relevant half-sandwich complex. The complex $[FeCl_2(dppe)]_n$ should be stored under inert atmosphere, prolonged storage in air results in a green colouration.

methanol (50 mL) and then with hexanes until the washings were colourless (~100 mL) affording 3.22 g of $[RuCl_2Cp^*]_n$ as a brown powder after drying in air. This solid was dissolved in ethanol (45 mL) along with 1,2-bis(diphenylphosphino)ethane (5.40 g, 13.6 mmol, 1.3 equiv. relative to $[RuCl_2Cp^*]_n$) and the mixture was heated to reflux for 18 h, followed by cooling to ambient temperature and then to 0°C. The resulting precipitate was collected by filtration and washed with hexanes until the washings were pale yellow affording RuCl(dppe)Cp* in 74 % yield as an orange solid (6.01 g, 8.96 mmol). Storage of the ethanolic reaction solution at 0°C yielded a further crop of RuCl(dppe)Cp* as red crystals (1.03 g, 1.54 mmol, 13 %). Total yield 87 % (7.04 g, 10.5 mmol) relative to $RuCl_3{\cdot}3H_2O$. δ_H (600.1 MHz $CDCl_3$) 1.43 (s, 15H, $C_5(CH_3)_5$), 2.13 (m, 2H, CH_2 (dppe)), 2.67 (m, 2H, CH_2 (dppe)), 7.19 (m, 4H, aryl dppe), 7.30 (m, 4H, aryl dppe), 7.36 (m, 8H, aryl dppe), 7.68 (m, 4H, aryl dppe). δ_P (242.9 MHz, $CDCl_3$) 75.2. Found: C 64.53, H 5.92. Anal. Calc. for $C_{36}H_{39}P_2ClRu$: C 64.52, H 5.87 %.

Synthesis of RuCl(dppe)Cp

A mixture of $RuCl(PPh_3)_2Cp$ (4.00 g, 5.51 mmol), 1,2-bis(diphenylphosphino)ethane (2.18 g, 5.47 mmol), and toluene (50 mL) was heated to reflux for 20 h, allowed to cool to ambient temperature, and concentrated to half of the original volume. Hexanes (30 mL) was added to the resulting orange slurry and the solids were collected by filtration, washed with hexanes (30 mL) and diethylether (30 mL), and dried in air to afford RuCl(dppe)Cp in 94 % yield as a yellow-orange solid (3.08 g, 5.14 mmol).δ_H (300.2 MHz, $CDCl_3$) 2.40 (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 4.54 (s, 5H, C_5H_5), 7.13–7.19 (m, 4H, C_6H_5), 7.24–7.31 (m, 8H, C_6H_5), 7.38–7.42 (m, 4H, C_6H_5), 7.87 (m, 4H, C_6H_5). δ_P (121.5 MHz, $CDCl_3$) 80.7. Found: C 62.18, H 4.94. Anal. Calc. for $C_{31}H_{29}P_2ClRu$: C 62.05, H 4.87 %.

Synthesis of trans-*RuCl*$_2$*(dppe)*$_2$

A mixture of 1,2-bis(diphenylphosphino)ethane (3.81 g, 9.56 mmol), ethanol (100 mL), and tetrahydrofuran (8 mL) was heated at high reflux until a colourless solution was obtained. Separately, $RuCl_3{\cdot}3H_2O$ (1.00 g, 3.82 mmol) was dissolved in hot ethanol (10 mL) and the dark brown solution was allowed to cool to room temperature before being added steadily dropwise over a 5 min period to the refluxing phosphine solution. Any remaining $RuCl_3{\cdot}3H_2O$ in the dropping funnel was washed into the reaction mixture with a further 10 mL of ethanol and reflux was continued for 10 min until the reaction mixture consisted of a yellow precipitate in a pale brown solution. The precipitate was recovered by filtration and washed with acetone (3 × 50 mL) to afford *trans*-$RuCl_2(dppe)_2$ in 88 % yield as a bright yellow crystalline solid (3.26 g, 3.37 mmol). δ_H (600.1 MHz, $CDCl_3$) 2.74 (m, 8H, CH_2), 7.01 (t, 16H, *J* 7.7, C_6H_5), 7.20 (t, 8H, *J* 7.4, C_6H_5), 7.26–7.28 (m, 16H, C_6H_5). δ_P (242.9 MHz, $CDCl_3$) 46.0. Found: C 64.56, H 4.88. Anal. Calc. for $C_{52}H_{48}P_4Cl_2Ru$: C 64.47, H 4.99 %.

Supplementary Material

Proton NMR spectra for FeCl(dppe)Cp*, FeCl(dppe)Cp, RuCl(dppe)Cp*, RuCl(dppe)Cp, and *trans*-$RuCl_2(dppe)_2$ are available on the Journal's website.

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