DALTON COMMUNICATION

Intramolecular S_NAr reactions as a route to complexes of hybrid cyclopentadienyl–phosphine ligands: synthesis of a rhodium complex of the first η^5,η^1,η^1-cyclopentadienyl–phosphine–thioether ligand

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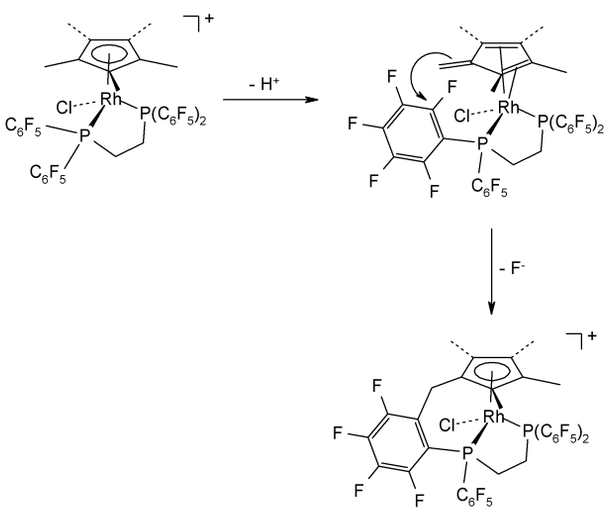
A convenient synthetic route to hybrid cyclopentadienyl–phosphine complexes is demonstrated by the high yield synthesis of the complex $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe\}][BF_4]$.

Cyclopentadienides and phosphines are two of the most common and important classes of ligand employed in organometallic chemistry. The coupling of these two ligand types in chelating bi- or tri-functional ligands is currently an area of intense activity since these hybrid cyclopentadienyl–phosphine ligands are expected to exert different effects on metal reactivity compared to the separated ligands.[1] For example, enhancement of the substrate selectivity and reaction regio- and stereoselectivity is anticipated. Despite these advantages the number of chelating hybrid cyclopentadienyl–phosphine ligands is limited.[1] One reason for this scarcity is the lack of convenient syntheses. Three synthetic approaches to complexes of hybrid ligands are envisaged: (i) prior synthesis of the ligand followed by coordination to the metal, (ii) coordination of both functionalities of the hybrid ligand to the metal followed by a metal-templated intramolecular coupling, (iii) coordination of one functionality of the hybrid ligand to the metal followed by intermolecular coupling to the second functionality and subsequent chelation.

The first strategy is currently the most commonly adopted route to metal complexes of hybrid cyclopentadienyl–phosphine ligands, but suffers from the disadvantage that ligand syntheses are often elaborate, involving multiple steps, and consequently poor overall yields are obtained.[1] The second approach provides a method of overcoming this problem. Since the two functionalities are held in close proximity by coordination to the metal, high yields coupled with high regioselectivities are expected. Despite the appeal of this approach there are very few reports of intramolecular reactions leading to complexes of hybrid cyclopentadienyl–phosphine ligands: the reaction of decafluoroazobenzene with $[RuMe(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ produces the hybrid cyclopentadienyl–phosphine ligand complex $[RuC_6F_4N{=}NC_6F_5(\eta^5,\eta^1\text{-}C_5H_4C_6H_4PPh_2)]$ in moderate yield,[2] the rhodium complex cation $[RhCl(PPh_2CH{=}CH_2)_2(\eta^5\text{-}C_5Me_5)]^+$ undergoes radical or base promoted hydroalkylation to give a mixture of the 1,2 and 1,3 isomers of $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3(CH_2CH_2CH_2PPh_2)_2\}]^+$ in 35% and 42% yield respectively,[3,4] and we have reported that in refluxing ethanol the salts $[MX\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}(\eta^5\text{-}C_5Me_4R)][BF_4]$ (M = Rh, X = Cl or Br, R = Me or Et; M = Ir, X = Cl, R = Me) undergo dehydrofluorinative C–C coupling to give $[MX\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_2R[CH_2C_6F_4P(C_6F_5)CH_2]_2\}][BF_4]$ in virtually quantitative yield.[5,6] Although the reaction between $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ and $(C_6H_3F_2\text{-}2,6)_2PCH_2CH_2P(C_6H_3F_2\text{-}2,6)_2$[7] and that between $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_4CF_3)]_2$ and $Ph_2PCH{=}CH_2$ to give $[RhCl_2\{\eta^5\text{-}C_5Me_3(CO_2Et)\text{-}2\text{-}CH_2CH_2CH_2PPh_2\}]$[4] appear to be examples of the third synthetic approach, it is more likely that these also occur by coordination of the phosphine and subsequent intramolecular reaction.

Although the intramolecular dehydrofluorinative C–C coupling reaction of $[RhCl\{(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2\}(\eta^5\text{-}C_5Me_5)][BF_4]$ is inhibited by the presence of triethylamine,[5] we now report that this reaction occurs rapidly at room temperature on addition of the non-nucleophilic base proton sponge 1,8-bis(dimethylamino)naphthalene. *In situ* NMR experiments in $CDCl_3$ show that $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_3[CH_2C_6F_4P(C_6F_5)CH_2]_2\text{-}1,3\}][BF_4]$ is formed quantitatively within 15 min of addition of a stoichiometric quantity of proton sponge. The reaction displays the same high yield and regiospecificity as that shown by the thermolysis in ethanol. On the basis of this observation we propose that the mechanism for this reaction involves initial formation of an η^4-fulvene complex by abstraction of a pentamethylcyclopentadienyl proton, followed by nucleophilic attack (S_NAr) of the methylene carbon atom at the *ortho* position of the pentafluorophenyl group (Scheme 1).



Scheme 1

Although, to date, we have been unable to verify this mechanism by direct observation of an η^4-fulvene complex, it has previously been established that the hydrogen atoms of a cationic η^5-pentamethylcyclopentadienyl rhodium complex are sufficiently acidic to be abstracted by strong base giving η^4-fulvene rhodium complexes which contain a nucleophilic methylene carbon atom,[8] and also that polyfluorinated arenes are susceptible to nucleophilic attack.[9] This mechanism has also been proposed for the similar intramolecular dehydrofluorinative C–C coupling reaction between η^5-pentamethylcyclopentadienyl and perfluorobenzyl ligands coordinated to cobalt.[10] This reaction scheme provides a simple, rational methodology for the synthesis of transition metal complexes of hybrid cyclopentadienyl–phosphine ligands. Here we validate and

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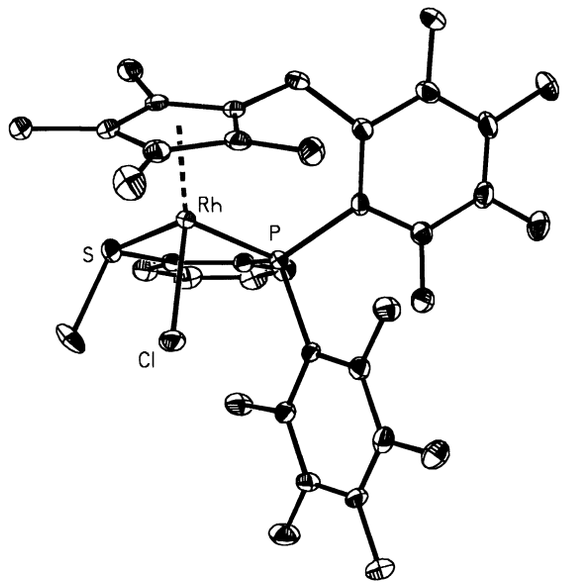
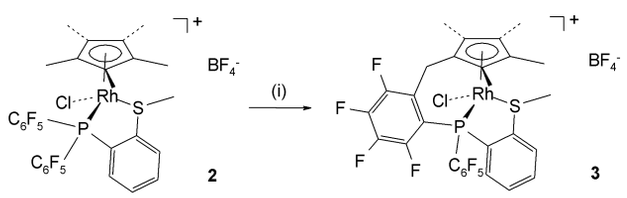


Fig. 1 Structure of the $R_{Rh}R_SS_P$ enantiomer of the cation of **3**. Thermal ellipsoids are at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (°): Cp′–Rh 1.815(4), Rh–P 2.2540(10), Rh–S 2.3502(10), Rh–Cl 2.3719(11); Cp′–Rh–P 126.6(1), Cp′–Rh–S 121.7(1), Cp′–Rh–Cl 124.4(1), P–Rh–S 86.10(4), P–Rh–Cl 93.19(4), S–Rh–Cl 94.71(4). Cp′ denotes the centroid of the cyclopentadienyl ring.

demonstrate the versatility of the methodology by the synthesis of a rhodium complex of the first hybrid η^5,η^1,η^1-cyclopentadienyl–phosphine–thioether ligand.

Treatment of $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ with an excess of sodium tetrafluoroborate and the bifunctional phosphine–thioether $(C_6F_5)_2PC_6H_4SMe$-1,2 **1** † gave the salt $[RhCl\{(C_6F_5)_2PC_6H_4SMe\text{-}1,2\}(\eta^5\text{-}C_5Me_5)][BF_4]$ **2** as an orange oil in *ca.* 80% yield.‡ Treatment of **2** with proton sponge in chloroform afforded the η^5,η^1,η^1-cyclopentadienyl–phosphine–thioether rhodium complex $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe\}][BF_4]$ **3** in *ca.* 90% yield (Scheme 2).§ The identity



Scheme 2 (i) Proton sponge, $CHCl_3$.

of **3** was confirmed by a single-crystal X-ray diffraction study (Fig. 1).¶ The structure clearly shows a C–C bond between an *ortho* carbon atom of a fluorinated phenyl ring and an exocyclic carbon of the pentamethylcyclopentadienyl ring, confirming that dehydrofluorinative C–C coupling has occurred. The cation possesses the expected three-legged geometry about rhodium and contains three stereogenic centres: the phosphorus, rhodium and sulfur atoms. In the crystal structure there is only one pair of enantiomers, $R_{Rh}R_SS_P$ and $S_{Rh}S_SR_P$, and both enantiomers are present within the unit cell. The spectroscopic data of **3** are completely consistent with the structure, and suggest that only this pair of enantiomers are present in solution. The thioether methyl singlet resonance at δ 2.60 shows no broadening on cooling to 228 K, suggesting that this resonance is due solely to one pair of enantiomers and is not the averaged signal of diastereoisomers differing in the configuration at sulfur. Further, ^{1}H spectroscopic studies reveal that this resonance shows an NOE correlation with two resonances assigned to aromatic hydrogen atoms, but not with any of the cyclopentadienyl methyl resonances. These data strongly suggest that only the enantiomers found in the crystal structure are present in solution and that there is configurational stability at the sulfur atom.

In summary we have established a simple and versatile synthetic rationale for hybrid cyclopentadienyl–phosphine complexes based on intramolecular nucleophilic attack by the methylene carbon atom of an η^4-fulvene complex at the *ortho* position of a fluorinated phenylphosphine. The approach was validated by the synthesis of the complex $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe\}][BF_4]$, which contains the first example of a hybrid η^5,η^1,η^1-cyclopentadienyl–phosphine–thioether ligand.

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Notes and references

† $(C_6F_5)_2PC_6H_4SMe$-1,2 **1**. A solution of Bu^{n}Li in hexane (1.5 cm^3, 1.6 M) was added to 2-bromothioanisole (0.50 g, 2.4 mmol) in diethyl ether (50 cm^3) at 0 °C. After stirring for 1 h the solution was added dropwise to $(C_6F_5)_2PBr$ (1.07 g, 2.4 mmol) at 0 °C. The solution was allowed to warm overnight. Water (*ca.* 2 cm^3) was added and the volatiles removed under reduced pressure. The product was obtained as a white solid on recrystallization from methanol. Yield 0.82 g (80%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.44 (m, 2H, C_6H_4), 7.20 (m, 1H, C_6H_4), 7.08 (m, 1H, C_6H_4), 2.51 (s, 3H, SMe). ^{19}F (282.4 MHz, $CDCl_3$): δ −129.15 (m, 4F, *o*-C_6F_5), −149.40 [t, ^3J(F–F) 21.2 Hz, 2F, *p*-C_6F_5), −160.30 (m, 4F, *m*-C_6F_5). ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$): δ −57.4 [quintet, ^3J(P–F) 37 Hz]. EI-MS: *m*/*z* 487 (25%, $[M - H]^+$), 472 (100%, $[M - CH_4]^+$) Found for $[M - H]^+$ 486.97691. $C_{19}H_6F_{10}PS$ requires 486.97682.

‡ $[RhCl\{(C_6F_5)_2PC_6H_4SMe\text{-}1,2\}(\eta^5\text{-}C_5Me_5)][BF_4]$ **2**. $[RhCl(\mu\text{-}Cl)(\eta^5\text{-}C_5Me_5)]_2$ (0.14 g, 0.22 mmol), **1** (0.28 g, 0.44 mol) and $NaBF_4$ (0.11 g, 1 mmol) were treated as for the synthesis of $[RhCl(dfppe)(\eta^5\text{-}C_5Me_5)][BF_4]$.[5] Salt **2** was obtained as an orange oil. Yield 0.40 g (79%). ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 7.95 (m, 1H, C_6H_4), 7.73 (m, 1H, C_6H_4), 7.65 (m, 1H, C_6H_4), 7.54 (m, 1H, C_6H_4), 3.08 (s, 3H, Me), 1.76 [d, J(P–H) 4.7 Hz, 15H, C_5Me_5]. ^{19}F (282.4 MHz, $CDCl_3$): δ −122.05 (m, 1F, *o*-C_6F_5), −126.75 (m, 1F, *o*-C_6F_5), −127.47 (m, 1F, *o*-C_6F_5), −131.36 (m, 1F, *o*-C_6F_5), −141.96 [t, 1F, ^3J(F–F) 19.8, *p*-C_6F_5], −144.39 [t, 1F, ^3J(F–F) 19.8 Hz, *p*-C_6F_5], −153.69 (s, 0.8F, $^{10}BF_4^-$), −153.74 (s, 3.2F, $^{11}BF_4^-$), −154.74 (m, 1F, *m*-C_6F_5), −156.91 (m, 1F, *m*-C_6F_5), −157.84 (m, 1F, *m*-C_6F_5), −160.31 (m, 1F, *m*-C_6F_5). ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$): δ 30.2 [dm, ^1J(Rh–P) 174 Hz].

§ $[RhCl\{\eta^5,\eta^1,\eta^1\text{-}C_5Me_4CH_2C_6F_4P(C_6F_5)C_6H_4SMe\}][BF_4]$ **3**. Salt **2** (0.4 g, 0.35 mmol) in chloroform (50 cm^3) was treated with proton sponge (1,8-bis(dimethylamino)naphthalene, 0.08 g, 0.35 mmol). The mixture was stirred for 30 min, and $NaBF_4$ (0.10 g, 0.9 mol) and water (*ca.* 20 cm^3) were added. The organic layer was separated and the solvent removed under reduced pressure. The resulting orange oil was washed with diethyl ether (2 × 50 cm^3) and dried *in vacuo*. Yield 0.36 g (92%). Crystals for analysis and X-ray diffraction were grown from chloroform. ^{1}H NMR (500.1 MHz, $CDCl_3$): δ 8.08 (m, 1H, C_6H_4), 7.80 (m, 2H, C_6H_4), 7.71 (m, 1H, C_6H_4), 4.36 [dd, J(P–H) 17.2, ^2J(H–H) 17.2, 1H, CH_2], 4.36 [d, J(H–H) 17.2, 1H, CH_2], 2.60 (s, 3H, Me), 2.17 [d, J(P–H) 8.9, 3H, Me], 1.95 [d, J(P–H) 3.5 Hz, 3H, Me], 1.65 (m, 3H, Me), 1.52 (s, 3H, Me). ^{19}F (282.4 MHz, $CDCl_3$): δ −119.73 (m, 1F), −126.32 (m, 1F), −132.89 (m, 1F), −134.35 (m, 1F), −142.43 (m, 1F), −145.50 [t, 1F, ^3J(F–F) 19.8 Hz, *p*-C_6F_5], −151.54 (m, 1F) −153.27 (s, 0.8F, $^{10}BF_4^-$), −153.33 (s, 3.2F, $^{11}BF_4^-$), −158.50 (m, 2F, *m*-C_6F_5). ^{31}P{^{1}H} (121.5 MHz, $CDCl_3$): δ 58.6 [dm, ^1J(Rh–P) 150 Hz]. (Found: C, 33.5; H, 2.1. Calc. for $C_{29}H_{21}BClF_{13}PRhS\cdot2.5CHCl_3$: C, 33.6; H, 2.1%).

¶ Crystal data for **3**·3$CHCl_3$: $C_{32}H_{24}BCl_{10}F_{13}PRhS$, M =1186.76, triclinic, $P\bar{1}$, a = 11.6484(9), b = 11.7516(10), c = 17.7351(14) Å, α = 93.233(2), β = 102.5490(10), γ = 112.3060(10)°, V = 2166.3(3) Å^3, Z = 2, μ(Mo-Kα) = 1.179 mm^{-1}, T = 153(2) K; 14538 reflections were measured, 8998 unique (R_{int} = 0.0521) which were used in all calculations. The final R and $wR(F^2)$ (all data) were 0.0470 and 0.1204 respectively. Data were collected on a Bruker AXS SMART diffractometer and the structure was solved by direct methods using the SHELXTL software package.[11] CCDC reference number 155415. See http://www.rsc.org/suppdata/dt/b0/b010244j/ for crystallographic data in CIF or other electronic format.

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