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Coordination chemistry of perfluoroalkylated phosphorus(III) ligands

David Gudmunsen, Eric G. Hope *, Danny R. Paige, Alison M. Stuart

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

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ABSTRACT

Palladium(II), platinum(II), rhodium(I), rhodium(III) and iridium(III) complexes of the tridecafluorohexyl-derivatised diphenylethylphosphinite ($PPh_2OC_2H_4R_f$), phenyldiethylphosphonite $\{PPh(OC_2H_4R_f)_2\}$, triethylphosphite $\{P(OC_2H_4R_f)_3\}$, triphenylphosphinite ($PPh_2OC_6H_4$-4-R_f), triphenylphosphonite $\{PPh(OC_6H_4\text{-}4\text{-}R_f)_2\}$, ethyldiphenylphosphine ($PPh_2C_2H_4R_f$), diethylphenylphosphine $\{PPh(C_2H_4R_f)_2\}$ and triethylphosphine $\{P(C_2H_4R_f)_3\}$ ligands are synthesized by conventional ligand displacement and/or halide-bridge cleaved reactions, and their spectroscopic parameters are compared with those for the related ligands lacking the tridecafluorohexyl ponytails.

1. Introduction

Since the introduction of *fluorous* chemistry by Horváth and Rábai [1] there has been considerable interest in the synthesis and applications of species incorporating long perfluoroalkyl substituents [2–4]. We have been particularly interested in the electronic and steric implications of the perfluoroalkyl substituents on the donor properties of perfluoroalkylated ligands in coordination chemistry and the structural impact of the fluorous ponytails on the solid state structures of the coordination compounds [5–10]. Phosphorus(III) ligands, primarily due to the widespread application in catalytic applications, have been the most extensively studied ligand class in fluorous chemistry, with considerable attention attached to electronically insulating the donor atom from the perfluoroalkyl substituents [5,6,11,12]. Theoretical calculations [13–15] and experimental studies, on alkyl- and aryl-phosphines, sometimes even with sophisticated spacer units [5,6,12,16–18], and triarylphosphites [19–22] have shown that complete electronic insulation is difficult, if not impossible. Recent work has inverted this rationale, by seeking to exploit this electronic influence to benefit the catalytic activity [23,24]. In order to be able to fully utilize such an electronic effect, it is necessary to have genuine insight into the influence of the perfluoroalkyl substituents and, here, we describe the coordination chemistry of a comprehensive series of perfluoroalkylated phosphorus(III) ligands with C_2H_4 and OC_2H_4 spacer units for comparison with our previously published C_6H_4 and OC_6H_4 systems.

2. Results and discussion

The preparation and characterization of the 1*H*,1*H*,2*H*,2*H*-tridecafluorooctyl-phosphine, phosphinite, phosphonite and phosphite ligands (**L1**–**L6**) and the related *para*-tridecafluorophenyl-phosphinite and phosphonite ligands (**L7**, **L8**) have been described previously [11]. We have shown that spectroscopic and structural properties of transition metal complexes [10] provide a clear guide to the electronic and steric impact of perfluoroalkyl substituents on the donor properties of ligands. For the most part, ligands (**L1**–**L8**) react with platinum metal starting materials in the same way as other phosphorus(III) ligands (Scheme 1); i.e. substitution of weakly coordinated ligands and cleavage of halide-bridged dimers. The new metal complexes (**1**–**52**) synthesized in this work have been characterized by a combination of elemental analysis, IR spectroscopy, mass spectrometry and multinuclear NMR spectroscopies (Table 1).

For the $[PtCl_2L_2]$ series (**1**–**8**), the thermodynamically favoured *cis*-isomers, clearly identified by the presence of two resonances assigned as ν(M-Cl) stretching vibrations in the IR spectra and large $^1J_{PtP}$ coupling constants (*ca.* L = phosphine, J = 3500–3600 Hz; L = phosphinite, J = 4100–4200 Hz; L = phosphonite, J = 4700–4900 Hz) are formed in all cases except when L = $P(C_2H_4C_6F_{13})_3$ (**L3**). Here, the single IR active M-Cl vibration together with

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* Corresponding author. Tel.: +44 116 252 2108; fax: +44 116 252 3789.
E-mail address: egh1@le.ac.uk (E.G. Hope).

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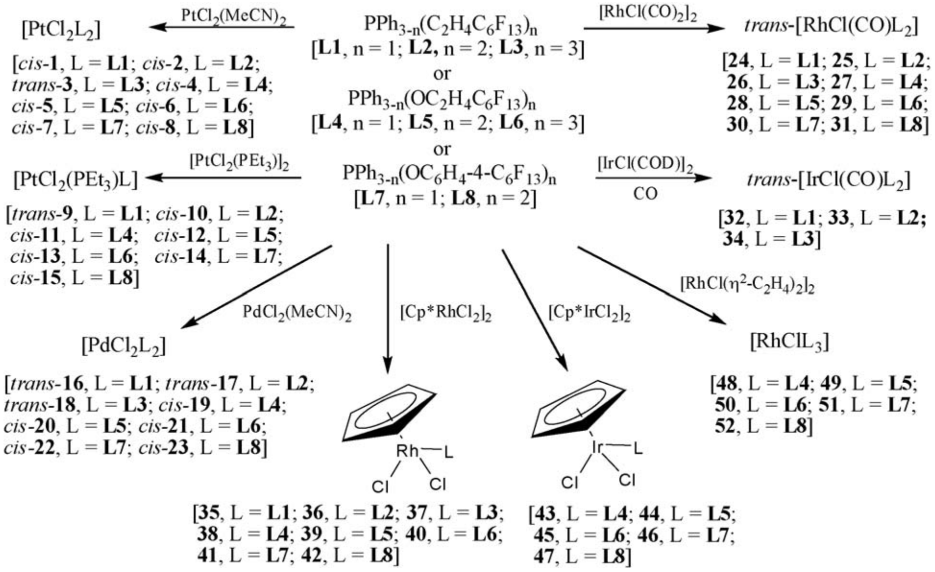

Scheme 1.

$^1J_{PtP}$ = 2941 Hz indicate formation of *trans*-$[PtCl_2L_2]$ (**3**). Previously, we have reported the formation of *trans*-isomers in comparable reactions of the bulky phosphite ligand $P(OC_6H_4\text{-}2\text{-}C_6F_{13})_3$ [22] or phosphine ligands $P(C_6H_4\text{-}4\text{-}C_6F_{13})_3$ [5] and $P(C_6H_4\text{-}3\text{-}C_6F_{13})_3$ [12], and presume that formation of *trans*-$[PtCl_2\{P(C_2H_4C_6F_{13})_3\}_2]$ (**3**) here is similarly related to the bulk of this tris-perfluoroalkylated ligand. We have previously highlighted the diastereotopic nature of the OCH_2 and CH_2CF_2 protons in the ^1H NMR spectrum of the free dialkylphosphonite ligand (**L5**) [11]. This effect is observed in the ^1H NMR spectrum of the platinum(II) dichloride complex of this ligand, (**5**), and all the other metal complexes of this ligand (**12**, **20**, **28**, **39**, **44**, **49**) prepared in this work. For illustration, the ^1H NMR spectrum of (**5**) reveals mutually coupled highly second order resonances for at 4.41 and 4.17 ppm associated with the OCH_2 protons and complicated overlapping multiplets for the CH_2CF_2 protons at 2.37 ppm. Here, for the first time, the diastereotopic inequivalence of the substituents along the carbon chain is also evident in the α-CF_2 resonances in the $^{19}F\{^1H\}$ NMR spectrum which appear as a highly asymmetric AB multiplet with $^2J_{FF}$ = 272 Hz.

Cleavage of the halide-bridges in $[PtCl_2(PEt_3)]_2$ with the phosphorus(III) ligands generates the related *cis*-$[PtCl_2(PEt_3)L]$ complexes (**10**–**15**) with diagnostic $^1J_{PtP}$ and $^2J_{PP}$ coupling constants. Interestingly, $\Delta^{31}P$ for (**10**–**15**) ($\Delta^{31}P = \delta^{31}P_{complex} - \delta^{31}P_{ligand}$) are virtually identical to those for the related bis-complexes (**2**, **4**–**8**). In marked contrast, the NMR spectral data for the product (**9**) from the reaction of $[PtCl_2(PEt_3)]_2$ with $PPh_2C_2H_4C_6F_{13}$ (**L1**) are conspicuously different. The $^{31}P\{^1H\}$ NMR spectrum is a highly asymmetric AB pattern in which $^1J_{PtP}$ (2500 Hz, **L1**; 2455 Hz, PEt_3) and $^2J_{PP}$ (515 Hz) are assignable to the *trans*-$[PtCl_2(PEt_3)(PPh_2C_2H_4C_6F_{13})]$ species (**9**). However, the formation of exclusively the *trans*-isomer in this particular reaction cannot be ascribed to the steric bulk of the incoming ligand, and must be a consequence of some highly specific electronic effect.

Turning now to the palladium(II) complexes, ^{31}P NMR chemical shifts and ν(Pd-Cl) absorptions in the infra-red spectra reveal *trans*-geometries for $[PdCl_2L_2]$ (L = phosphine; **16**–**18**) and *cis*-geometries (L = phosphinite, phosphonite, phosphite; **19**–**23**), in line with the relative *trans*-effect for these ligands at palladium(II). Here, the reactions of $[PdCl_2(MeCN)_2]$ with the ligands were unremarkable, except in the reaction of the triarylphosphinite (**L7**) where the crude ^1H NMR spectrum was complicated and the $^{31}P\{^1H\}$ NMR spectrum revealed two singlet resonances at δ 113.1 and 78.2 in an approximate 2:1 ratio. The desired product, (**22**), a pale yellow solid, and this impurity, pale yellow crystals, were readily separated by fractional crystallization from acetone. The ^{19}F NMR spectrum of the impurity had no resonances and a single crystal X-ray structural determination revealed the product to be the previously synthesized [25] and structurally characterized [26] chloride bridged dimer $[Pd_2Cl_2\{Ph_2PO\cdots H\cdots OPPh_2\}]$ containing two diphenylphosphinito groups from which the perfluoroalkyl-substituted aryl rings have, apparently, been hydrolysed. The providence of such a hydrolysis is unclear, since no related hydrolytic reactions were observed in any other reactions of **L7**, or indeed any of the, more hydrolytically unstable, phosphonite or phosphite ligands in this work.

Cleavage of the halide-bridges in $[RhCl(CO)_2]_2$ with the monodentate phosphorus(III) ligands readily generates the *trans*-$[RhCl(CO)L_2]$ (**24**–**31**); the members of this series (**26**) [27,28], (**27**) and (**29**) [29] have been described previously. *trans*-$[IrCl(CO)L_2]$ (L = **L1**, **L2**, **L3**; **32**, **33**, **34**) are prepared by carbonylation of the product from the cleavage of $[IrCl(COD)]_2$ with the respective phosphines; *trans*-$[IrCl(CO)(\mathbf{L3})_2]$ (**34**) has been described previously [28]. For these complexes, the spectroscopic parameters ($^1J_{RhP}$, ν(CO)) are highly consistent with each of the aryl/alkyl-phosphine, -phosphinite and -phosphonite ligand classes; however, we note a significant difference for our perfluoroalkylated phosphite ligands where, whilst *trans*-$[RhCl(CO)(\mathbf{L6})_2]$ (**29**) is generated in high yield, the analogous reaction with L = $P(OC_6H_4\text{-}4\text{-}C_6F_{13})_3$ yields exclusively the halide-bridged dimeric $[RhClL_2]_2$ [22].

The piano-stool $[Cp^*MCl_2L]$ {M = Rh (**35**–**42**); M = Ir (**43**–**47**)}, similarly formed by halide-bridge cleavage reactions in high yields, display comparable spectroscopic data for each of the three ligand classes (Table 1). Finally, although the combined ligand displacement and halide-bridge cleavage reactions of $[Rh(\eta^2\text{-}C_2H_4)_2Cl]_2$ with an excess of each of the ligands (**L1**–**L8**) readily afforded the tris-ligand complexes $[RhClL_3]$, only the phosphinite, phosphinite and phosphite ligands generated analytically pure and sufficiently solution stable products (**48**–**52**) to allow full characterization. Here, the complexes are readily identified from mutually coupled resonances in the $^{31}P\{^1H\}$ NMR spectra where $^1J_{RhP}$ vary systematically with both the donor ligand ($J_{phosphite} > J_{phosphonite} > J_{phosphinite}$) and *trans*-ligand ($J_{trans\text{-}Cl} > J_{trans\text{-}P}$) in line with the established ligand effects at rhodium(III).