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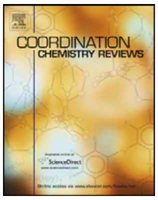

Review

Coordination chemistry of the noble gases and noble gas fluorides

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Contents

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ABSTRACT

Recent developments in the synthesis and characterisation of transition metal coordination and organometallic compounds, incorporating either the noble gases or the noble gas fluorides as ligands, are reviewed together for the first time, and placed in an historical context.

1. Introduction

In the 50 years since Neil Barlett's demonstration of the reactivity of the noble gases [1], perhaps the most surprising, interesting and thought provoking observations have been in their coordination chemistry. In this review article, the quite disparate but clearly related four strands of noble gas coordination chemistry; organometallic noble gas complexes, metal oxide noble gas complexes, homoleptic transition metal xenon complexes and noble gas fluorides as ligands are considered together for the first time.

2. Organometallic noble gas complexes

The study of the coordination of the noble gases, principally xenon, krypton and argon, interestingly, celebrates its 40th anniversary in 2012 [2]. However, in comparison to the recently reported isolable homoleptic xenon coordination compounds and complexes of the noble gas fluorides (Section 4), these highly reactive species have only be generated and studied at low temperatures, in the gas phase or using ultra-fast detection techniques. The history and developments in this field were elegantly reviewed in 2001 [3], so only the work in key reports and more recent developments are outlined here; by way of a summary, Table 1 lists all the organometallic noble gas complexes reported to-date.

It could be viewed that the first transition–metal noble gas complex, $Cr(CO)_5Ar$ [2], was not generated by design, being identified by Turner et al. using matrix isolation techniques during photolysis experiments of chromium hexacarbonyl in an argon matrix. Indeed, the importance of the metal–argon interaction was not really discussed until the report of detailed photochemical studies of the group VI hexacarbonyls in noble gas, methane and other matrices at cryogenic temperatures in 1975 [4]. Here, shifts in the UV/vis absorption maxima and the $\upsilon(CO)$ IR stretching frequencies of the products from the photolysis of $M(CO)_6$ (M = Cr, Mo, W) in both pure and doped noble gas matrices were shown to provide clear evidence for noble gas coordination, with the strength of the metal–noble gas interaction increasing in the order $Ne \ll Ar < Kr < Xe$. Kinetic data on the bonding of xenon and krypton atoms to $M(CO)_5$ fragments has also been studied using time resolved IR spectroscopy in the gas phase [5], and the nature of these "relatively" weak bonds have been

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Table 1
Organometallic noble gas complexes.

Group V	Ref.	Group VI	Ref.	Group VII	Ref.	Group VIII	Ref.	Group IX	Ref.
$CpV(CO)_3Xe$	[17]	$Cr(CO)_5Ne$	[4]	$Mn(CO)_5Kr$	[8]	$Fe(CO)_4Xe$	[23–25]		
		$Cr(CO)_5Ar$	[2,4]	$CpMn(CO)_2Xe$	[16]	$[Fe(CO)_5Kr]^+$	[8]		
		$Cr(CO)_5Kr$	[4,15]	$CpMn(CO)_2Kr$	[16]				
		$Cr(CO)_5Xe$	[4,9,15]	$Cp^*Mn(CO)_2Xe$	[16]				
		fac-$Cr(CO)_3(dfepe)Ar$	[19]	$Cp^*Mn(CO)_2Kr$	[16]				
		fac-$Cr(CO)_3(dfepe)Xe$	[19]	$Cp^{Et}Mn(CO)_2Xe$	[16]				
		mer-$Cr(CO)_3(dfepe)Xe$	[19]	$Cp^{Et}Mn(CO)_2Kr$	[16]				
		η^6-$C_6H_6Cr(CO)_2Ar$	[20]						
		η^6-$C_6H_6Cr(CO)_2Xe$	[21]						
$CpNb(CO)_3Xe$	[17]	$Mo(CO)_5Ne$	[4]			$Ru(CO)_2(PMe_3)_2Ar$	[7]	$CpRh(CO)Kr$	[18]
		$Mo(CO)_5Ar$	[4]			$Ru(CO)_2(PMe_3)_2Xe$	[7]	$CpRh(CO)Xe$	[18]
		$Mo(CO)_5Kr$	[4,15]			$Ru(CO)_2(dmpe)Ar$	[26]	$Cp^*Rh(CO)Kr$	[27]
		$Mo(CO)_5Xe$	[4,15]			$Ru(CO)_2(dmpe)Xe$	[26]	$Cp^*Rh(CO)Xe$	[27]
								η^3-$Tp^*Rh(CO)Xe$	[28]
								η^2-$Tp^*Rh(CO)Xe$	[28]
								$Bp^*Rh(CO)Xe$	[28]
$CpTa(CO)_3Xe$	[17]	$W(CO)_5Ne$	[4]	$CpRe(CO)_2Kr$	[22]				
		$W(CO)_5Ar$	[4,15]	$CpRe(CO)_2Xe$	[11,22]				
		$W(CO)_5Kr$	[4,15]	$Cp^*Re(CO)_2Kr$	[16]				
		$W(CO)_5Xe$	[4,10,15]	$Cp^*Re(CO)_2Xe$	[16]				
				$CpRe(CO)(PF_3)Xe$	[13]				
				$^iPrCpRe(CO)_2Xe$	[13]				
				$^iPrCpRe(CO)(PF_3)Xe$	[13]				

accurately modelled using *ab initio* and DFT methods and shown to be dominated by interactions between the noble gas p-orbitals and those of the equatorial carbonyl groups [6]. Subsequently, a varied range of other d^6 and d^8 (*e.g.* $Ru(CO)_2(PMe_3)_2L$ (L = Ar, Xe) [7]) complexes have been generated and characterised following photolysis in cryogenic matrices. Even the paramagnetic radicals $Mn(CO)_5Kr$ and $[Fe(CO)_5Kr]^+$ have been detected by EPR spectroscopy following γ-radiolysis in krypton matrices [8]. However, the limitations of matrix isolation techniques in terms of our understanding of the generation, reactivity and stability of complexes with metal–noble gas bonds, has led researchers to undertake investigations in liquid and supercritical noble gas solutions.

The first solution stable organometallic noble gas complex, $Cr(CO)_5Xe$, was also reported by Turner et al. [9]. It was generated by uv photolysis of chromium hexacarbonyl in both liquefied xenon and liquefied krypton doped with xenon at −98 °C, and identified by its characteristic IR spectrum. The relatively long lifetime of the complex at this temperature ($t_{1/2} \approx 2$ s) was ascribed to the high xenon concentration (*ca.* 1.5–27 M) in comparison to that of the other reactants (*ca.* 10^{-5} to 10^{-7} M). Enhanced lifetimes can be achieved by using 5d metals, *e.g.* $W(CO)_5Xe$ is reported to have a lifetime of *ca.* 1.5 min at −103 °C in liquid xenon [10], and cyclopentadienyl co-ligands, *e.g.* $CpRe(CO)_2Xe$ is reported to have a lifetime of *ca.* 3.5 min at −103 °C in liquid xenon [11]. The comparability of the exceptionally long lifetime for this rhenium complex with those for closely related CpRe(CO)(alkane) complexes which, crucially, had been characterised by NMR techniques in solution [12], led this group to speculate whether it could be possible to undertake the first NMR study of an organometallic noble gas complex. Unfortunately (or fortunately), $CpRe(CO)_3$, the photolytic precursor to $CpRe(CO)_2Xe$, is poorly soluble in liquid xenon at low temperatures and this hinders the chance of getting reliable NMR data. So, the team prepared $CpRe(CO)_2(PF_3)$ and $(^iPrCp)Re(CO)_2(PF_3)$ [$^iPrCp = \eta^5$-C_5H_4-$CH(CH_3)_2$] as their starting materials, with the valuable additional ^{19}F and ^{31}P NMR handles and much greater solubility in liquid xenon [13]. For each of these complexes FTIR studies in liquid xenon or liquid krypton doped with xenon at −107 °C revealed that two photoproducts were formed on irradiation; $CpRe(CO)_2Xe$ and $CpRe(CO)(PF_3)Xe$ from $CpRe(CO)_2(PF_3)$, and $(^iPrCp)Re(CO)_2Xe$ and $(^iPrCp)Re(CO)(PF_3)Xe$ from $(^iPrCp)Re(CO)_2(PF_3)$. In both cases, the monocarbonyl complexes have much longer lifetimes than the dicarbonyl adducts. The multinuclear NMR studies on the photolysis of these complexes at −110 °C in liquid xenon supports the assignments made in the IR experiments, and provides the first spectroscopic evidential link between the bound xenon ligands and the other metal bound ligands. ^{19}F NMR experiments initially reveals new doublets at δ −5.1 ($^1J_{PF} = 1220$ Hz) for both the Cp and ^{i}PrCp photoproducts (the ^{i}Pr substituent is not expected to have a significant impact upon the fluorine environment) before, on further photolysis, the doublet for free PF_3 builds into the spectra. In the analogous ^1H NMR spectra, the Cp region is not particularly informative. However, for the isopropyl-substituted complex, the generation of two, equal intensity, doublets for the methyl protons (that both show coupling through a COSY experiment to the CH proton) is compelling evidence for the formation of $(^iPrCp)Re(CO)(PF_3)Xe$ in which symmetry renders the two isopropyl methyl groups inequivalent. Direct information on the rhenium—xenon bond is obtained when 100% isotopically enriched ^{129}Xe ($I = 1/2$) is used as the solvent during photolysis of $(^iPrCp)Re(CO)_2(PF_3)$. A series of 2D experiments reveal $\delta(Xe) = -6179$, $^2J_{XeF} = 42$ Hz and $^3J_{XeP} = 5$ Hz and the lifetime to xenon exchange in solution >27 ms, all of which clearly indicate that it is entirely appropriate to consider the xenon as a discrete ligand and not just a weakly solvating atom [13]. DFT calculations have been used to probe the bonding in $CpRe(CO)_2Xe$ and $CpRe(CO)(PF_3)Xe$, from which the authors conclude that the Re–X interactions are closed-shell and indicative of charge-induced dipole and dispersive bonding, in which the rhenium d-orbitals appear to contribute little. The Re—Xe bond lengths are computed to be 2.910 and 2.901 Å, respectively [14].

In the quest for room temperature stable organometallic xenon complexes, researchers have turned their attention to the application of supercritical fluids. The now familiar range of $M(CO)_5Ng$ complexes are each available through photolysis of the appropriate group VI metal hexacarbonyl in the supercritical noble gas, and their spectroscopic properties and reactivity (*e.g.* with doped CO) studied at room temperature [15]. As might be expected, the rates of reaction of $M(CO)_5(Ng)$ with CO in pure supercritical noble gas were found to decrease Ar > Kr > Xe and Cr ≈ Mo > W, and from the temperature dependency of the reaction kinetics the authors conclude that the reaction of $W(CO)_5Xe$ with CO in scXe occurs by a dissociative mechanism, as reported for the same reaction in