Crystallographic and Spectroscopic Assessment of Chelate-stabilized Aryl Halide Complexes at a Seven-coordinate d⁴ Molybdenum Centre

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A new series of chelate stabilized aryl halide coordination complexes of molybdenum are prepared by a novel oxidative addition strategy; quantitative equilibrium measurements suggest that the structure of the chelate ring, rather than the identity of the halide (X = Cl, Br, I), controls the strength of aryl halide binding in these complexes.

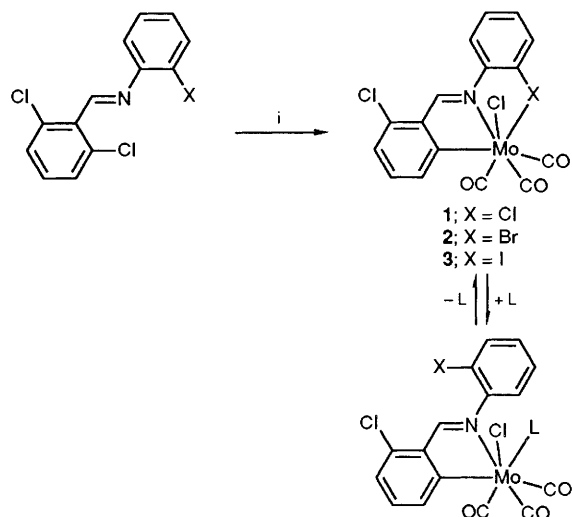Although the pioneering work of Beck and Schloter[1] provided vibrational evidence for dichloromethane coordination at $[C_5H_5M(CO)_3]^+$ Lewis acids (M = Mo, W) over a decade ago, no crystallographic analysis of halocarbon binding at a d⁴ metal centre has been reported.[2] The continuing interest[3] in this class of compounds prompts us to report that chelate assisted oxidative addition[4] of aromatic C–X bonds in a series of Schiff base ligands provides a novel synthetic entry into a new family of aryl halide coordination complexes one of which has been characterized by X-ray diffraction.
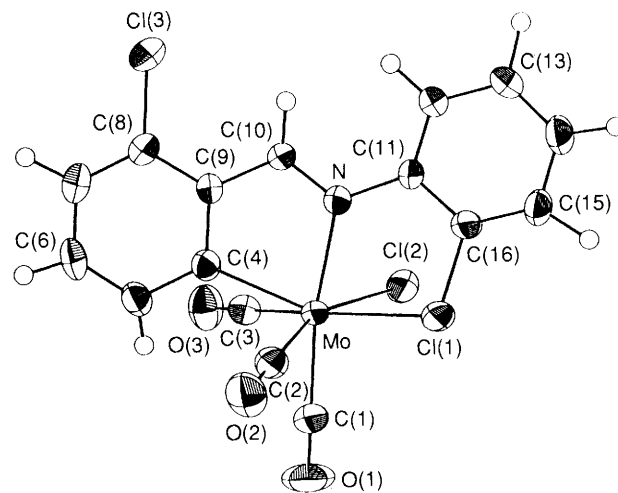
Table 1 v_{CO} Data for compounds 1–5 and equilibrium data for displacement of the coordinated aryl halide by thf recorded in toluene

Compound	X	v_{CO}/cm^{-1}			K^a	ΔH/kJ mol^{-1b}	ΔS/J K^{-1} mol^{-1b}
1	Cl	2036	1966	1939	2.6	−20(3)	−59(17)
2	Br	2034	1966	1937	0.8	−20(2)	−69(17)
3	I	2033	1966	1933	0.2	−11(2)	−50(21)
4	OMe	2028	1958	1928	c	—	—
5	NH$_2$	2025	1956	1917	c	—	—

^{a} In units of (mol dm^{-3})$^{-1}$ at 298 K. ^{b} Measured by quantitative FTIR spectroscopy from 213–303 K in 10% thf solution; estimated errors are given in parenthesis. ^{c} thf does not displace this ligand from molybdenum.

Scheme 1 *Reagents*: i, (C$_7$H$_8$)Mo(CO)$_3$, thf, −C$_7$H$_8$

1; X = Cl
2; X = Br
3; X = I

Fig. 1 ORTEP representation of **1**. Selected bond lengths (Å) and angles (°): Mo–C(4) 2.226(4), Mo–N 2.189(4), Mo–C(1) 1.994(5), Mo–C(2) 1.979(6), Mo–C(3) 1.957(6), Cl(1)–C(16) 1.753(5), Cl(3)–C(8) 1.738(5); Cl(1)–Mo–Cl(2) 82.17(5), Cl(1)–Mo–C(3) 162.9(1), N–Mo–C(1) 171.1(2), Cl(2)–Mo–C(2) 159.3(1), Cl(1)–Mo–C(4) 128.9(4).

As shown in Scheme 1, treatment of appropriately designed Schiff base ligands with an equivalent of Mo(CO)$_3$(thf)$_3$ (thf = tetrahydrofuran) generated *in situ* from the toluene complex,[5] as indicated by quantitative spectroscopic measurements, affords conversion into the capped octahedral molybdenum(II) aryl halide coordination complexes **1–3** which can be crystallized as air-stable solids in approximately 80% isolated yields. The aryl chloride complex **1** was further characterized by X-ray crystallography as illustrated in Fig. 1.†‡ The Mo–Cl(1) distance of 2.624(1) Å is somewhat longer than the Mo–Cl(2) distance of 2.473(1) but clearly indicative of a covalent Mo–aryl chloride bond. Other structural features are unexceptional for this class of compounds[4] and the Mo–Cl(1)–C(16) angle is 98.5(2)° consistent with donation of a halide lone pair to molybdenum. The Cl(1)–C(16) bond

shows a slight, but statistically not significant,[6] lengthening compared to Cl(3)–C(8). The Mo–Cl interaction was further characterized in the solid state by nuclear quadrupole resonance (NQR) spectroscopy at 77 K. This complex exhibits a coordination shift of the ^{35}Cl NQR signal of 3.685 MHz, the largest difference yet recorded and consistent with a strong Mo–Cl interaction.[7]

In part as a consequence of their chelated structure, the aryl halides are competitive ligands with typical solvents such as thf and Et$_2$O. Interestingly, the IR spectroscopic data (Table 1) suggest that the donor abilities of the three aryl halides are rather similar, albeit less than the more classical methyl ether **4** or amine **5** complexes. Accordingly we have measured the equilibrium constants for displacement of the halides by thf as a function of temperature (Table 1). These values indicate that the ligating ability of the three aryl halides groups are indeed quite similar. The entropy change for binding is less than half of what would be expected based on statistical mechanical estimates[8] and much lower than what we have measured in a similar reaction involving replacement of an agostic C–H ligand by thf at a six-coordinate tungsten(0) centre.[9] This suggests that significant strain energies are involved in the present seven-coordinate system which we plan to clarify by further thermochemical investigations.[10] Although the three lower aryl halides have very similar coordinating abilities in these complexes, attempts to prepare the analogous aryl fluoride complex have to date proved unsuccessful.[11]

References

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