Synthesis of Binuclear and Trinuclear Cluster Halides of Molybdenum and Rhenium, and of Carbonyl Halides of Rhenium, Iridium, Ruthenium, and Platinum using Metal Atoms

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Reactive halocarbons such as 1,2-dibromo- (or dichloro-) ethane or allyl chloride will halogenate atoms of molybdenum and rhenium under co-condensation conditions giving solvated transition metal halides in lower valency states, *e.g.* $[Re_3Cl_9(THF)_3]$ (THF = tetrahydrofuran), which are useful synthetic precursors; co-condensation of rhenium with oxalyl chloride gives $[Re(CO)_4Cl]_2$, ruthenium atoms when co-condensed with oxalyl chloride give a carbonyl halide compound which adds trimethylphosphine forming $[Ru(Me_3P)_3(CO)Cl_2]$, and similarly, iridium atoms with oxalyl chloride and then triphenylphosphine give $[Ir(CO)_2(PPh_3)Cl_3]$.

Oxidative addition of carbon–halogen bonds to transition metal atoms is well established.[1] We set out to exploit this reactivity for the synthesis of lower halides and carbonyl halides of the more refractory transition metals.

Co-condensation of rhenium atoms generated from a positive hearth electron-gun furnace, using the large scale apparatus described elsewhere,[2] with 1,2-dibromoethane followed by extraction of the reaction matrix at room temperature with tetrahydrofuran (THF) gave the compound $[Re_3Br_9(OC_4H_8)_3]$ (**1**). The yield, based on metal leaving the furnace, was *ca.* 90% and in a typical reaction 7 g of rhenium atoms evaporated from the furnace gave 12 g of (**1**) after 4 h. Treatment of (**1**) with trimethylphosphine in THF for 15 min at 40 °C gave the binuclear compound $[(Me_3P)_2Br_2Re{\equiv}ReBr_2(PMe_3)_2]$, (**2**), in *ca.* 65% yield. Compounds of the class $[Re_3X_9L_3]$ and $[Re_2X_4L_4]$, where X = Cl or Br and L = R_3P, are well established[3-5] although (**1**) itself has not been previously described. The reported synthetic routes have involved three to four separate stages, starting from the element.

(**1**) $[Re_3Br_9(OC_4H_8)_3]$
(**2**) $[(Me_3P)_2Br_2Re{\equiv}ReBr_2(PMe_3)_2]$
(**3**) $[(Me_3P)_2Br_2Mo{\equiv}MoBr_2(PMe_3)_2]$
(**4**) $[Mo(PMe_3)_3Br_3]$
(**5**) $[Mo_2Cl_4(PEt_3)_4]$
(**6**) $[Re(CO)_4Cl]_2$
(**7**) $[Ru(PMe_3)_3(CO)Cl_2]$
(**8**) $[Ir(CO)_2(PPh_3)Cl_3]$
(**9**) *trans*-$[Pt(CO)_2Cl_2]$

When molybdenum atoms were co-condensed with an excess of 1,2-dibromoethane and the resulting mixture was extracted with THF a deep red solution was obtained. Addition of trimethylphosphine to this solution gave the compounds $[(Me_3P)_2Br_2Mo{\equiv}MoBr_2(PMe_3)_2]$, (**3**), and $[Mo(Me_3P)_3Br_3]$, (**4**), which were separated by chromatography on a short alumina column. The yields of (**3**) and (**4**) were 40% and 25% respectively, and in a typical experiment 5 g of (**3**) could be isolated. Co-condensation of molybdenum atoms in an excess of 1,2-

dichloroethane followed by extraction with tetrahydrofuran gave a red solution. Addition of triethylphosphine gave [$Mo_2Cl_4(PEt_3)_4$], (**5**), in 35% yield. When allyl chloride was used in place of 1,2-dichloroethane then essentially similar results were obtained. The compounds (**3**) and (**4**) are new although closely related analogues, including (**5**), are well known.[3,6] Previous syntheses have required three to four separate reactions starting from molybdenum hexacarbonyl.

Co-condensation of rhenium atoms with an excess of oxalyl chloride gives the well known [$Re(CO)_4Cl]_2$, (**6**) in *ca.* 40% yield. Ruthenium atoms when co-condensed into an excess of oxalyl chloride followed by extraction with THF give a red solution which on removal of the solvent gives a red solid. Extraction with THF and addition of toluene yields a green solid. The i.r. spectra of the red and green materials show the bands assignable to terminal carbon monoxide ligands at 2150w, 2985s, 2025s, and 1960s; and at 2079s, 2088s, and 1970s cm^{-1}, respectively. Characterisation of these materials is in progress. Addition of trimethylphosphine to the green solid caused a steady reaction and yellow crystals of [$Ru(Me_3P)_3(CO)Cl_2$], (**7**), were formed in *ca.* 70% yield [*m/e* = 428; ν_{CO} 1955s cm^{-1} (mull)]. In a typical small scale experiment *ca.* 1.0 g of (**7**) was obtained.

Co-condensation of iridium atoms with oxalyl chloride yields an orange solid which shows bands in the i.r. mull spectrum assignable to terminal carbonyl stretching frequencies at 2155s, 2102s, and 2080s cm^{-1}. Treatment of this carbonyl compound with triphenylphosphine gives white crystals of one isomer of [$Ir(CO)_2(PPh_3)Cl_3$], (**8**), in essentially quantitative yield based on the iridium atoms leaving the furnace [ν_{CO} (THF) 2060s and 2036s cm^{-1}].

When platinum is co-condensed with oxalyl chloride then white *trans*-[$Pt(CO)_2Cl_2$], (**9**), may be sublimed from the dried reaction mixture in essentially quantitative yield: typically 2.0 g of (**9**) were obtained in a small scale experiment.

The compounds (**1**)—(**9**) have been characterised by microanalysis and relevant spectroscopic methods. The above observations show that metal atoms can provide new synthetic routes to mono- and poly-nuclear lower oxidation state transition metal halides and also to carbonyl halide derivatives. We find that these laboratory scale syntheses are considerably less laborious and time-consuming than using conventional methods. Furthermore, the metallic state is the least expensive source of the pure noble metals.

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References

1 'Chemistry of Free Atoms and Particles,' K. J. Klabunde, Academic Press, 1980.
2 M. L. H. Green, *J. Organomet. Chem.*, 1980, **200**, 119; F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc.*, *Dalton Trans.*, 1981, 1938.
3 R. A. Walton, *Prog. Inorg. Chem.*, 1976, **21**, 114; J. R. Ebner and R. A. Walton, *Inorg. Chem.*, 1975, **14**, 1987.
4 H. D. Gicksman and R. A. Walton, *Inorg. Synth.*, 1979, **20**, 46.
5 F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, 1965, **4**, 508.
6 J. S. Filippo, Jr., *Inorg. Chem.*, 1972, **11**, 3140.