CHEMICAL SOCIETY REVIEWS

Seven-coordinate halocarbonyl complexes of the type [$MXY(CO)_3(NCMe)_2$] (M = Mo, W; X, Y = halide, pseudo halide) as highly versatile starting materials

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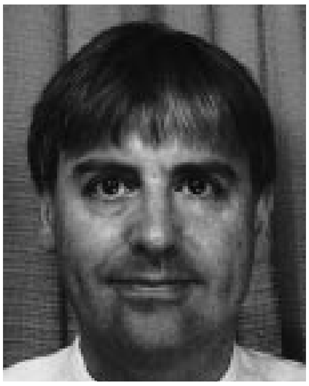
The fortuitous discovery of the seven-coordinate complexes [$MI_2(CO)_3(NCMe)_2$] (M = Mo or W) is described; the wide-ranging chemistry of these compounds is discussed together with the use of the effective atomic number rule in predicting their reactions. The four structural types of seven-coordinate halocarbonyl complexes derived from [$MI_2(CO)_3(NCMe)_2$] are described. The applications of the [$MXY(CO)_3(NCMe)_2$] (X = Y = Br, I; X = Cl, Br, Y = I; X = Cl, Y = $GeCl_3$, $SnCl_3$) system in both alkene metathesis catalysis and nitrogen fixation are also discussed. The synthesis of organometallic complexes containing six different ligands together with the preparation and stereochemical properties of the first structurally characterised {M_{ABCDEF}}$_2$ dimer, [$Cl(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)Mo(\mu\text{-}NCS)(\mu\text{-}SCN)MoCl(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)$] are described.

1 Introduction

The availability of suitable starting materials has always been of considerable importance to the synthetic chemist. Since the first halocarbonyl donor ligand complex of molybdenum(II), namely [$MoI_2(CO)_2(diars)$] {diars = $C_6H_4(AsMe_2)_2$-1,2} was prepared by Nigam and Nyholm in 1957 using reaction (1),[1] six- and seven-coordinate halocarbonyl complexes have received considerable attention.[2]

Paul K. Baker (born Isleworth, Middlesex 1954) obtained his BSc (1976) and PhD (1979) from the University of Bristol. His thesis entitled 'The Synthesis and Reactions of Cationic Organotransition-metal Complexes' was obtained under the guidance of Neil G. Connelly and Michael Green. He held temporary Lectureships at the University of Strathclyde (1980) and the University of Manchester (1981), followed by a Lectureship in Chemistry at Thames Polytechnic (now the University of Greenwich). In 1984, he was appointed to a Lectureship in Chemistry at the University of Wales, Bangor, and was promoted to Senior Lecturer in 1989, and subsequently to a Readership in 1994. He is co-author of over 180 research publications mainly in the field of the organometallic chemistry of molybdenum and tungsten. He has given lectures on his research in over 40 UK Universities and Industrial Companies, and he has lectured extensively in Australia, Austria, Belgium, France, Germany, Holland, Hong Kong, Hungary, Italy, Poland, Portugal, South Africa, Spain and the USA on various aspects of his research work. He is a Fellow of the Royal Society of Chemistry. In July 1997, the author was awarded the Teaching Fellowship for the Faculty of Science at the University of Wales, Bangor.



$$[Mo(CO)_4(diars)] + I_2 \longrightarrow [MoI_2(CO)_2(diars)] + 2CO \qquad (1)$$

In the early days, the two most commonly used routes to seven-coordinate halocarbonyl complexes were (*i*) the oxidation of complexes of molybdenum(0) or tungsten(0) containing strong field ligands, and (*ii*) reactions of the reactive halo-bridged dimers, [{$M(\mu\text{-}X)X(CO)_4$}$_2$] (M = Mo, W; X = Cl, Br, I) with strong field ligands. An early example of type (*i*) is given in reaction (2).[3]

$$[M(CO)_4(2,5\text{-dithiahexane})] + X_2 \longrightarrow [MX_2(CO)_3(2,5\text{-dithiahexane})] + CO \qquad (2)$$

M = Mo, W; X = Br, I

In 1966, Colton and Tomkins[4] described the synthesis of the chloro-bridged dimer, [{$Mo(\mu\text{-}Cl)Cl(CO)_4$}$_2$] [reaction (3)].

$$2[Mo(CO)_6] + 2Cl_2 \xrightarrow{-78\ °C} [\{Mo(\mu\text{-}Cl)Cl(CO)_4\}_2] + 4CO \qquad (3)$$

From 1966 to 1971, Colton *et al.* investigated the chemistry of [{$M(\mu\text{-}X)X(CO)_4$}$_2$] (M = Mo, W; X = Cl, Br, I) with strong field ligands to give a range of six- and seven-coordinate complexes of molybdenum(II) and tungsten(II) and some of their results are published in a review article.[5] The molecular structure of the tungsten bromo-bridged dimer [{$W(\mu\text{-}Br)Br(CO)_4$}$_2$] has been crystallographically determined by Cotton *et al.*,[6] and shows each tungsten atom to be in a capped octahedral environment, with a carbonyl group capping an octahedral face (Fig. 1). In 1972, Westland and Muriithi[7] described the reactions of the halo-bridged dimers, [{$Mo(\mu\text{-}X)X(CO)_4$}$_2$] (X = Cl, Br) with weaker field ligands such as pyridine, tetrahydrofuran and acetonitrile, which eventually gave the non-carbonyl containing products [MoX_3L_3] and zero-valent [$Mo(CO)_6$] *via* disproportionation of the six-coordinate molybdenum(II) intermediates, [$MoX_2(CO)_2L_2$]. They were apparently unable to isolate these intermediates in a pure state.

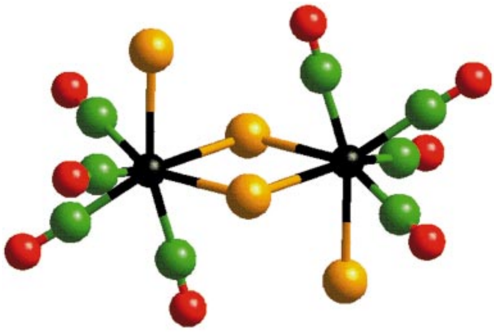


Fig 1. Molecular structure of [{$W(\mu\text{-}Br)Br(CO)_4$}$_2$][6]

In 1962, Tate, Knipple and Augl[8] published the seminal paper on the synthesis of the important starting materials, *fac*-[$M(CO)_3(NCMe)_3$] (M = Cr, Mo or W) by refluxing [$M(CO)_6$]

in acetonitrile for various periods of time. These zero-valent tris(acetonitrile) complexes have been used as starting materials for the preparation of a wide range of organotransition-metal complexes including π-allyl halocarbonyl complexes.[2] In their paper,[8] Tate, Knipple and Augl showed that the reaction of $[W(CO)_3(NCMe)_3]$ with iodine in methanol evolved three moles of gas and gave a non-carbonyl containing product. They did not isolate the seven-coordinate bis(acetonitrile) complex $[WI_2(CO)_3(NCMe)_2]$. In view of these observations we decided to reinvestigate the halogen oxidation of *fac*-$[M(CO)_3(NCMe)_3]$ (M = Mo or W) by reacting them in acetonitrile rather than methanol, in the hope of obtaining the seven-coordinate complexes $[MX_2(CO)_3(NCMe)_2]$, with two potentially labile acetonitrile ligands. These reactions (4), first carried out in November 1984, have been extremely successful and quantitative yields of the diiodo-complexes $[MI_2(CO)_3(NCMe)_2]$, were prepared.[9] More recently,[10] we have developed a better route to the dibromo-complexes $[MBr_2(CO)_3(NCMe)_2]$, by carrying out the reaction of *fac*-$[M(CO)_3(NCMe)_3]$ (prepared *in situ*) with Br_2 at −78 °C.

$$fac\text{-}[M(CO)_3(NCMe)] + X_2 \xrightarrow{0\ °C} [MX_2(CO)_3(NCMe)_2] + NCMe \quad (4)$$

M = Mo or W; X = Br or I

We have also studied the oxidation of *fac*-$[Mo(CO)_3(NCMe)_3]$ (prepared *in situ*[8]) with a range of other oxidizing agents XY (XY = ICl,[11] IBr,[12] $GeCl_4$,[13] $SnCl_4$[14]) to give $[MoXY(CO)_3(NCMe)_2]$ (X = Cl, Y = I; X = Br, Y = I; X = Cl, Y = $GeCl_3$; X = Cl, Y = $SnCl_3$). During the past 12 years we have prepared and characterised over 1900 new organometallic complexes derived from the highly versatile starting materials, $[MXY(CO)_3(NCMe)_2]$.[2]

This article will describe the versatility of the $[MI_2(CO)_3(NCMe)_2]$ complexes in Section 2, and discusses how the effective atomic number rule can be used to predict the products of these reactions. Section 3 will give an overview on the structures of seven-coordinate complexes derived from $[MI_2(CO)_3(NCMe)_2]$, and Section 4 discusses the applications of the $[MXY(CO)_3(NCMe)_2]$ system in alkene metathesis and nitrogen fixation research. Section 5 discusses the synthesis of complexes of molybdenum(II) containing six-different monodentate ligands. The conclusion (Section 6) discusses current and future developments of the $[MXY(CO)_3(NCMe)_2]$ system.

2 Investigation of the chemistry of the highly versatile complexes $[MI_2(CO)_3(NCMe)_2]$

Although the chemistry of the $[MXY(CO)_3(NCMe)_2]$ (M = Mo or W; X = Y = Br, I; for M = Mo only, X = Cl, Y = I; X = Br, Y = I; X = Cl, Y = $GeCl_3$, $SnCl_3$) has been extensively investigated,[2] and differences in reactivity are apparent as discussed in Section 5, this section will concentrate on the diiodo-complexes $[MI_2(CO)_3(NCMe)_2]$, which have received the most attention. The complexes $[MI_2(CO)_3(NCMe)_2]$ (M = Mo or W) have proved ideal starting materials for a wide range of reactions. Although they are air-sensitive in both the solid state and solution, they can be weighed in air and standard vacuum/Schlenk line techniques are very suitable for carrying out all manipulations with this system. These starting materials can be easily prepared in multigram quantities in a pure state. We have modified Tate, Knipple and Augl's[8] early report for the synthesis of *fac*-$[M(CO)_3(NCMe)_3]$ complexes, by reacting $[Mo(CO)_6]$ under reflux in NCMe for 24 h, and $[W(CO)_6]$ under reflux in NCMe for 72 h. It is essential to have very careful and thorough degassing of the $[M(CO)_6]$–NCMe mixture before refluxing, as shown on the BBC Open University video made in Bangor in 1988,[15] for the Third Level Inorganic Chemistry Course, CHEM 777, S343. This video, together with an associated student book[15] uses the $[MXY(CO)_3(NCMe)_2]$ system to illustrate Schlenk line techniques, spectroscopic and X-ray techniques and various other techniques used in modern day synthetic inorganic chemistry.

Scheme 1 illustrates the diverse chemistry of $[MI_2(CO)_3(NCMe)_2]$. Although Scheme 1 is reasonably complete, there are many subtle reactions which are not given in the scheme. These reactions, depending on the electronic and steric effects of the ligands added, can give a diverse range of different products. The top half of the scheme from $[MI_2(CO)_3(NCMe)_2]$ describes the reactions with neutral and anionic ligands, whereas the bottom half concentrates on the alkyne derivatives of $[MI_2(CO)_3(NCMe)_2]$. We have found that the complexes $[MI_2(CO)_3(NCMe)_2]$ react with almost any potential ligand in the current chemical catalogues, including poor donor ligands, for example $BiPh_3$.[16] The starting materials, $[MI_2(CO)_3(NCMe)_2]$ and all the reaction products shown in Scheme 1 obey the effective atomic number rule.

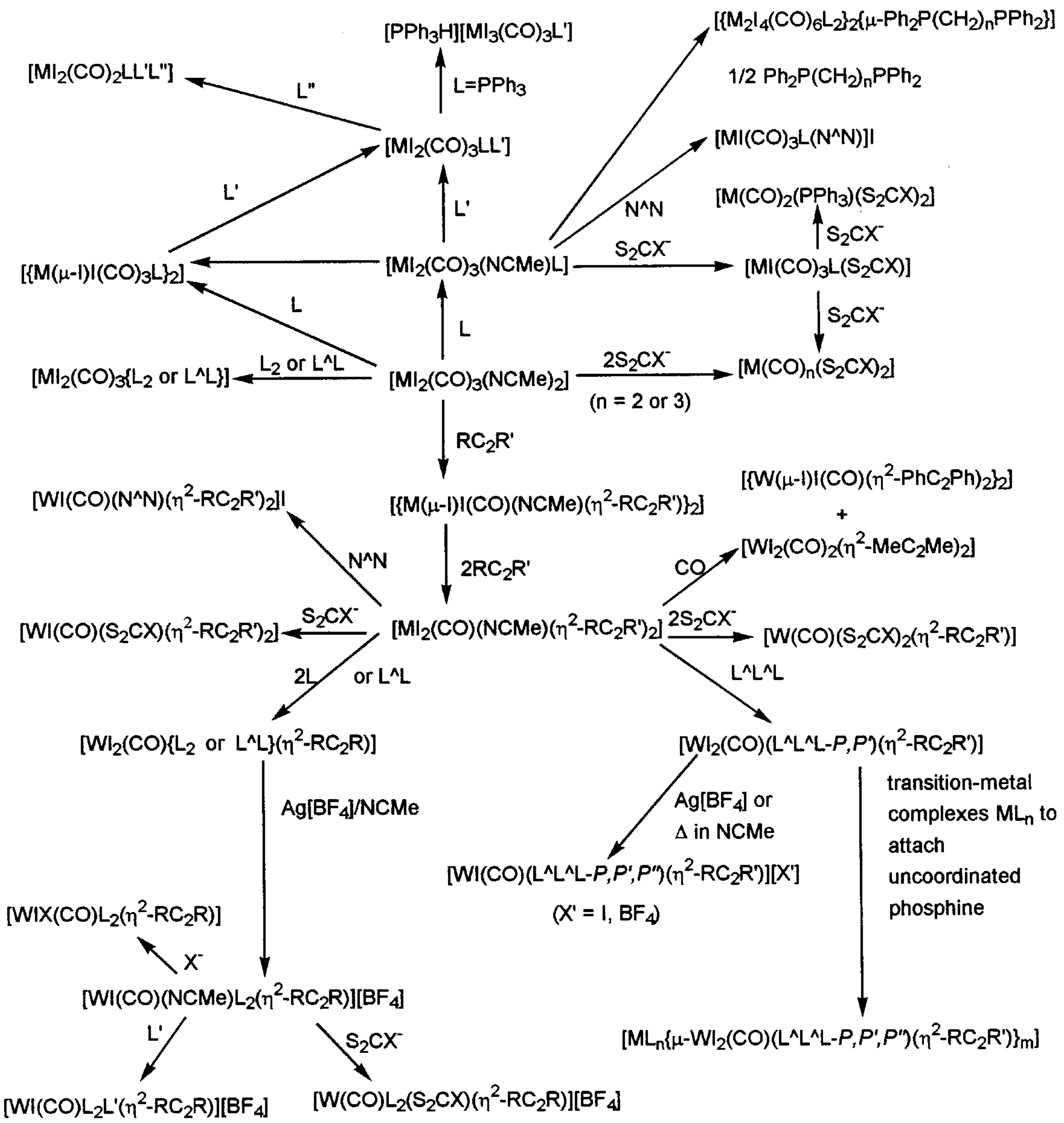
Although over 1900 new complexes have been made from the $[MXY(CO)_3(NCMe)_2]$ system, which has provided a good training for research students in the synthesis and characterisation of moderately air-sensitive complexes; the main significance is in the catalytic activity of many of these complexes (see Sections 4 and 6).

Alkyne ligands can donate two or four electrons to a transition-metal centre,[17] and in the early transition-metal complexes, alkynes generally utilize both their filled pπ-orbitals and donate four electrons to the metal. It is interesting to note that in the bis(alkyne) complexes, $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$[18] shown in Scheme 1, each alkyne must donate an average of three electrons to the metal for the complexes to obey the effective atomic number rule. The ^{13}C NMR chemical shifts for the alkyne carbon atoms in the complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ are generally in the region of 150 ppm, which agrees with Templeton and Ward's[17] correlation indicating that the alkynes are donating an average of three electrons to the metal in these systems. The reaction products of $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ with both phosphine[19] and phosphite[20] donor ligands, give mono(alkyne) products $[WI_2(CO)L_2(\eta^2\text{-}RC_2R')]$, which have alkyne carbon chemical shifts above 200 ppm which indicates[17] they are donating four electrons to the metal, thus enabling them to obey the effective atomic number rule. Very recently,[21] we have described the reactions of $[WI_2(CO)_3L_2]$ {L = PEt_3, PPh_3; L_2 = $Ph_2P(CH_2)_2PPh_2$} with $Na_2[S\hat{}S]$ {$S\hat{}S$ = C_3S_5 (C_3S_5 = 4,5-disulfanyl-1,3-dithiole-2-thionate) or maleonitriledithiolate} or H_2bdt (bdt = benzene-1,2-dithiol) in acetonitrile and ethanol to give the six-coordinate complexes $[W(S\hat{}S)(CO)_2L_2]$, which do not obey the effective atomic number rule. Hence, although the vast majority of our reactions are predicted by the effective atomic number rule, there are several exceptions to the rule.

Research workers in other countries have also used the $[MI_2(CO)_3(NCMe)_2]$ complexes as starting materials in their research. For example, Krishnamurthy *et al.*[22] have reported the reactions of the diphosphazane ligands $RN\{P(OPh)_2\}_2$ (R = Me, Ph) with $[MI_2(CO)_3(NCMe)_2]$ to afford the acetonitrile replaced seven-coordinate complexes $[MI_2(CO)_3(\{P(OPh)_2\}_2NR)]$, which has been crystallographically characterised for M = W, R = Ph. Very recently, Cano *et al.*[23] have described the reactions of $[MoI_2(CO)_3(NCMe)_2]$ with the hydrotris(3,5-dimethylpyrazol-1-yl)borate ligand to yield a range of products depending upon the solvent and the initial concentration of the starting materials, including $[Mo_4O_4(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OH)_2(Hpz^{Me2})_6]I_2\cdot 4NCMe$ which has been crystallographically characterised.

3 Structures of seven-coordinate complexes derived from $[MI_2(CO)_3(NCMe)_2]$

Seven-coordination is an unusual geometry in transition-metal chemistry, and there are four main types of structure exhibited by seven-coordinate complexes; these are (*i*) capped octahedral,



Scheme 1 M = Mo or W; for the reaction of $[MI_2(CO)_3(NCMe)_2]$ with donor ligands described in the top half of the page, L, L′ and L″ represent a wide range of neutral carbon, nitrogen, phosphorus, arsenic, antimony, bismuth, oxygen and sulfur donor ligands. L^L represents a neutral bidentate phosphine donor ligand, N^N represents a neutral bidentate nitrogen donor ligand such as 2,2′-bipy, 1,10-phen *etc.* For the top and bottom half of the scheme S_2CX^- (X = NR_2, R = Me, Et, CH_2Ph *etc.*; X = OEt, SEt *etc.*). For the reactions of the bis(alkyne) complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RC_2R')_2]$ (R, R′ = Me, Ph *etc.*), L, L^L and L^L^L represent mono-, bi- and tri-dentate phosphine ligands respectively, and X^-; X = Cl, Br, I, NO_2, NO_3, NCS, OH, SR (R = Et, Bu^t, Ph, CH_2Ph).

(*ii*) capped trigonal prismatic, (*iii*) the so-called '4 : 3 geometry', and (*iv*) pentagonal bipyramidal geometry. Several important reviews concerned with the structures of seven-coordinate complexes have been published,[2,24,25] which also discuss the structures of the $[MX_2(CO)_3L_2]$ type complexes. In reality, some of the structures we have found derived from the $[MI_2(CO)_3(NCMe)_2]$ system do not exhibit one of the four perfect geometries described above, but crystallise in some intermediate structure, often in between two structural types. It has been shown that very few coordination polyhedra have regular structures and the majority lie on the reaction coordinates connecting the ideals. The majority of the structures which have been determined of seven-coordinate complexes derived from $[MI_2(CO)_3(NCMe)_2]$ are capped octahedral or distorted capped octahedral, although all four principal geometries have been observed. In order to clarify the main geometries of seven-coordinate complexes derived from $[MI_2(CO)_3(NCMe)_2]$, accurate coloured diagrams of crystal structures, together with simple model pictures of complexes for all four representative structures are shown in Figs. 2–5.

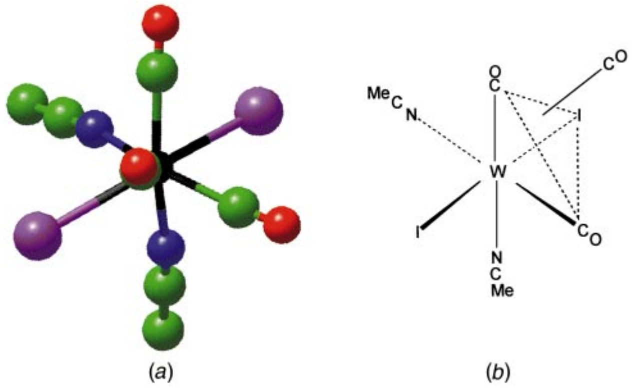


Fig. 2 (*a*) Molecular structure of $[WI_2(CO)_3(NCMe)_2]$.[26] (*b*) Simple representation of the capped octahedral structure of $[WI_2(CO)_3(NCMe)_2]$.

The molecular structure of the tungsten starting material $[WI_2(CO)_3(NCMe)_2]$ has been crystallographically determined

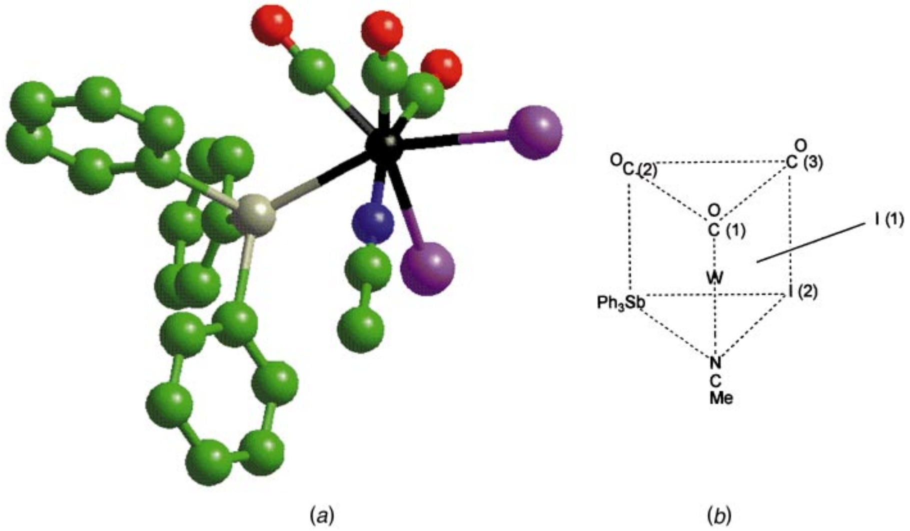


Fig. 3 (*a*) Molecular structure of [$WI_2(CO)_3(NCMe)(SbPh_3)$].[10] (*b*) Simple representation of the capped trigonal prismatic geometry of [$WI_2(CO)_3(NCMe)(SbPh_3)$].

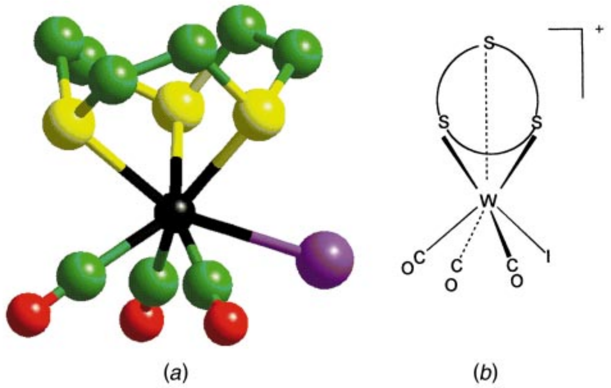


Fig. 4 (*a*) Molecular structure of the cation [$WI(CO)_3([9]aneS_3)$]$^+$.[28] (*b*) Simple representation of the 4 : 3 geometry or piano-stool geometry of [$WI(CO)_3([9]aneS_3)$]$^+$.

(Fig. 2),[26] and has distorted capped octahedral geometry with a carbonyl ligand in the unique capping position, which is capping an octahedral face containing two carbonyl ligands and one of the iodine atoms as shown in Fig. 2(*b*). The large iodide ligands are *trans* to each other in this complex. Colton and Kevekordes[27] have shown how the solution state ^{13}C NMR spectra of capped octahedral complexes containing a capping carbonyl ligand can be correlated with the crystallographically determined solid-state structure. For example, the low temperature ^{13}C NMR spectrum (−70 °C, 250 MHz, CD_2Cl_2) of [$WI_2(CO)_3(NCMe)_2$],[26] has two carbonyl resonances at δ = 228.48 and 202.36, with an intensity ratio of 1 : 2. The lower field resonance is due to the capping carbonyl group.[27] The resonance at δ = 202.36 is in the typical range for octahedral carbonyl ligands. The room temperature ^{13}C NMR spectrum (+25 °C, 250 MHz, CD_2Cl_2) of [$WI_2(CO)_3(NCMe)_2$] has a single carbonyl resonance which as expected suggests the complex is fluxional due to the small amount of energy required for these seven-coordinate complexes to rearrange. Many seven-coordinate halocarbonyl complexes exhibit this fluxional behaviour.[2,27]

The other three less commonly observed geometries of complexes derived from [$MI_2(CO)_3(NCMe)_2$] are exemplified by (*a*) [$WI_2(CO)_3(NCMe)(SbPh_3)$],[10] which has a distorted capped trigonal prismatic geometry with one triangular face having three CO groups, and the other having I(2), Sb and N, with I(1) capping the rectangular face defined by C(1), I(2), N and C(3) {see Fig. 3(*a*) and (*b*)}; (*b*) the S_3-bonded macrocyclic complex [$WI(CO)_3([9]aneS_3)$][BPh_4][28] which can be considered to have the so called '4 : 3 geometry' with the three

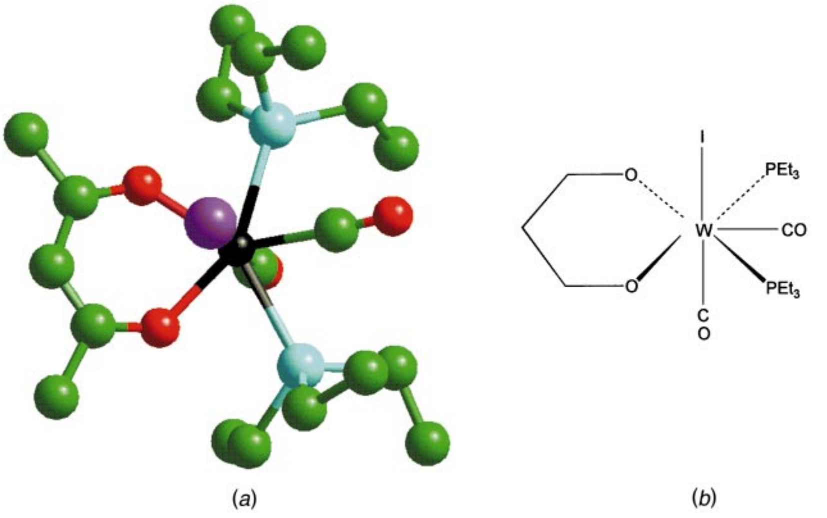


Fig. 5 (*a*) Molecular structure of [$WI(acac)(CO)_2(PEt_3)_2$].[29] (*b*) Simple representation of the pentagonal bipyramidal geometry of [$WI(acac)(CO)_2(PEt_3)_2$].

sulfur atoms forming the seat, and the three carbonyl ligands and an iodide group forming the four legs of this, often called 'piano stool' geometry {refer to Fig. 4(*a*) and (*b*)}; and (*c*) the least commonly observed structure in this system which is the pentagonal bipyramidal geometry, and which has only been found in very recently[29] observed structures of [MI(acac)-$(CO)_2(PEt_3)_2$] (M = Mo, W) {for M = W, see Fig. 5(*a*) and (*b*)}. It should be noted that many seven-coordinate lanthanide and actinide complexes do exhibit the pentagonal bipyramidal geometry.[24]

There is obviously a complex interplay between steric and electronic effects and multidenticity of the ligands attached to the metal in these systems which governs the geometry of these complexes. It is important to note that the geometry observed in the solid state appears to be preserved in solution as evidenced by ^{13}C NMR spectroscopy.[27]

4 Applications of the complexes [$MXY(CO)_3(NCMe)_2$] and their derivatives

Throughout the course of our work with the [MXY-$(CO)_3(NCMe)_2$] system, we have been conscious of the importance of the potential applications of these complexes in other areas of research. Two of the main potential applications of the complexes [$MXY(CO)_3(NCMe)_2$] and their derivatives we have been exploring are in (*i*) alkene metathesis catalysis, and (*ii*) nitrogen fixation research.

Our interest in developing the chemistry of [MXY-$(CO)_3(NCMe)_2$] with a very wide range of ligands results partly from a paper published by Bencze and Kraut-Vass[30] in 1985, which describes the catalytic activity of the halocarbonyl complexes [$MX_2(CO)_3L_2$] (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$). Complexes of this type were found to be single component catalysts for the ring opening polymerisation of norbornene and norbornadiene.[30] The best catalyst was found to be [$WCl_2(CO)_3(AsPh_3)_2$] which polymerises norbornadiene to give a vinylcyclopentene polymer with a high *cis*-content. Bencze and Kraut-Vass also found[30] that the mechanism of these reactions (5) involved loss of L in the rate-determining step, followed by coordination of the alkene (6).

$$[MX_2(CO)_3L_2] \overset{\text{RDS}}{\rightleftharpoons} [MX_2(CO)_3L] + L \qquad (5)$$

$$[MX_2(CO)_3L] + \text{alkene} \rightleftharpoons [MX_2(CO)_3L(\eta^2\text{-alkene})] \qquad (6)$$

Further studies by Bencze *et al.*[31] showed that the next step in the mechanism involves a 1,2-hydrogen shift on the coordinated alkene to give a carbene intermediate. In view of these observations we have been studying the catalytic activity of [$MXY(CO)_3(NCMe)_2$] and many of their derivatives shown in Scheme 1 towards the metathesis of a wide range of acyclic and cyclic alkenes with considerable success. Since Bencze and Kraut-Vass[30] showed the rate-determining step in these catalytic reactions involved loss of donor ligand {see reaction (5)}, it is significant that in our system the complexes [MXY-$(CO)_3(NCMe)_2$] and [$MXY(CO)_3(NCMe)L$] have at least one labile acetonitrile ligand, and many of the complexes in Scheme 1, including the alkyne complexes are highly active alkene metathesis catalysts.[32] For example, the complexes [$MBr_2(CO)_3(NCMe)_2$] (M = Mo or W) and [$WBr_2(CO)_3$(NCMe)(EPh_3)] (E = P, As, Sb) all rapidly initiate the room temperature polymerisation of norbornadiene.[32] Since the nature of L can be varied inexhaustibly in this system the stereochemistry of the products can, in principle, be controlled in these reactions.

The chemical industry puts a high emphasis on water soluble homogeneous catalysts, and during the course of our work in conjunction with Dr Aidan J. Lavery, ZENECA Specialties, we have discovered the cheap and readily available water solubilising substituted pyridine ligands such as sodium [pyridine-4-carboxylate], which forms completely water-soluble complexes, such as [$WI_2(CO)_3(4\text{-}NaO_2CC_5H_4N)_2$].[33] This and related water-soluble seven-coordinate complexes are being explored as potential biphasic catalysts.

Over the years much research has been directed to synthesising simple models that mimic the active site of the nitrogenase enzyme, which contains molybdenum, iron and sulfur in the active site. Recently, the X-ray structure analysis of the three forms of the active site of the FeMo protein which was isolated from *Azobacter vinelandii* and *Clostridium pasteurianum* has been described,[34] and is shown in Fig. 6. From our point of view it has a molybdenum centre with three attached sulfur atoms together with a bidentate anionic oxygen donor ligand, and a histidine group. In conjunction with Dr Raymond L. Richards *et al.*[28,29] at the Nitrogen Fixation Laboratory, we have been investigating the [$MXY(CO)_3(NCMe)_2$] system in nitrogen fixation research, by firstly investigating the chemistry of [$MXY(CO)_3(NCMe)_2$] and derivatives with a wide variety of neutral and anionic oxygen and sulfur donor ligands, and with iron–sulfur clusters such as [$Fe_4Cp_4S_6$], in order to attempt to mimic the active site of nitrogenase shown in Fig. 6. In order to get three sulfur atoms attached to molybdenum or tungsten we have used[28] the reactions of equimolar amounts of [MI_2-$(CO)_3(NCMe)_2$] with, for example, the macrocycle [9]aneS_3 in the presence of Na[BPh_4] to give the cationic complexes [$MI(CO)_3$([9]aneS_3)][BPh_4]. This has been crystallographically characterised for M = W, shown in Fig. 4(*a*). We are also investigating the reduction of the sulfur donor ligand complexes in the presence of dinitrogen, in order to form dinitrogen complexes containing sulfur donor ligands.

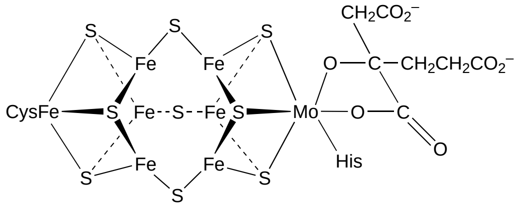
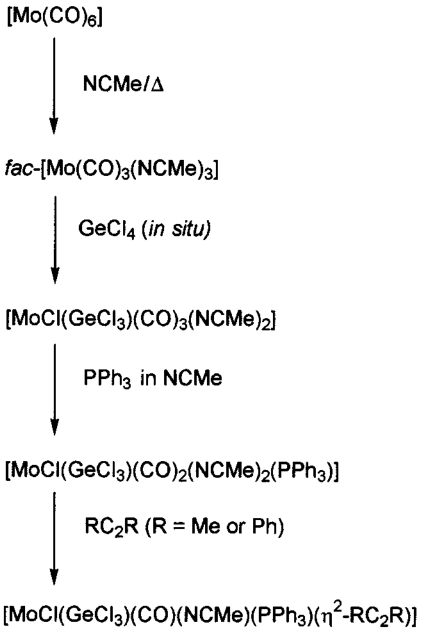


Fig. 6 Structure of the active site of FeMoco from an X-ray structural analysis[34]

5 Complexes containing six different monodentate ligands derived from [$MXY(CO)_3(NCMe)_2$]

Very few octahedral transition-metal complexes containing six different monodentate ligands have been described. An early example of a [M_{ABCDEF}] complex is [PtCl(Br)I-(NO_2)(NH_3)(py)] reported in 1958.[35] In order to illustrate the subtle differences in the chemistry of [$MI_2(CO)_3(NCMe)_2$] and other [$MXY(CO)_3(NCMe)_2$] type complexes, this section describes the strategic synthesis of [M_{ABCDEF}] molybdenum complexes, and the X-ray crystal structure of a dinuclear complex which has two identical M_{ABCDEF} centres.

The complete synthetic scheme for the synthesis of the [M_{ABCDEF}] complexes [$MoCl(GeCl_3)(CO)(NCMe)(PPh_3)(\eta^2$-$RC_2R$)] (R = Me or Ph) is shown in Scheme 2.[36] It is interesting to note that reaction of [$MoXY(CO)_3(NCMe)_2$] with an equimolar amount of PPh_3 in NCMe for X = Y = I gives the acetonitrile displaced product [$MoI_2(CO)_3(NCMe)(PPh_3)$], whereas, for X = Cl, Y = $GeCl_3$ the carbon monoxide displaced product, [$MoCl(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] is obtained. This is likely to be due to the combined higher electronegativity of the Cl and $GeCl_3$ groups which weakens the M–C bond due to decreased back-bonding and strengthens the Mo–N bond due to increased σ-bonding compared with the two iodo ligands. As previously discussed,[17] alkynes can act as 'four-electron donors', and hence the reaction of [MoCl-$(GeCl_3)(CO)_2(NCMe)_2(PPh_3)$] with one equivalent of RC_2R yielded the chiral [M_{ABCDEF}] complexes [$MoCl(GeCl_3)$-



Scheme 2

(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)] *via* displacement of a CO and an NCMe ligand. There are 15 possible simple geometrical isomers of an [M$_{\rm ABCDEF}$] octahedral complex, and each one will have its own diastereoisomer. Over the years, many hitherto unsuccessful attempts have been made to grow suitable single crystals for X-ray analysis of [M$_{\rm ABCDEF}$] complexes derived from [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-RC$_2$R)]. However, treatment of [MoCl(GeCl$_3$)(CO)(NCMe)(PPh$_3$)(η^2-MeC$_2$Me)] with an equimolar amount of [NBu$^n{}_4$][NCS] gave the anionic complex [NBu$^n{}_4$][MoCl(GeCl$_3$)(NCS)-(CO)(PPh$_3$)(η^2-MeC$_2$Me)], which reacted in acetone with a slight trace of water to afford the dimeric {M$_{\rm ABCDEF}$}$_2$ complex [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-NCS)(μ-SCN)MoCl(CO)-(PPh$_3$)(η^2-MeC$_2$Me)]. This is the first {M$_{\rm ABCDEF}$}$_2$ complex to be structurally characterised (Fig. 7).[37] Each molybdenum atom has terminal chloride, carbon monoxide, triphenylphosphine and but-2-yne ligands, and a nitrogen and sulfur of two bridged thiocyanate groups. One of the reasons for preparing mononuclear M$_{\rm ABCDEF}$ complexes was to synthesise and characterise new chiral catalysts. However, the dinuclear complex above is very interesting from a stereochemical point of view which was not discussed in the original communication.[37] The dimer (Fig. 7), is not a chiral molecule as there is a centre of symmetry located at the centre of the eight-membered ring and hence the dimer is the achiral *meso* form of the molecule (point group $C_{\rm i}$). The two Mo atoms are both stereocentres, but have opposite absolute configurations which can be classified as C and A using the Cahn–Ingold–Prelog priority rules by analogy with the well known *R/S* nomenclature system for tetrahedral stereocentres.

6 Conclusions and future developments of the [MXY(CO)$_3$(NCMe)$_2$] system

The main purpose of this article has been to illustrate how the easily prepared seven-coordinate complexes [MI$_2$-(CO)$_3$(NCMe)$_2$] have proved to be highly versatile starting materials for a wide range of reaction types as shown in Scheme 1. The diversity of this research is also highlighted by the use of a number of other oxidizing agents in place of I$_2$ such as XY (XY = ICl,[11] IBr,[12] GeCl$_4$[13] or SnCl$_4$[14]) which, when reacted with *fac*-[M(CO)$_3$(NCMe)$_3$] (prepared *in situ*[8]), give the products [MXY(CO)$_3$(NCMe)$_2$]. The [MXY(CO)$_3$(NCMe)$_2$] series of complexes have proved to be extremely useful as starting materials for a wide range of chemistry.

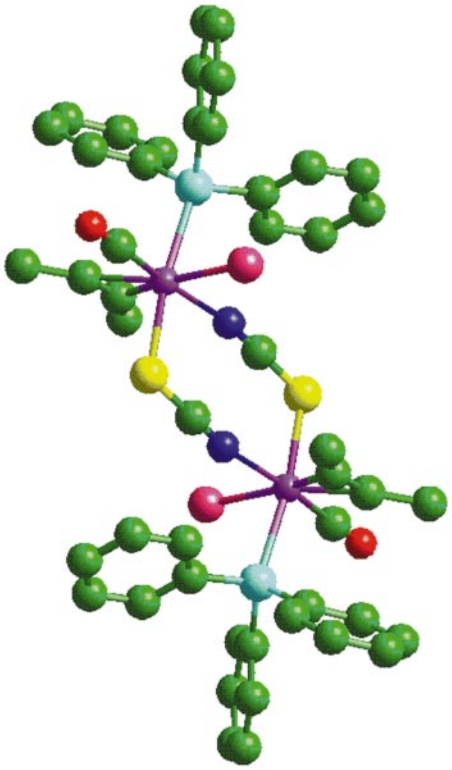


Fig. 7 Molecular structure of [Cl(CO)(PPh$_3$)(η^2-MeC$_2$Me)Mo(μ-NCS)(μ-SCN)MoCl(CO)(PPh$_3$)(η^2-MeC$_2$Me)][37]

I believe the most significant current and future potential uses of the [MXY(CO)$_3$(NCMe)$_2$] system are in homogeneous catalysis. Apart from the previously described,[32] uses of [MXY(CO)$_3$(NCMe)$_2$] and derivatives in alkene metathesis (Section 4) which we are continuing to develop; a very recent result[38] has shown that the bis(phosphite) complex [MoI$_2$(CO)-{P(OPr^i)$_3$}$_2$(η^2-MeC$_2$Ph)] catalyses the trimerisation of 1-phenylpropyne to give 1,2,4-trimethyl-3,5,6-triphenylbenzene. We are currently exploring the applications of [MoI$_2$-(CO){P(OPr^i)$_3$}$_2$(η^2-MeC$_2$Ph)] and related complexes for the trimerisation of other alkynes. The uses of the organometallic phosphines, such as [WI$_2$(CO){PhP(CH$_2$CH$_2$PPh$_2$)$_2$-*P,P′*}(η^2-MeC$_2$Me)][39] which exists as two diastereoisomers in a single crystal as shown in {Fig. 8(*a*) and (*b*)}, for the synthesis and applications of mixed-metal catalysts are also being investigated.

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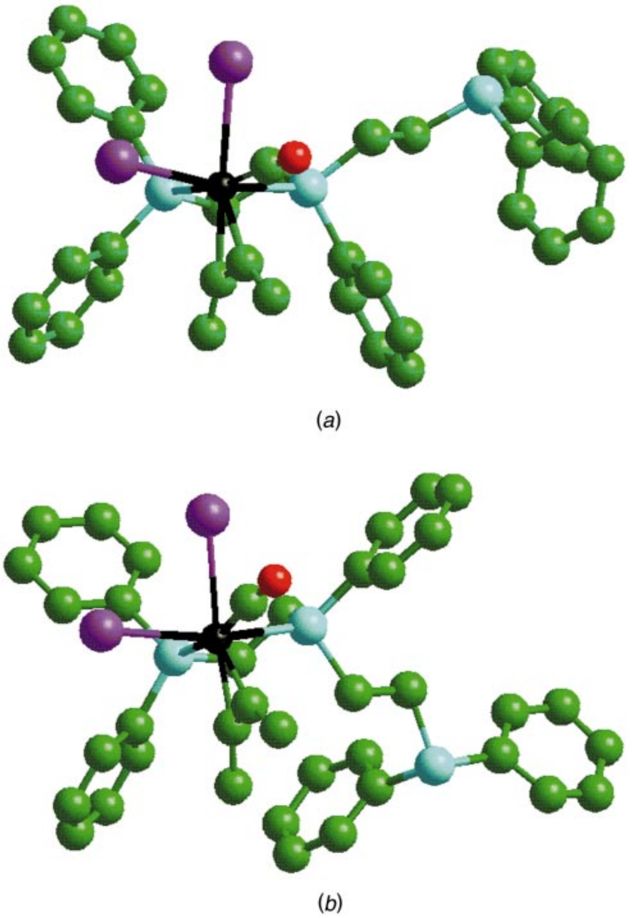

Fig. 8 Molecular structure of the two diastereoisomers of $[WI_2(CO)\{PhP(CH_2CH_2PPh_2)_2\text{-}P,P'\}(\eta^2\text{-}MeC_2Me)]$[39]

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