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Homoleptic alkylisocyanide complexes of molybdenum(0) and tungsten(0), useful precursors for the synthesis of low-valent dialkylaminocarbyne complexes

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Abstract

A large scale, high yield synthesis of the homoleptic alkylisocyanide complexes $M(RNC)_6$ (R = Et, ^{t}Bu) and carbonyl-free diethylaminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ starting from $M(CO)_6$ (M = Mo, W) is reported. The synthetic procedure begins with the conversion of $M(CO)_6$ into *fac*-$M(CO)_3(MeCN)_3$, followed by substitution of the acetonitrile ligands in *fac*-$M(CO)_3(MeCN)_3$ by RNC to give the isocyanide complexes *fac*-$M(CO)_3(RNC)_3$ (**1a–2b**) (**1**: M = Mo, **2**: M = W; **a**: R = Et, **b**: R = ^{t}Bu). Compounds **1a–2b** are then oxidatively decarbonylated with Br_2 to give the seven-coordinate M^{II} complexes $M(CO)_2(RNC)_3(Br)_2$ (**3a–4b**) (**3**: M = Mo, **4**: M = W). Subsequent reaction of **3a–4b** with an excess of RNC results in the elimination of the residual CO ligands and formation of the ionic compounds $[M(RNC)_6Br]Br$ (**5a–6b**) (**5**: M = Mo, **6**: M = W). Compounds **5a–6b** are then reduced with Na/Hg to yield $M(RNC)_6$ (**7a–8b**) (**7**: M = Mo, **8**: M = W), the isoelectronic congeners of $M(CO)_6$. Reaction of the ethylisocyanide derivatives $M(EtNC)_6$ (**7a**, **8a**) with Et_3OBF_4 leads finally to $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ (**9a**: M = Mo, **10a**: M = W). This route to electron-rich, isocyanide-substituted diethylaminocarbyne complexes is compared with the established procedure involving the stepwise decarbonylation of the Fischer-type carbyne complex *trans*-$I(CO)_4W{\equiv}CNEt_2$ with RNC.

Introduction

Since 1952, when the synthesis of the first zerovalent homoleptic isocyanide complex of the chromium triad, $Cr(PhNC)_6$, was accomplished by reaction of $Cr_2(OAc)_4 \cdot 2H_2O$ with PhNC [1], several methods have been developed for the preparation of these isoelectronic congeners of $M(CO)_6$ (M = Cr, Mo, W). They

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have utilized ligand displacement reactions of zerovalent, carbonyl-free precursors such as $M(bipy)_3$ (M = Cr, Mo, W; bipy = 2,2'-bipyridyl), $Cr_2(COT)_3$ (COT = cyclooctatetraene) and $Cr(C_{10}H_8)_2$ ($C_{10}H_8$ = naphthalene) with RNC [R = Ph, ^{t}Bu, Cy(Cyclohexyl)] [2–5], reduction of halide compounds such as $CrCl_3(THF)_3$, $MoCl_3$, $MoCl_4(EtCN)_2$ and WCl_6 by Na/Hg or Mg in the presence of RNC (R = Aryl, ^{t}Bu) [6–8], reductive elimination of isopropyl groups from $Cr(^iPr)_4$ [9], and finally reductive cleavage of the metal–metal multiple bond in the dinuclear complexes $M_2(OAc)_4$ (M = Cr, Mo), $W_2(dmhp)_4$ (dmhpH = 2,4-dimethyl-6-hydroxypyrimidine) and $W_2(mhp)_4$ (mhpH = 2-hydroxy-6-methylpyridine) by arylisocyanides [1,7,10] or Na/Hg and ^{t}BuNC [11–13]. However these methods have, with few exceptions, two disadvantages: (a) they give relatively low yields and (b) the preparation of the starting materials is tedious. Therefore studies of the reactivity of $M(RNC)_6$ are rather limited. They involve ligand displacement reactions, as in the photosubstitution of one isocyanide ligand in $M(RNC)_6$ by pyridine to give $M(RNC)_5(py)$ (M = Cr, Mo, W; R = Ph, $C_6H_3{}^iPr_2$-2,6) [14], oxidative additions of electrophiles as in the alkylation of $Mo(^tBuNC)_6$ with MeI or $PhCH_2Br$ to yield $[Mo(^tBuNC)_6Me]I$ [11] or $[(^tBuNC)_5Mo[\eta^2\text{-}C(N^tBu)CH_2Ph]]Br$ [13], electrochemical investigations by cyclic voltammetry [10,15–19], and chemical oxidations of $M(RNC)_6$. Illustrative examples of the latter are the reactions of $M(PhNC)_6$ (M = Mo, W) with $NOPF_6$ and I_2 to afford the cations $[M(PhNC)_5NO]^+$ and $[M(PhNC)_6I]^+$ [10,15] and the reaction of $Cr(RNC)_6$ (R = aryl) with $AgPF_6$ to yield, depending on the ratio of the reactants, the one or two electron oxidation products $[Cr(RNC)_6]PF_6$ or $[Cr(RNC)_6](PF_6)_2$ [16].

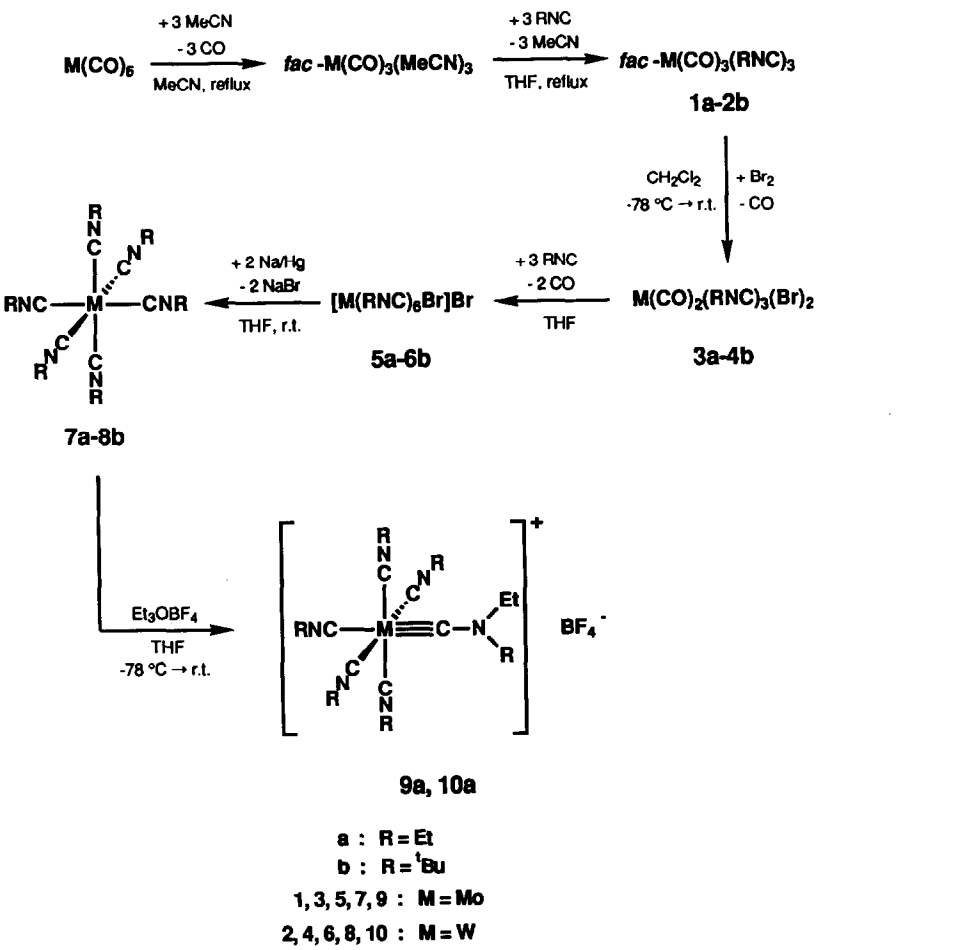
Our previous studies on reactivity of the isocyanide complexes *cis,trans*-$(\eta^5\text{-}C_5R_5)M(CO)_2(EtNC)I$ (R = H, Me; M = Mo, W) have shown that reduction of the metal centre activates the ethylisocyanide ligand for an electrophilic attack at nitrogen and provides a good route to low-valent diethylaminocarbyne complexes [20,21]. Moreover we have found that low-valent phenyl- and diethylaminocarbyne complexes such as $X(CO)_n(^tBuNC)_{4-n}W{\equiv}CPh$ (X = Br, I; n = 0, 1) and $I(CO)_n(^tBuNC)_{4-n}W{\equiv}CNEt_2$ (n = 1, 2) undergo a clean proton-induced isocyanide-carbyne coupling reaction with HX (X = Br, I) to give the acetylene complexes $(X)_2(CO)_n(^tBuNC)_{3-n}W[\eta^2\text{-}PhC{\equiv}CN(H)^tBu]$ (X = Br, I; n = 0, 1) [22] and $(I)_2(CO)_n(^tBuNC)_{3-n}W[\eta^2\text{-}Et_2NC{\equiv}CN(H)^tBu]$ (n = 1, 2) [23], respectively. These observations are important for understanding the reductive coupling of two adjacent isocyanide ligands in $[M(RNC)_6X]^+$-complexes (M = Mo^{II}, W^{II}; R = ^{t}Bu, Cy; X = Cl, Br, I, CN) to give bis(alkylamino)acetylene compounds, reported by Lippard and coworkers [24,25]. Initially these authors suggested that the crowded coordination sphere and the reduction of the metal centre promotes C–C bond formation in the seven coordinate isocyanide complexes [26]. Later they proposed the intermediate formation of an isocyanide-substituted aminocarbyne complex, but gave no experimental evidence in support of this proposal [27]. For rhenium they isolated such a complex, but failed to demonstrate coupling to give the acetylene compounds [28]. However, we recently verified that reductive coupling of isocyanide ligands in $[M(RNC)_6Br]Br$ (M = Mo, W; R = Et, ^{t}Bu) proceeds via two subsequently formed six coordinate key intermediates, a homoleptic zerovalent isocyanide complex and an isocyanide-substituted aminocarbyne complex. The aminocarbyne complex then undergoes an acid promoted isocyanide-carbyne coupling reaction to give the bis(amino)acetylene compounds [29].

In this paper high yield syntheses of the M^{II} complexes $[M(RNC)_6Br]Br$ (M = Mo, W; R = Et, ^{t}Bu), their reduction products $M(RNC)_6$ and the carbonyl-free diethylaminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ starting from $M(CO)_6$ are described, and compared with previously reported routes to related compounds.

Results and discussion

Treatment of the trisacetonitrile complexes *fac*-$M(CO)_3(MeCN)_3$ (M = Mo, W) with three equivalents of RNC (R = Et, ^{t}Bu) proceeds rapidly in refluxing THF to give the isocyanide complexes *fac*-$M(CO)_3(RNC)_3$ (**1a–2b**) (**1**: M = Mo, **2**: M = W; **a**: R = Et, **b**: R = ^{t}Bu) (Scheme 1) [30].

Compared with other methods such as the direct thermal replacement of three CO ligands from $M(CO)_6$ catalyzed by $CoCl_2$ or PdO [31–33] or the substitution reaction of olefinic derivatives of $M(CO)_6$ with RNC [34–38], this route to the



Scheme 1. Synthesis of homoleptic alkylisocyanide complexes and carbonyl-free diethylaminocarbyne complexes of molybdenum(0) and tungsten(0).

fac-$M(CO)_3(RNC)_3$ complexes has several advantages: (a) the starting compounds, *fac*-$M(CO)_3(MeCN)_3$, are readily obtained in practically quantitative yields by refluxing $M(CO)_6$ in acetonitrile [39,40]; (b) no other members of the substitution series $M(CO)_n(RNC)_{6-n}$ ($n = 0$–2 or 4–6) are formed during the reaction of *fac*-$M(CO)_3(MeCN)_3$ with RNC, so that *fac*-$M(CO)_3(RNC)_3$ are readily isolated in pure form (product purity has been checked by IR-spectroscopy and total elemental analyses to be > 99%); (c) the yields are essentially quantitative.

The compounds **1a–2b** react rapidly with one equivalent of Br_2 in CH_2Cl_2 at −78 °C to give the seven-coordinate M^{II} complexes $M(CO)_2(RNC)_3(Br)_2$ (**3a–4b**) (**3**: M = Mo, **4**: M = W), which are isolated as thermally stable, yellow solids in quantitative yields (Scheme 1). They are soluble in CH_2Cl_2 and THF but insoluble in Et_2O and n-pentane. High purity and exact stochiometry of the reactants are essential in these reactions to avoid formation of other mixed isocyanide-carbonyl M^{II} complexes such as $M(CO)(RNC)_4(Br)_2$ or further oxidation of **3a–4b** by bromine to M^{IV} complexes [30,41–43]. If these precautions are not taken, separation of **3a–4b** from these byproducts becomes difficult (since decomposition of **3a–4b** on silica gel or alumina prevents their purification by column chromatography) and results in lower yields.

Oxidative decarbonylation of substituted carbonyl complexes of M^0 (M = Mo, W) has been previously shown to offer a convenient preparative route to diamagnetic, seven-coordinate M^{II} complexes [30,41,42,44–48]. Using this method, Lippard and coworkers made **3b** from *fac*-$Mo(CO)_3(^tBuNC)_3$ (**1b**) and the diiodocompound $W(CO)_2(^tBuNC)_3(I)_2$ from *fac*-$W(CO)_3(^tBuNC)_3$ (**2b**), albeit in lower yields than reported here [41,49].

The reaction of **3a–4b** with an excess of RNC (R = Et, ^{t}Bu) in THF results in elimination of two carbonyl ligands and one bromide ligand from the coordination sphere to give the ionic compounds $[M(RNC)_6Br]Br$ (**5a–6b**) (**5**: M = Mo, **6**: M = W) (Scheme 1). The complexes **5a–6b** are isolated as thermally stable, yellow solids, which are very soluble in CH_2Cl_2, sparingly soluble in THF, but insoluble in Et_2O and n-pentane.

It should be noted that careful control of the reaction conditions is necessary for the preparation of the ethyl isocyanide derivatives **5a** and **6a**, otherwise the obtained products are not analytically pure (probably due to contamination with the dicationic compounds $[M(EtNC)_7](Br)_2$ (M = Mo, W)). Thus the molybdenum complex **3a** is best treated with an excess of EtNC in THF at room temperature, whereas the analogous but less reactive tungsten compound **4a** is best treated with an excess of EtNC in THF at 50–60 °C (bath temperature). In comparison the t-butylisocyanide derivatives $[M(^tBuNC)_6Br]Br$ (**5b**, **6b**) are exclusively formed even when **3b** and **4b** are refluxed in THF with an excess of ^{t}BuNC.

Previously a variety of methods have been described for the the synthesis of compounds with the general formula $[M(RNC)_6X]^+$ [M = Mo, W; R = Me, ^{t}Bu, Cy; X = Cl, Br, I, CF_3CO_2]. These methods include chemical oxidation of $M(CO)_6$ or isocyanide derivatives of $M(CO)_6$ with halogens in the presence of isocyanide [41], thermal displacement of CO ligands in M^{II}-dihalo-complexes such as $W(CO)_4(^tBuNC)(I)_2$ and $[W(CO)_4(I)_2]$ by RNC [45,50], and cleavage of the quadruple bond in the dinuclear complexes $Mo_2(O_2CCF_3)_4$ and $K_4Mo_2Cl_8$ by RNC [51]. However the present method is clearly superior since: (a) the products $[M(RNC)_6Br]Br$ are obtained quantitatively and in analytically pure form, and (b)

the starting materials, $M(CO)_2(RNC)_3(Br)_2$ (**3a–4b**), are readily available in large quantities by high yield reactions from $M(CO)_6$.

Reduction of **5a–6b** with Na/Hg in THF leads to the formation of $M(RNC)_6$ (**7a–8b**) (**7**: M = Mo, **8**: M = W), the isoelectronic congeners of $M(CO)_6$. These products are isolated as thermally stable, yellow (**7a**), orange (**7b, 8a**), or red (**8b**) solids in high yields (90–99%). They are all soluble in THF, toluene and Et_2O. The t-butylisocyanide derivatives **7b** and **8b** are also soluble in n-pentane. All complexes are very air sensitive and decompose in CH_2Cl_2 solution (probably due to oxidative degradation by the solvent).

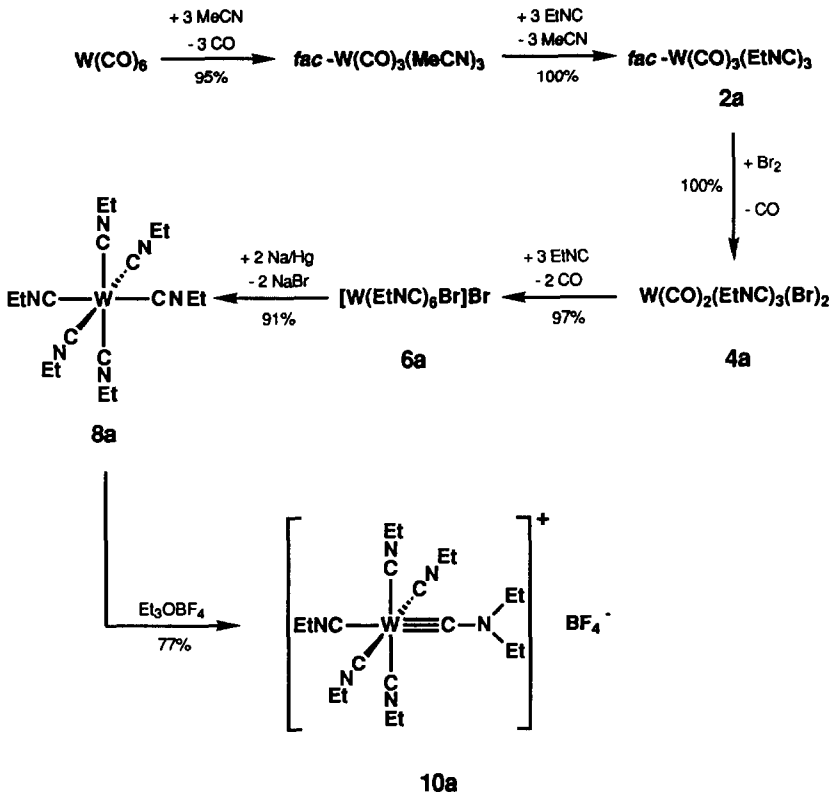
The t-butylisocyanide compounds $M(^tBuNC)_6$ (M = Cr, Mo, W) have been previously prepared by reductive cleavage of the metal–metal multiple bond in $Cr_2(OAc)_4$, $Mo_2(OAc)_4$ and $W_2(mhp)_4$ with Na/Hg and ^tBuNC [11–13]. It is noteworthy, that the only other reported homoleptic alkylisocyanide complexes of Group VI metals are the chromium compounds $Cr(RNC)_6$ (R = ^nBu, ^tBu, Cy, CF_3), which are not easily accessible [3–5,9,52].

We have previously shown that ethyl isocyanide ligands become susceptible to electrophilic attack at nitrogen by coordination to an electron-rich metal centre. This reaction has opened up a superior alternative to the classical Fischer route for the synthesis of low-valent, carbonyl-containing diethylaminocarbyne complexes [20,21]. Additionally it can be now used for the synthesis of a rare class of low-valent, carbonyl-free diethylaminocarbyne complexes, of which to our knowledge only two derivatives, *trans*-$I(^tBuNC)_4W{\equiv}CNEt_2$ and $[(^tBuNC)_5W{\equiv}CNEt_2]I$, are known to date [53]. Thus, ethylation of **7a** and **8a** with Et_3OBF_4 in THF occurs at the isocyanide nitrogen and yields the complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ (**9a, 10a**) (**9a**: M = Mo, **10a**: M = W), which are isolated, after purification by column chromatography on silylated silica gel, as purple solids in high yields (Scheme 1). They are very soluble in CH_2Cl_2 and THF but insoluble in Et_2O and n-pentane. **9a** and **10a** have remarkable thermal stability, melting at 114 and 110 °C, respectively, without decomposition. In contrast, the analogous carbonyl complexes $[(CO)_5Mo{\equiv}CNEt_2]BF_4$ and $[(CO)_5W{\equiv}CNEt_2]Y$ (Y = BF_4, SbF_6, BCl_4, $SbCl_6$) decompose in solution far below room temperature [54–56].

The ethylation of **7a** and **8a** with Et_3OBF_4 to give **9a** and **10a** is closely related to previously reported reactions involving electrophilic attack at an isocyanide coordinated at an electron-rich metal centre. Illustrative examples are the protonation of *trans*-$M(MeNC)_2(dppe)_2$ (M = Mo, W), *trans*-$ReCl(RNC)(dppe)_2$ (R = Me, ^tBu) and $ReCl(^tBuNC)_n(PMe_3)_{5-n}$ (n = 2, 3) with HX (X = BF_4, HSO_4, FSO_3) to give the alkylaminocarbyne complexes *trans*-$[(MeNC)(dppe)_2M{\equiv}CN(H)Me]X$ [57,58], *trans*-$[Cl(dppe)_2Re{\equiv}CN(H)R]BF_4$ [59] and $[Cl(^tBuNC)_{n-1}(PMe_3)_{5-n}Re{\equiv}CN(H)^tBu]BF_4$ [12] respectively, or the methylation of *trans*-$M(MeNC)_2(dppe)_2$ (M = Mo, W) with $MeFSO_3$ to give the dimethylaminocarbyne complex *trans*-$[(MeNC)(dppe)_2M{\equiv}CNMe_2]FSO_3$ [60].

The new synthetic route described here and the classical Fischer-route (i.e. stepwise transformation of a carbonyl to a carbene and then a carbyne ligand) to low-valent, carbonyl-free diethylaminocarbyne complexes are illustrated in Schemes 2 and 3.

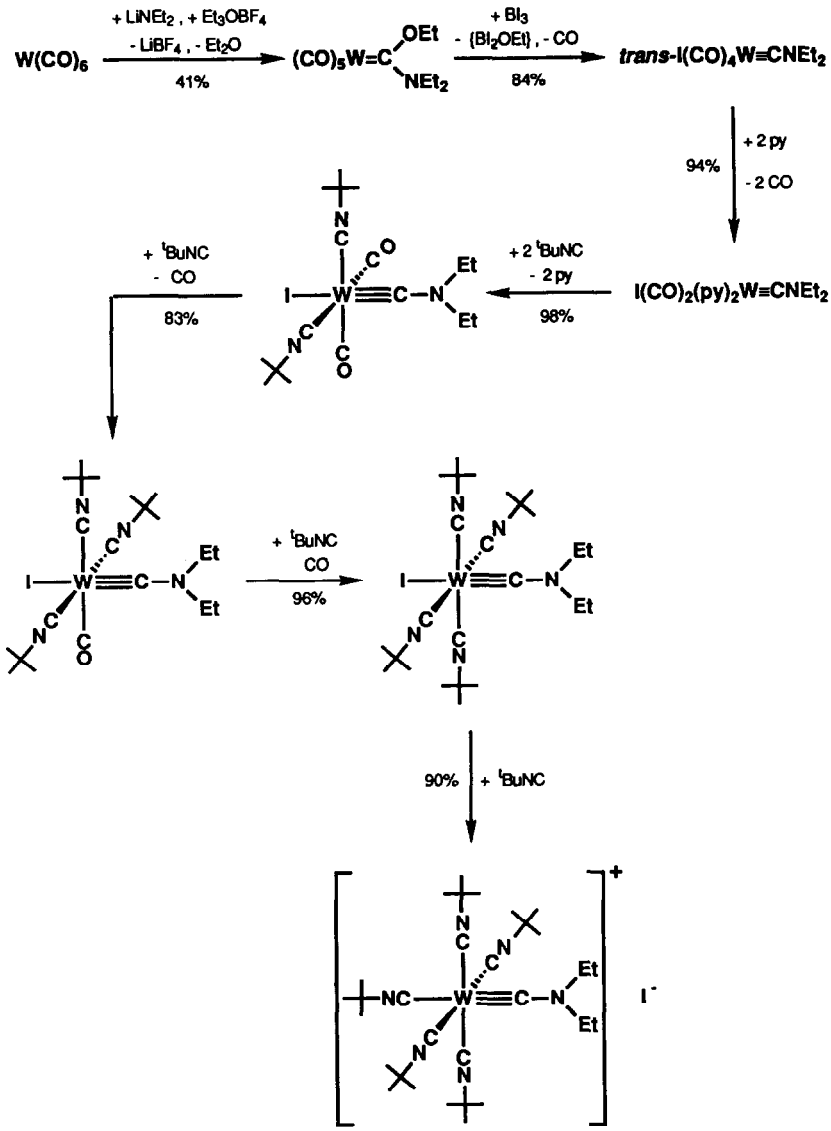
Each step of the new route involves an essentially quantitative, clean reaction (Scheme 2). Complicated purification procedures are therefore avoided and the overall yield of **10a** is very high [65% relative to $W(CO)_6$].



Scheme 2. New synthetic route to low-valent tungsten diethylaminocarbyne complexes via ethylisocyanide precursors.

In contrast, the Fischer-route to $[(^tBuNC)_5W{\equiv}CNEt_2]I$, the analogous complex to **10a** has several disadvantages: (a) the overall yield is low (23% relative to $W(CO)_6$) due to the poor yield for the transformation of $W(CO)_6$ to $(CO)_5W[C(OEt)NEt_2]$ [61]; (b) tedious purification of the thermolabile complex *trans*-$I(CO)_4W{\equiv}CNEt_2$ by low-temperature column chromatography is necessary [61]; and (c) extension of this method to analogous molybdenum complexes is restricted, since the key intermediate *trans*-$X(CO)_4Mo{\equiv}CNEt_2$ cannot be obtained from $(CO)_5Mo[C(OEt)NEt_2]$ and BX_3 (X = Br, I) [62]. (Note: the only hitherto known synthesis of *trans*-$X(CO)_4Mo{\equiv}CNEt_2$ in moderate yields involves the reaction of the extremely thermolabile $[(CO)_5Mo{\equiv}CNEt_2]BF_4$ with $NR_4{}^+X^-$ (R = ^{n}Bu, Et; X = Br, I) [54].)

In contrast to the observed reaction of $M(EtNC)_6$ (**7a**, **8a**) with Et_3OBF_4 to give diethylaminocarbyne complexes, reaction of $Mo(^tBuNC)_6$ with MeI has been previously reported to give either the methyl complex $[Mo(^tBuNC)_6Me]I$ [11] or the iminoacyl complex $[(^tBuNC)_5Mo[\eta^2\text{-}C(N^tBu)Me]]I$ [13]. These results are consistent with previous observations that for electron-rich isocyanide complexes the site of electrophilic attack (i.e. at the isocyanide nitrogen or the metal centre) is strongly influenced by the metal centre and the nature of the electrophile [12,20,21,28,57–60,63,64].



Scheme 3. Classical Fischer-route to low-valent tungsten diethylaminocarbyne complexes.

Spectroscopic investigations

IR spectra

The solution IR-spectra of **1a–10a** exhibit in the region 2200–1500 cm^{-1} characteristic absorptions for the ν(C≡NR) and ν(C≡O) stretching vibrations of the coordinated isocyanide and carbonyl ligands (Table 1).

The numbers and relative intensities of the ν(C≡NR) and ν(C≡O) absorption bands are consistent with the facial arrangement of the isocyanide and carbonyl ligands in the octahedral complexes **1a–2b** [30,35,36,65,66] and, in accord with the

Table 1

ν(C≡NR)-, ν(C≡O)- and ν(C=N) stretching vibrations of the complexes **1a–10a** in cm^{-1}; solvent CH_2Cl_2 (a), THF (b)

Complex	ν(C≡NR)	ν(C≡O)	ν(C=N)	Solvent
fac-$Mo(EtNC)_3(CO)_3$ (**1a**)	2169 m, 2134 m, 2108 w,sh	1940 vs, 1863 s,br	–	a
fac-$Mo(^tBuNC)_3(CO)_3$ (**1b**)	2154 m, 2114 m 2068 w,sh	1936 vs, 1860 s,br	–	a
fac-$W(EtNC)_3(CO)_3$ (**2a**)	2170 m, 2129 m 2103 w,sh	1935 vs, 1861 s,br	–	a
fac-$W(^tBuNC)_3(CO)_3$ (**2b**)	2155 m, 2108 m 2065 w,sh	1929 vs, 1858 s,br	–	a
$Mo(CO)_2(EtNC)_3(Br)_2$ (**3a**)	2204 s, 2184 s	1993 s, 1933 s	–	a
$Mo(CO)_2(^tBuNC)_3(Br)_2$ (**3b**)	2179 s, 2169 s,sh	1990 s, 1930 s		a
$W(CO)_2(EtNC)_3(Br)_2$ (**4a**)	2205 s,sh, 2183 s	1979 s, 1916 s	–	a
$W(CO)_2(^tBuNC)_3(Br)_2$ (**4b**)	2175 s, 2160 s,sh	1975 s, 1912 s	–	a
$[Mo(EtNC)_6Br]Br$ (**5a**)	2193 w,sh 2159 vs, 2141 s, 2103 m,sh	–	–	a
$[Mo(^tBuNC)_6Br]Br$ (**5b**)	2184 w, 2139 vs, 2116 s, 2069 m	–	–	a
$[W(EtNC)_6Br]Br$ (**6a**)	2199 w,sh, 2152 vs, 2131 s,sh, 2102 m,sh	–	–	a
$[W(^tBuNC)_6Br]Br$ (**6b**)	2188 w, 2132 vs, 2108 s,sh 2063 m	–	–	a
$Mo(EtNC)_6$ (**7a**)	1991 vs,br, 1868 s	–	–	b
$Mo(^tBuNC)_6$ (**7b**)	1966 s,br, 1869 vs,br	–	–	b
$W(EtNC)_6$ (**8a**)	1987 vs,br, 1868 s	–	–	b
$W(^tBuNC)_6$ (**8b**)	1960, s,br, 1856 vs,br	–	–	b
$[(EtNC)_5Mo{\equiv}CNEt_2]BF_4$ (**9a**)	2183 m, 2154 w, 2112 s, 2087 vs	–	1531 m	a
$[(EtNC)_5W{\equiv}CNEt_2]BF_4$ (**10a**)	2180 m, 2139 m,sh 2109 s, 2082 vs	–	1540 m	a

^1H and ^{13}C NMR data, rule out the presence of the meridional isomers *mer*-$M(CO)_3(RNC)_3$ [37].

A comparison of the IR data of **1a–2b** with those of **7a–8b** shows a considerable decrease in the ν(C≡NR) frequencies upon replacement of the carbonyl ligands (**1a–2b**) by the weaker π-acceptors EtNC and ^{t}BuNC (**7a–8b**) [35–37,66]. This decrease is a consequence of the enhancement of the electron density at the metal centre and the simultaneous strengthening of the metal–isocyanide back bonding in **7a–8b**. The fact that two ν(C≡NR) absorption bands are observed for **7a–8b** in solution strongly suggests a molecular geometry of symmetry lower than O_h, since for O_h-symmetry only one ν(C≡NR) fundamental is IR-allowed. In addition, the values of the ν(C≡NR) frequencies for the complexes **7a–8b** are very low relative to those of the free alkylisocyanides [ν(C≡NEt) in THF: 2149 cm^{-1}; ν(C≡N^{t}Bu) in CH_2Cl_2: 2140 cm^{-1}] [21,67]. In terms of the valence bond theory these results are interpreted in terms of a strong contribution by the canonical form **B** to the structure of **7a–8b**.

$$\bar{M}-C\equiv\overset{+}{N}-Et \longleftrightarrow M=C=\dot{N}\diagdown Et$$

(A) **(B)**

A similar interpretation has been previously given for the low ν(C≡NR) frequencies observed for other electron-rich isocyanide complexes such as *trans*-$M(MeNC)_2(dppe)_2$ [M = Mo, ν(C≡NMe) in THF: 1886 cm^{-1}; M = W, ν(C≡NMe) in THF: 1850 cm^{-1}] [68], *trans*-$ReCl(MeNC)(dppe)_2$ [ν(C≡NMe) in Nujol: 1830 and 1800 cm^{-1}] [59], $Cr(^tBuNC)_6$ [ν(C≡N^{t}Bu) in methylcyclohexane: 1960 and 1880 cm^{-1}] [5], $(\eta^5\text{-}C_5H_5)(CO)(^tBuNC)W{\equiv}CNEt_2$ [ν(C≡N^{t}Bu) in n-pentane: 1933 cm^{-1}] [69] and $Na[(\eta^5\text{-}C_5Me_5)W(CO)_2(EtNC)]$ [ν(C≡NEt) in THF: 1855 cm^{-1}] [20], and is supported by X-ray structural data, which show a multiple bond character of the $M\text{–}C_{isocyanide}$ bonds and an extensive bending of the isocyanide ligands at nitrogen in such complexes [57,70–72].

The complexes **9a** and **10a**, consistent with other diethylaminocarbyne complexes, exhibit a characteristic absorption band at ~ 1550 cm^{-1}, which may be assigned to a ν(C=N) vibration [20,21,53,60,69,73,74]. This band reveals the strong interaction of the metal–carbon triple bond with the lone pair of nitrogen as represented by the canonical form **D**:

(C) **(D)**

In keeping with previous results, this band is observed for the molybdenum complex **9a** at a slightly lower frequency than that for the analogous tungsten complex **10a** [21].

^{1}H NMR spectra

The proton NMR spectra of **1a–2b** and **7a–8b** (Table 2) exhibit one triplet and quartet from the methyl and methylene protons of the equivalent ethylisocyanide ligands (**1a, 2a, 7a, 8a**) and one singlet from the equivalent t-butylisocyanide ligands (**1b, 2b, 7b, 8b**), and in agreement with the IR-spectra, confirm the assigned structures for these octahedral complexes.

Equivalent isocyanide ligands are also found in **3a–6b** due to the fluxionality of these complexes on the proton NMR time scale at room temperature in solution [30]. Stereochemical nonrigidity has also been previously observed for other seven-coordinate complexes and studied by NMR-spectroscopy [75,76]. By contrast, two triplets and two quartets with 4 : 1 intensity ratio respectively are obtained for the inequivalent ethyl isocyanide ligands (*cis* and *trans* relative to the diethylaminocarbyne ligand) in **9a** and **10a**.

^{13}C NMR spectra

Further support for the structural assignment of **1a–10a** is given by the ^{13}C NMR spectra, which show signals from equivalent isocyanide ligands in the octahedral complexes **1a–2b** and **7a–8b** and the fluxional seven-coordinate complexes **3a–6b**, but two different environments for the ethyl isocyanide ligands in **9a** and **10a** (Table 3).

A comparison of the isocyanide carbon resonances of **1a–2b** with those of **7a–8b** reveals that deshielding occurs upon substitution of the carbonyl ligands in **1a–2b** (δ_C = 149.1–158.4 ppm) by the weaker π-acceptors ligands EtNC or ^{t}BuNC in **7a–8b** (δ_C = 178.6–192.5 ppm). This trend is consistent with previous NMR studies

Table 2

^{1}H NMR data of the complexes **1a–10a** in CD_2Cl_2 (a) and C_6D_6 (b) at +20 °C; relative intensities and multiplicities in parentheses, coupling constants in Hz

Complex	$(CH_3)_3CNC$	$N(CH_2CH_3)_2$	CH_3CH_2NC	$N(CH_2CH_3)_2$	CH_3CH_2NC	Solvent
1a	–	–	1.37 (9,t) ^3J(HH) 7.3	–	3.60 (6,q) ^3J(HH) 7.3	a
1b	1.46 (27,s)	–	–	–	–	a
2a	–	–	1.38 (9,t) ^3J(HH) 7.3	–	3.65 (6,q) ^3J(HH) 7.3	a
2b	1.47 (27,s)	–	–	–	–	a
3a	–	–	1.46 (9,t) ^3J(HH) 7.3	–	3.87 (6,q) ^3J(HH) 7.3	a
3b	1.54 (27,s)	–	–	–	–	a
4a	–	–	1.46 (9,t) ^3J(HH) 7.3	–	3.96 (6,q) ^3J(HH) 7.3	a
4b	1.54 (27,s)	–	–	–	–	a
5a	–	–	1.43 (18,t) ^3J(HH) 7.3	–	3.88 (12,q) ^3J(HH) 7.3	a
5b	1.50 (54,s)	–	–	–	–	a
6a	–	–	1.43 (18,t) ^3J(HH) 7.3	–	4.01 (12,q) ^3J(HH) 7.3	a
6b	1.51 (54,s)	–	–	–	–	a
7a	–	–	0.94 (18,t) ^3J(HH) 7.3	–	3.16 (12,q) ^3J(HH) 7.3	b
7b	1.31 (54,s)	–	–	–	–	b
8a	–	–	0.96 (18,t) ^3J(HH) 7.3	–	3.23 (12,q) ^3J(HH) 7.3	b
8b	1.32 (54,s)	–	–	–	–	b
9a	–	1.25 (6,t) ^3J(HH) 7.3	1.37 (15,t) ^3J(HH) 7.3 [a]	3.12 (4,q) ^3J(HH) 7.3	3.68 (10,q) ^3J(HH) 7.3 [b]	a
10a	–	1.26 (6,t) ^3J(HH) 7.3	1.38 (15,t) ^3J(HH) 7.3 [a]	3.14 (4,q) ^3J(HH) 7.3	3.73 (2,q) ^3J(HH) 7.3; 3.80 (8,q) ^3J(HH) 7.3	a

[a] Signals for the methyl protons of the ethylisocyanide ligands with *cis*- and *trans*-orientation relative to the diethylaminocarbyne ligand are by accident coincident. [b] Signals for the methylene protons of the ethylisocyanide ligands with *cis*- and *trans*-orientation relative to the diethylaminocarbyne ligand are by accident coincident.

on isocyanide complexes of zerovalent Group VI metals. These have shown that a stronger metal–isocyanide back bonding, which reduces the CN bond order, causes an increased deshielding of the isocyanide carbon [53,69,74,77].

Isocyanide–carbon, carbonyl–carbon and carbyne–carbon signals of the tungsten complexes appear at higher field than those of the analogous molybdenum compounds (Table 3) [21]. This is a consequence of the previous observed group VI metal triad ^{13}C shielding trend [77,78].

Mass spectra

Complexes **7a–8b** under EI conditions give characteristic fragmentation patterns, which involve successive loss of isocyanide ligands from the parent molecule ion, cleavage of an ethyl group from the ethyl isocyanide ligand (**7a, 8a**) or cleavage of a

Table 3

^{13}C-NMR data of the complexes **1a–10a** in CD_2Cl_2 (a) or C_6D_6 (b) at +20 °C

Complex	$N(CH_2CH_3)_2$	CH_3CH_2NC	Me_3CNC	CH_3CH_2NC	$N(CH_2CH_3)_2$	Me_3CNC	RNC	CO	M≡C	Solvent
1a	–	15.5	–	39.0	–	–	158.4	214.3	–	a
1b	–	–	31.0	–	–	56.5	158.3	215.0	–	a
2a	–	15.7	–	39.2	–	–	149.6	204.8	–	a
2b	–	–	31.1	–	–	56.1	149.1	205.6	–	a
3a	–	14.9	–	40.8	–	–	150.5	239.3	–	a
3b	–	–	28.9	–	–	57.2	148.7	237.3	–	a
4a	–	15.3	–	40.9	–	–	143.6	231.8	–	a
4b	–	–	30.3	–	–	58.7	143.0	231.9	–	a
5a	–	15.9	–	41.3	–	–	162.7	–	–	a
5b	–	–	30.8	–	–	58.1	163.0	–	–	a
6a	–	16.1	–	40.8	–	–	152.8	–	–	a
6b	–	–	31.1	–	–	58.2	153.5	–	–	a
7a	–	16.6	–	39.0	–	–	187.1	–	–	b
7b	–	–	32.1	–	–	55.1	192.5	–	–	b
8a	–	16.7	–	39.2	–	–	178.6	–	–	b
8b	–	–	32.2	–	–	55.4	184.8	–	–	b
9a	14.3	15.1; [a]	–	39.3; [a]	45.9	–	151.3; [a]	–	251.2	a
		16.0		39.5			167.4			
10a	14.3	15.2; [a]	–	39.5; [a]	44.5	–	143.2; [a]	–	243.8	a
		16.3		39.8			159.2			

[a] Signal for the ethylisocyanide ligand with *trans*-orientation relative to the diethylaminocarbyne ligand.

Table 4
Mass spectra of the complexes **7a–8b**; m/z values relative to the ^{98}Mo and ^{184}W isotope

Complex	m/z	tentative assignment
7a	428	M^+
	373	$[M-EtNC]^+$
	318	$[M-2EtNC]^+$
	289	$[M-2EtNC-Et]^+$
	263	$[M-3EtNC]^+$
	234	$[M-3EtNC-Et]^+$
	208	$[M-4EtNC]^+$
	179	$[M-4EtNC-Et]^+$
	153	$[M-5EtNC]^+$
7b	596	M^+
	513	$[M-^tBuNC]^+$
	430	$[M-2^tBuNC]^+$
8a	514	M^+
	459	$[M-EtNC]^+$
	430	$[M-EtNC-Et]^+$
	404	$[M-2EtNC]^+$
	375	$[M-2EtNC-Et]^+$
	320	$[M-3EtNC-Et]^+$
8b	682	M^+
	625	$[M-^tBu]^+$
	599	$[M-^tBuNC]^+$
	569	$[M-^tBu-Me_2C{=}CH_2]^+$
	542	$[M-^tBuNC-^tBu]^+$
	516	$[M-2^tBuNC]^+$
	486	$[M-^tBuNC-^tBu-Me_2C{=}CH_2]^+$
	430	$[M-^tBuNC-^tBu-2Me_2C{=}CH_2]^+$
	374	$[M-^tBuNC-^tBu-3Me_2C{=}CH_2]^+$
	318	$[M-^tBuNC-^tBu-4Me_2C{=}CH_2]^+$
	291	$[M-2^tBuNC-^tBu-4Me_2C{=}CH_2]^+$

t-butyl group and elimination of isobutene from the t-butyl isocyanide ligand **(8b)** (Table 4).

Conclusion

The described high yield synthesis of the homoleptic alkylisocyanide compounds $M(RNC)_6$ and the per-substituted diethylaminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ starting from $M(CO)_6$ is distinguished by a sequence of clean, large scale reactions via the easily accessible and well-characterized precursors *fac*-$M(CO)_3(RNC)_3$, $M(CO)_2(RNC)_3(Br)_2$ and $[M(RNC)_6Br]Br$ (M = Mo, W; R = Et, ^{t}Bu). The products have been recently shown to be key intermediates in the reductive isocyanide coupling reaction of $[M(RNC)_6X]^+$-complexes (X = halogen) and to undergo electrophile-induced CC-coupling reactions. The exploration of these fundamental CC-coupling steps and an extension to other reactivity studies of these rare, electron-rich compounds is considerably facilitated by the presented procedure.

Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulation. The solvents were dried by standard methods (n-pentane, toluene, Et_2O and THF over Na/benzophenone; CH_2Cl_2 over P_2O_5 and Na/Pb alloy) and distilled under nitrogen prior to use or stored in bottles over 4Å molecular sieves. All column chromatography was performed on silylated silica gel 60 (Merck, 0.063–0.2 mm, dried in vacuo and stored under nitrogen) as the stationary phase and a thermostated column of 45 cm length and 1.5 cm diameter.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were run on a Nicolet DX 5 FT spectrophotometer. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded in dry, de-oxygenated methylene-d_2-chloride and benzene-d_6 on a Jeol GX 400 FT instrument. Chemical shifts were referenced to residual solvent signals (CD_2Cl_2 δ_H 5.32 and δ_C 53.8 ppm; C_6D_6 δ_H 7.15 and δ_C 128.0 ppm). Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer.

The complexes *fac*-$M(CO)_3(MeCN)_3$ (M = Mo, W), *fac*-$W(CO)_3(RNC)_3$ (**2a**: R = Et; **2b**: R = ^{t}Bu) and $W(CO)_2(RNC)_3(Br)_2$ (**4a**: R = Et; **4b**: R = ^{t}Bu) were prepared as reported earlier [30,39,40]. EtNC and ^{t}BuNC were synthesized according to published procedures [79,80] distilled and stored under nitrogen. Et_3OBF_4 was obtained by Meerwein's method [81].

1. fac-*$Mo(CO)_3(EtNC)_3$ (1a)*

To a suspension of 1.47 g (4.85 mmol) of *fac*-$Mo(CO)_3(MeCN)_3$ in 80 ml of THF was added 1.2 ml (16.17 mmol) of EtNC, and the mixture was refluxed for 1 h. The resulting slight cloudy solution was filtered to remove some insoluble material, the solvent was removed from the pale yellow filtrate at reduced pressure, and **1a** isolated as a colourless, microcrystalline solid after reprecipitation of the residue from Et_2O/n-pentane. m.p.: 111°C. Yield: 1.66 g (99%). Found: C, 41.78; H, 4.26; N, 12.58; O, 14.10. $C_{12}H_{15}MoN_3O_3$ (345.21) calc.: C, 41.75; H, 4.38; N, 12.17; O, 13.90%.

2. fac-*$Mo(CO)_3(^tBuNC)_3$ (1b)*

To a suspension of 3.80 g (12.54 mmol) of *fac*-$Mo(CO)_3(MeCN)_3$ in 100 ml of THF was added 5.00 ml (44.20 mmol) of ^{t}BuNC and the mixture refluxed for 1.5 h. The resulting slight cloudy, pale yellow solution was worked up as described above for the preparation of **1a** (under 1.) and complex **1b** isolated as a colourless, microcrystalline solid. m.p.: 175°C. Yield: 5.35 g (99%). Found: C, 50.51; H, 6.36; Mo, 22.88; N, 10.12; O, 11.36. $C_{18}H_{27}MoN_3O_3$ (429.37) calc.: C, 50.35: H, 6.34; Mo, 22.34; N, 9.79; O, 11.18%.

3. $Mo(CO)_2(EtNC)_3(Br)_2$ (3a)

To a pale yellow solution of 1.14 g (3.30 mmol) of **1a** in 100 ml of CH_2Cl_2 was added dropwise at −80°C a solution of 0.17 ml (3.30 mmol) of Br_2 in 20 ml of CH_2Cl_2. The colour of the bromine disappeared immediately to give a yellow solution. The mixture was warmed to room temperature and stirred for 5 min. The solvent was then reduced in volume and an Et_2O/n-pentane mixture added to precipitate **3a**. The supernatant colourless solution was decanted and the yellow residue dried in vacuo. m.p.: 80°C (dec.). Yield: 1.57 g (quantitative). Found: C,

27.61; H, 3.37; Br, 34.03; Mo, 20.39, N, 8.98, O, 6.90. $C_{11}H_{15}Br_2MoN_3O_2$ (477.01) calc.: C, 27.70; H, 3.17; Br, 33.50; Mo, 20.11; N, 8.81; O, 6.71%.

*4. $Mo(CO)_2(^tBuNC)_3(Br)_2$ (**3b**)*

To a pale yellow solution of 1.54 g (3.59 mmol) of **1b** in 100 ml of CH_2Cl_2 was added dropwise at −80 °C a solution of 0.184 ml (3.57 mmol) of Br_2 in 20 ml of CH_2Cl_2, and the resulting yellow solution was worked up as described above for the preparation of **3a**. The complex **3b** was isolated as a yellow solid. m.p.: 106 °C (dec.). Yield: 2.00 g (99%). Found: C, 36.24; H, 4.85; Br, 29.21; Mo, 17.34, N, 7.53, O. 5.80. $C_{17}H_{27}Br_2MoN_3O_2$ (561.18) calc.: C, 36.38; H, 4.85; Br, 28.48; Mo, 17.10; N, 7.49; O, 5.70%.

*5. $[Mo(EtNC)_6Br]Br$ (**5a**)*

A solution of 1.60 g (3.35 mmol) of **3a** in 100 ml of THF was treated with 2.0 ml (26.95 mmol) of EtNC and the mixture stirred for 5 h at room temperature, during which gas evolution was observed and a yellow solid separated. The solvent was then removed in vacuo and the bright yellow solid washed with Et_2O. m.p.: 148 °C. Yield: 1.95 g (99%). Found: C, 36.86; H, 5.22; N, 13.73. $C_{18}H_{30}Br_2MoN_6$ (586.23) calc.: C, 36.88; H, 5.16; N, 14.34%.

*6. $[Mo(^tBuNC)_6Br]Br$ (**5b**)*

To a yellow solution of 1.41 g (2.51 mmol) of **3b** in 50 ml of THF was added 2.0 ml (17.68 mmol) of ^{t}BuNC. Gas evolution was immediately observed and the solution became cloudy. The mixture was then heated for 1 h at 60 °C. The resulting suspension was allowed to cool to room temperature and an Et_2O/n-pentane mixture was added. The almost colourless supernatant, solution was decanted and the bright yellow solid dried in vacuo. Yield: 1.89 g (quantitative). Found: C, 47.68; H, 7.20; N, 11.10. $C_{30}H_{54}Br_2MoN_6$ (754.55) calc.: C, 47.75; H, 7.21; N, 11.14%.

*7. $[W(EtNC)_6Br]Br$ (**6a**)*

A yellow solution of 1.97 g (3.49 mmol) of **4a** in 50 ml of THF was treated with 1.00 ml (13.48 mmol) of EtNC and the mixture was heated at 50–60 °C for 15 h. The resulting yellow suspension was reduced in volume and Et_2O was added. The almost colourless supernatant solution was decanted and the yellow residue dried in vacuo. m.p.: 112 °C. Yield: 2.28 g (97%). Found: C, 32.20; H, 4.52; Br, 22.93; N, 12.89; W, 27.42. $C_{18}H_{30}Br_2N_6W$ (674.14) calc.: C, 32.07; H, 4.48; Br, 23.71; N, 12.47; W, 27.27%.

*8. $[W(^tBuNC)_6Br]Br$ (**6b**)*

A yellow solution of 0.70 g (1.08 mmol) of **4b** in 50 ml of THF was treated with 1.2 ml (10.61 mmol) of ^{t}BuNC and the mixture refluxed for 5 h. The solvent was removed from the resulting suspension and the intense yellow solid washed with Et_2O. m.p.: 183 °C (dec.). Yield: 0.91 g (quantitative). Found: C, 43.00; H, 6.63; Br, 18.47; N, 10.00, W, 21.19. $C_{30}H_{54}Br_2N_6W$ (842.46) calc.: C, 42.77; H, 6.46; Br, 18.97; N, 9.98; W, 21.82%.

*9. $Mo(EtNC)_6$ (**7a**)*

A suspension of 1.50 g (2.56 mmol) of **5a** in 100 ml of THF was treated with 1.31 ml of 0.92% (w/w) Na/Hg (7.20 mmol Na) and the mixture stirred at room

temperature for 48 h, until all yellow solid had dissolved. The grey precipitate, consisting of NaBr and Na/Hg, was allowed to settle and the supernatant brown-yellow solution filtered through a filter canula. The solvent was removed from the filtrate at reduced pressure and the residue extracted with Et_2O. The Et_2O-solution was reduced in volume and cooled to −78 °C to complete the precipitation of **7a** as a yellow, microcrystalline solid. m.p.: 109 °C. Yield: 1.08 g (99%). Found: C, 50.32; H, 6.95; Mo, 22.60; N, 20.08. $C_{18}H_{30}MoN_6$ (426.42) calc.: C, 50.70; H, 7.09; Mo, 22.50; N, 19.71%.

10. $Mo(^tBuNC)_6$ (7b)

A suspension of 0.50 g (0.66 mmol) of **5b** in 75 ml of THF was treated with 0.55 ml of 0.92% (w/w) Na/Hg (3.02 mmol Na) and the mixture stirred at room temperature for 60 h, until all yellow solid had dissolved. The grey precipitate consisting of NaBr and Na/Hg, was allowed to settle and the supernatant orange solution filtered through a filter canula. The solvent was removed from the filtrate at reduced pressure and the residue extracted with n-pentane. The n-pentane solution was reduced in volume and the product allowed to crystallize at −78 °C to give **7b** as an orange, microcrystalline solid. m.p.: 127 °C. Yield: 0.39 g (99%). Found: C, 60.29; H, 9.20; Mo, 16.62; N, 14.40. $C_{30}H_{54}MoN_6$ (594.74) calc.: C, 60.59; H, 9.15; Mo, 16.13; N, 14.13%.

11. $W(EtNC)_6$ (8a)

By the method used for the preparation of **7a**, **8a** was obtained as an orange solid by reaction of a yellow suspension of 0.95 g (1.41 mmol) of **6a** with 1.10 ml of 0.92% (w/w) Na/Hg (6.05 mmol Na) in 75 ml of THF. m.p.: 109 °C. Yield: 0.66 g (91%). Found: C, 41.42; H, 5.80; N, 16.34; W, 35.13. $C_{18}H_{30}N_6W$ (514.33) calc.: C, 42.03; H, 5.88; N, 16.34; W, 35.75%.

12. $W(^tBuNC)_6$ (8b)

By the method used for the preparation of **7b**, **8b** was obtained as a red, microcrystalline solid by reaction of a yellow suspension of 1.20 g (1.42 mmol) of **6b** with 1.20 ml of 0.92% (w/w) Na/Hg (6.60 mmol Na) in 90 ml of THF at room temperature. m.p.: 132 °C. Yield: 0.96 g (99%). Found: C, 52.33; H, 7.98; N, 12.10. $C_{30}H_{54}N_6W$ (682.65) calc.: C, 52.79; H, 7.97; N, 12.31%.

13. $[(EtNC)_5Mo{\equiv}CNEt_2]BF_4$ (9a)

To a yellow solution of 0.30 g (0.70 mmol) of **7a** in 40 ml of THF was added 0.13 g (0.68 mmol) of Et_3OBF_4 at −80 °C. The resulting suspension was warmed to room temperature and stirred for 2 h during which the insoluble Et_3OBF_4 dissolved and the solution became dark red. The solvent was then evaporated and the residue purified by column chromatography on silylated silica gel at +5 °C. Elution with CH_2Cl_2/Et_2O (1/2) gave a purple band, which yielded complex **9a** as a purple solid after evaporation of the solvent and reprecipitation of the residue from CH_2Cl_2/Et_2O/n-pentane. m.p.: 114 °C. Yield: 0.32 g (84%). Found: C, 44.22; H, 6.43; F, 14.35; Mo, 17.70; N, 15.41. $C_{20}H_{35}BF_4MoN_6$ (542.28) calc.: C, 44.30; H, 6.51; F, 14.01; Mo, 17.69; N, 15.50%.

*14. $[(EtNC)_5W{\equiv}CNEt_2]BF_4$ (**10a**)*

A yellow solution of 0.39 g (0.76 mmol) of **8a** was treated with 0.14 g (0.74 mmol) of Et_3OBF_4 in 50 ml of THF at −78 °C. The suspension was allowed to warm to room temperature and stirred for 2 h. The solvent was removed from the resulting dark red solution and the residue purified as described for the preparation of **9a**, to give **10a** as a deep purple solid. m.p.: 110 °C. Yield: 0.37 g (77%). Found: C, 38.32; H. 5.57; F, 12.32; N, 13.21; W, 28.41. $C_{20}H_{35}BF_4N_6W$ (630.19) calc.: C, 38.12; H, 5.60; F, 12.06; N, 13.34; W, 29.17%.

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