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Carbyne–carbyne coupling at a single metal center. Synthesis and structure of bis(diethylamino)acetylene complexes of molybdenum(II) and tungsten(II)

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Abstract

A high-yield synthesis of Mo^{II} and W^{II} bis(diethylamino)acetylene complexes starting from $M(CO)_6$ (**1**, **2**) is reported. This begins with the stepwise transformation of $M(CO)_6$ to the M^{II} isocyanide complexes $M(CO)_2(CNR)_3(Br)_2$ (**7a**–**8b**) (**7**: M = Mo; **8**: M = W; **a**: R = Et; **b**: R = ^tBu). Complexes **7a**–**8b** react with $Et_2NC{\equiv}CNEt_2$ to give the cationic alkyne complexes *mer*-$[Br(CO)(RNC)_3M(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**9a**–**10b**) (**9**: M = Mo; **10**: M = W). Thermal decarbonylation of **9a**–**10b** with RNC affords the carbonyl-free derivatives *trans*-$[Br(RNC)_4M(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**11a**–**12b**) (**11**: M = Mo; **12**: M = W). Complexes **11a** and **12a** can be also obtained from the homoleptic isocyanide complexes $M(CNEt)_6$ (**13**: M = Mo; **14**: M = W) by a sequence of reactions resulting in coupling of two ethyl isocyanide ligands to give a bis(diethylamino)acetylene ligand. This sequence is initiated by the regioselective ethylation of $M(CNEt)_6$ with one equivalent of $[Et_3O]BF_4$ to give the diethylaminocarbyne complexes $[(EtNC)_5M{\equiv}CNEt_2]BF_4$ (**15**: M = Mo; **16**: M = W). Addition of another equivalent $[Et_3O]BF_4$ to **15** and **16** results in the formation of the bis-diethylaminocarbyne complexes $[(EtNC)_4M(CNEt_2)_2](BF_4)_2$ (**17**: M = Mo; **18**: M = W). On treatment with $[NEt_4]Br$ these undergo a carbyne–carbyne coupling reaction to give the alkyne complexes **11a** and **12a**, respectively. Spectroscopic data for the novel transition-metal complexes of bis(diethylamino)acetylene **9a**–**12b** indicate substantial bond delocalization in the metal–alkyne fragment and restricted rotation of the diethylamino groups around the C_{alkyne}–N bonds. The alkyne ligand acts as a four-electron donor and allows the metal center to achieve a closed-shell configuration. These observations are supported by the results of a single-crystal X-ray diffraction study of the complex *trans*-$[Br(^tBuNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]PF_6$ (**12b'**), obtained from **12b** and $TlPF_6$.

Introduction

Ynamines ($R_2NC{\equiv}CR'$) have proved to be a versatile species for organic syntheses, undergoing a variety of addition and cycloaddition reactions with

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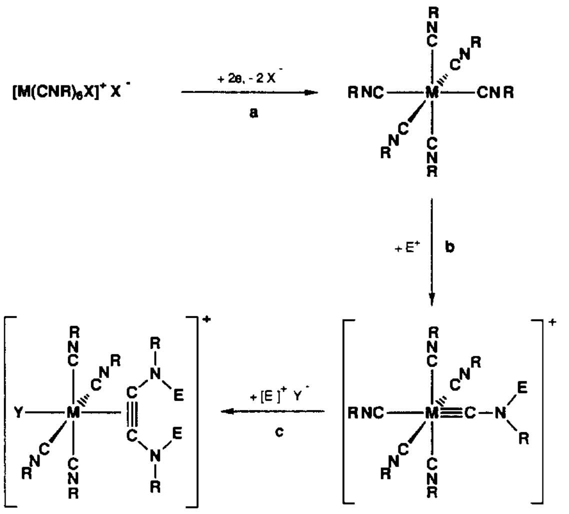


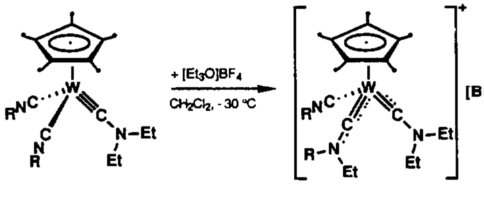
M = Mo W X Y = Halogen R = Et ᵗBu E = H Et $SiMe_3$, E = H

Scheme 1. Stepwise mechanism for the reductive coupling of two isocyanide ligands in $[M(CNR)_6X]^+$ complexes

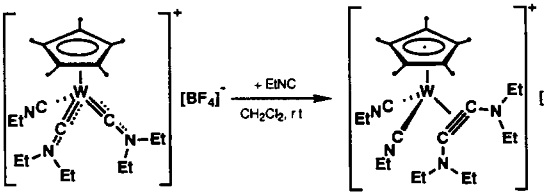
electrophiles [1]. This reactivity can be attributed to their enhanced nucleophilic character. In contrast, little is known about the reactivity of the closely related ynediamines ($R_2NC{\equiv}CNR'_2$), although convenient methods for the synthesis of these rare heterosubstituted acetylenes involving reactions of trichloroethylene with lithium dialkylamides or the decarbonylation of bis(dialkylamino)cyclopropenons have been known for more than 25 years [2]. Thus only a few reactions of ynediamines with organic substrates have been reported to date, *viz.* [2 + 1] cycloadditions to carbon monosulfide [3a] and aryl isocyanides [3b], [2 + 2] cycloadditions to *N*-sulfinylamines, sulfines and sulfur diimides [3c,d], and 1,4-dipolar cycloadditions to pyrimidin-1-ium-olates [3e–g]. Reactions of ynediamines with inorganic substrates are also limited to reactions of $Et_2NC{\equiv}CNEt_2$ with metal carbonyls [4], insertion reactions of $Et_2NC{\equiv}CNEt_2$ to the metal–carbon bond of Fischer type carbene complexes [5], [2 + 2] cycloadditions of $Et_2NC{\equiv}CNEt_2$ across the X=C bond (X = S, Se, Te) of coordinated heteroaldehydes- and ketones [6], and a metathesis reaction of $Et_2NC{\equiv}CNEt_2$ with the alkylidyne complex $(^tBuO)_3W{\equiv}CMe$ [7].

Our interest in the chemistry of ynediamines arose from mechanistic studies [8] of the reductive coupling of two alkyl isocyanide ligands in $[M(CNR)_6X]^+$ complexes (M = Mo^{II}, W^{II}; X = halide) to form coordinated bis(alkylamino)acetylenes [9]. These studies showed that reductive isocyanide–isocyanide coupling is a multistep process. The initial step involves a two-electron reduction of the seven-coordinate starting materials to give the octahedral M^0 isocyanide complexes $M(CNR)_6$ (Scheme 1, step a) [8a,9e]. This step is followed by the addition of a Lewis acid to one isocyanide nitrogen atom of $M(CNR)_6$ to give an octahedral cationic aminocarbyne complex (Scheme 1, step b). Addition of a second equivalent of an acid (HX) finally induces coupling of the aminocarbyne with the adjacent isocyanide ligand to give the diaminoacetylene complex [8b,c] (Scheme 1, step c).

This carbyne–isocyanide coupling is observed for a number of electron-rich Group VI transition metal carbyne complexes [10]. Recently experimental observations indicated that this reaction proceeds in two steps [8d]. The initial step involves an electrophile-induced transformation of the carbyne complex to a bis-carbyne intermediate (eq. a). This is followed by the nucleophile-promoted carbyne–carbyne coupling reaction of the bis-carbyne intermediate to yield the alkyne product (eq. b).



(a)



(b)

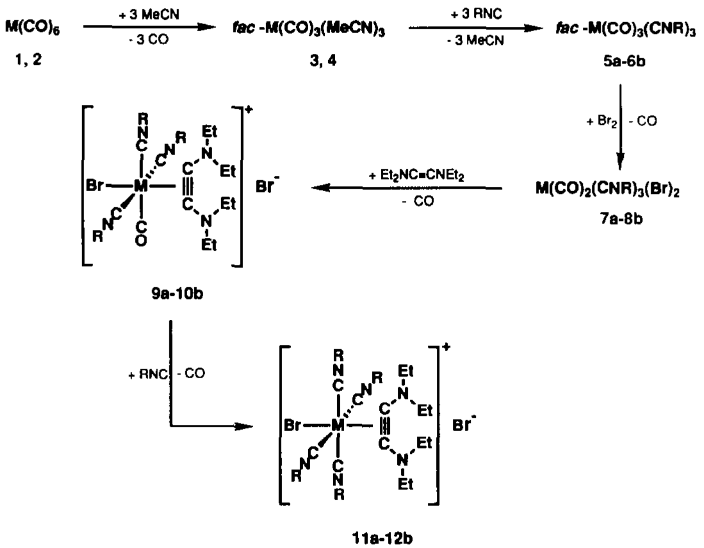
In continuation of our work on transition-metal mediated formation of C_2-units from C_1 fragments, we describe below two different routes for the synthesis of M^{II} bis(diethylamino)acetylene complexes starting from $M(CO)_6$ (M = Mo, W).

Results and discussion

The molybdenum(II) and tungsten(II) bis(diethylamino)acetylene complexes were made starting from the metal hexacarbonyls $M(CO)_6$ (**1**: M = Mo; **2**: M = W). The hexacarbonyls were first converted into the M^0 isocyanide complexes *fac*-$M(CO)_3(CNR)_3$ (**5a**–**6b**) (Scheme 2) [8a,10d]. The latter were then treated with one equivalent of bromine to give the halo-isocyanide complexes $M(CO)_2(CNR)_3(Br)_2$ (**7a**–**8b**) (**7**: M = Mo; **8**: M = W; **a**: R = Et; **b**: R = ^{t}Bu) (Scheme 2) [8a,10d].

The complexes **7a**–**8b** are convenient precursors for the synthesis of other mononuclear Mo^{II} and W^{II} compounds because they can be obtained pure from the hexacarbonyls $M(CO)_6$ by high yield reactions, which can be scaled up to 30 g [8a,10d]. In addition, they are stable enough to be stored at room temperature but at the same time exhibit high reactivity owing to the presence of labile CO ligands. Thus, treatment of the molybdenum derivatives **7a** and **7b** with $Et_2NC{\equiv}CNEt_2$ in CH_2Cl_2 at 20°C is accompanied by rapid evolution of CO gas, resulting in the formation of the cationic alkyne complexes *mer*-$[Br(CO)(RNC)_3Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**9a**: R = Et; **9b**: R = ^{t}Bu) (Scheme 2).

Complexes **9a** and **9b** were isolated after purification by column chromatography on a silylated silica support as orange microcrystalline solids in 80 and 94%



Scheme 2. Synthesis of M^{II} bis(diethylamino)acetylene complexes starting from $M(CO)_6$ (M = Mo, W) and $Et_2NC{\equiv}CNEt_2$.

yields, respectively. They are very soluble in CH_2Cl_2, moderate soluble in THF, but insoluble in Et_2O and n-pentane, and decompose upon heating under argon at 102 and 70°C, respectively.

The tungsten complexes $W(CO)_2(CNR)_3(Br)_2$ (**8a**, **8b**) were found to be less reactive than the analogous molybdenum compounds **7a** and **7b**. For example, no reaction was observed between **8a** or **8b** and $Et_2NC{\equiv}CNEt_2$ in CH_2Cl_2 at ambient temperature. However, when a THF solution of **8a** and **8b** was refluxed in the presence of the alkyne CO replacement occurred to give the bis(diethylamino)acetylene complexes *mer*-$[Br(CO)(RNC)_3W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**10a**: R = Et; **10b**: R = ^tBu) (Scheme 2). Evidence for this was provided by the IR spectra of the reaction solutions, which showed a gradual decrease in the intensity of the two strong $\nu(CO)$ absorptions of the starting materials at 1971 and 1905 cm^{-1} (**8a**) and 1970 and 1910 cm^{-1} (**8b**) and concomitant increase in the intensity of the $\nu(CO)$ absorption of the products **10a** and **10b** at 1966 and 1967 cm^{-1}, respectively.

Complexes **10a** and **10b** were isolated after purification by column chromatography on a silylated silica support as orange microcrystalline solids in 91 and 89% yields, respectively. They are thermally more stable than the analogous molybdenum compounds **9a** and **9b**, decomposing under argon at 123 and 116°C, respectively.

It is noteworthy that reactions of the dibromo complexes $M(CO)_2(CNR)_3(Br)_2$ (**7a–8b**) or the analogous diiodo compound $W(CO)_2(CNEt)_3(I)_2$ with alkynes such as $PhC{\equiv}CBr$, $PhC{\equiv}CH$ and $RO_2CC{\equiv}CCO_2R$ (R = Me, Et) have been previously shown to undergo elimination of both CO ligands to give the neutral alkyne products *mer*-$(Br)_2(RNC)_3M(\eta^2\text{-}R_1C{\equiv}CR_2)$ (R = Et, ^tBu; M = Mo, W) and *mer*-$(I)_2(EtNC)_3W(\eta^2\text{-}R_1C{\equiv}CR_2)$, respectively [10d,11]. No formation of cationic monocarbonyl derivatives analogous to **9a–10b** was observed in these reactions. In contrast, diaminoacetylene complexes of the type $(I)_2(CO)_n(^tBuNC)_{3-n}W[\eta^2\text{-}$

$Et_2NC{\equiv}CN(H)^tBu$] ($n = 1, 2$) were reported to react with ^tBuNC to give the cationic monocarbonyl complex *mer*-$[(I)(CO)(^tBuNC)_3W[\eta^2\text{-}Et_2NC{\equiv}CN(H)^tBu]]I$, the latter being analogous with **10b** [10b].

Reaction of the molybdenum complexes **9a** and **9b** with RNC in refluxing THF gave the carbonyl-free alkyne complexes *trans*-$[Br(RNC)_4Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**11a**, **11b**) (**a**: R = Et; **b**: R = ^tBu) (Scheme 2). These were isolated as green solids in 94 and 96% yields, respectively. In contrast, the less reactive tungsten compounds **10a** and **10b** undergo an analogous CO substitution reaction only in refluxing DME; the purple alkyne complexes *trans*-$[Br(RNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**12a**, **12b**) were obtained in 91 and 87% yields, respectively (Scheme 2). Reaction of the t-butyl isocyanide derivative **12b** with $TlPF_6$ in CH_2Cl_2 at room temperature results in an exchange of the counter-anion to give *trans*-$[Br(^tBuNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]PF_6$ (**12b′**). Exchange of the bromo ligand in **12b** by t-butyl isocyanide to give the dicationic complex $[(^tBuNC)_5W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)](PF_6)_2$ did not occur even when complex **12b** was treated with an excess of $TlPF_6$ and ^tBuNC in refluxing CH_2Cl_2.

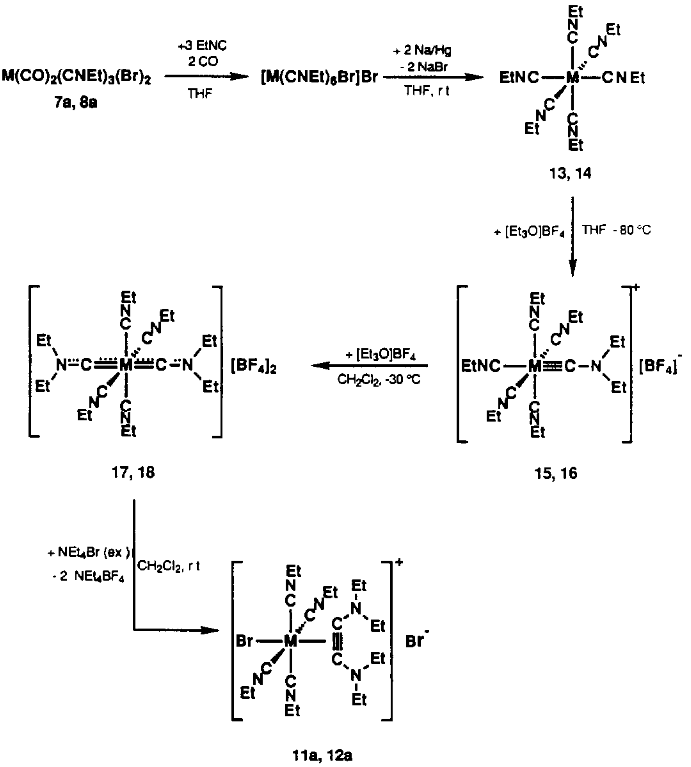
Complexes **11a–12b′** show considerable thermal stability, melting without decomposition between 136 and 150°C. They are all soluble in CH_2Cl_2, sparingly soluble in THF and DME, but insoluble in Et_2O and *n*-pentane. The molybdenum compounds **11a** and **11b** exhibit thermochromic behavior in the solid state. Thus, at ambient temperature they are green but at −80°C purple colored. In contrast, CH_2Cl_2 solutions of **11a** and **11b** are purple over the temperature range −80 to +20°C.

Bis(diethylamino)acetylene in complexes **9a–12b′** acts as a four-electron donor ligand and helps the metal center to attain a noble gas configuration. This is indicated by the spectroscopic data for these compounds and the crystal structure of **12b′**. The existence of four-electron donation by the alkyne ligand is further supported by the low reactivity of **9a–12b′**, as demonstrated by the thermal stability and the slow decomposition of these compounds in the presence of water and oxygen.

All these properties are inconsistent with a formulation of **9a–12b′** as 16e complexes containing a two-electron donor alkyne ligand [12]. Further evidence for the ionic nature of the alkyne complexes **9a–12b′** was provided by the molar conductances of **10b** and **12b**, which are close to those reported for 1:1 electrolytes (**10b**: c 8.80×10^{-4} mol/dm^3, T 22°C, Λ_M 134.2 Ω^{-1} cm^2 mol^{-1}; **12b**: c 7.06×10^{-4} mol/dm^3, T 22°C, Λ_M 125.5 Ω^{-1} cm^2 mol^{-1}) [13,14].

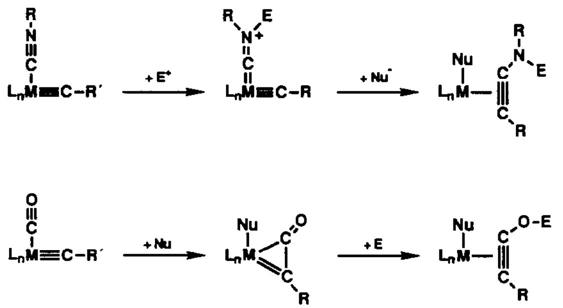
An alternative route to molybdenum(II) and tungsten(II) bis(diethylamino)-acetylene complexes was developed starting from the halo-isocyanide compounds **7a** and **8a**. These were first transformed to the diethylaminocarbyne complexes **15** and **16** (Scheme 3). The transformation was carried out as previously described by a sequence of reactions involving substitution of the CO ligands in **7a** and **8a** by RNC to give the M^{II} complexes $[M(CNEt)_6Br]Br$, followed by reductive dehalogenation of the latter with Na/Hg to give the homoleptic ethyl isocyanide complexes $M(CNEt)_6$ (**13**, **14**) [8a]. These were subsequently treated with one equivalent of $[Et_3O]BF_4$ to give complexes **15** and **16** (Scheme 3).

Reaction of the mono-diethylaminocarbyne complexes **15** and **16** in CH_2Cl_2 with a second equivalent of $[Et_3O]BF_4$ yielded the bis-diethylaminocarbyne complexes **17** and **18**, respectively (Scheme 3). Unfortunately isolation of the bis-dieth-



Scheme 3. Transition-metal centered formation of bis(diethylamino)acetylene by coupling two ethyl isocyanide ligands.

ylaminocarbyne complexes **17** and **18** in pure form was prevented by the concomitant formation of ionic by-products, which were difficult to remove. However formation of these compounds was evidenced by the IR spectra of the reaction solutions, which revealed a gradual decrease in intensity of the two strong $\nu(\mathrm{C{\equiv}NEt})$ absorptions of the starting materials at 2112 and 2087 cm^{-1} (**15**) and 2109 and 2082 cm^{-1} (**16**) and a concomitant increase in intensity of the $\nu(\mathrm{C{\equiv}NEt})$ absorptions of the products at 2201 and 2157 cm^{-1} (**17**) and 2195 and 2144 cm^{-1} (**18**). Furthermore the IR spectra of the reaction solutions showed a gradual increase in intensity of the characteristic $\nu(\mathrm{C{=}N})$ absorption of the bis-diethylaminocarbyne complexes **17** and **18** at 1550 and 1558 cm^{-1} at the expense of the analogous absorption of the mono-diethylaminocarbyne complexes **15** and **16** at 1531 and 1540 cm^{-1}, respectively (see *IR spectra*). Additional evidence for the formation of the bis-diethylaminocarbyne complexes **17** and **18** was provided by their subsequent nucleophile-induced carbyne–carbyne coupling reaction. Thus, treatment of **17** and **18**, prepared *in situ* from **15** and **16**, with an excess of NEt$_4$Br resulted in coupling of the two carbyne ligands to give the alkyne compounds **11a** and **12a**, respectively (Scheme 3). Complexes **11a** and **12a** were isolated after purification by column chromatography on a silylated silica support in 38 and 36% yields, respectively. Formation of ionic by-products in the reaction of [(EtNC)$_5$M≡CNEt$_2$]BF$_4$ with [Et$_3$O]BF$_4$ may be attributed to the competitive



Scheme 4 Mechanism of the carbyne–isocyanide and carbyne–carbonyl coupling reaction of mononuclear Group VI transition metal carbyne complexes

ethylation of the metal center or the carbyne ligand in **15** and **16**. These side reactions probably do not lead to carbyne–carbyne coupling, and so lower the yields of the alkyne products **11a** and **12a**.

The metal-centered formation of bis(diethylamino)acetylene by coupling two single carbon-based ligands (conversion of **13** and **14** into **11a** and **12a**, respectively) is analogous to the acid-induced isocyanide–isocyanide coupling reaction of $M(CNR)_6$ ($M = Mo$, W; $R = Et$, ^tBu) with HX ($X = Br$, I) to give the bis(alkylamino)acetylene complexes $[X(RNC)_4M[\eta^2\text{-}R(H)NC{\equiv}CN(H)R]]X$ [8b,c]. This analogy is reinforced by the observation that the latter reaction also proceeds via mono-aminocarbyne complexes [8b,c]. The IR spectroscopic identification of the bis-aminocarbyne intermediates **17** and **18** on the reaction pathway between the mono-aminocarbyne complexes **15** and **16** and the coupling products **11a** and **12a** supports our previous hypothesis [8,10] that the actual C–C bond forming step in the reductive coupling of alkyl isocyanide ligands in the Mo^{II} and W^{II} complexes $[M(CNR)_6X]^+$ to give coordinated ynediamines (Scheme 1) involves coupling of two aminocarbyne ligands at a single metal center (eq. b). It also supports our earlier suggestion that different mechanisms are operative in the carbyne–isocyanide [8b–d,10] and the well-established carbyne–carbonyl coupling reaction [15] of Group VI transition metal carbyne complexes to give coordinated ynamines and ynol ethers, respectively (eq. b, Scheme 4). Finally it implies that factors promoting the regioselective transformation of a d^6-metal poly-isocyanide complex to a bis-aminocarbyne complex will also promote the reductive isocyanide–isocyanide coupling reaction. Studies aimed at elucidating such factors are currently under way.

Spectroscopic investigations

IR spectra

The solution IR spectra of the alkyne complexes **9a–12b'** and the bis-carbyne complexes **17** and **18** exhibit in the region 2250–1500 cm^{-1} characteristic absorptions for the (C≡N) stretching vibrations of the isocyanide ligands and the (C=N) stretching vibrations of the bis(diethylamino)acetylene and diethylaminocarbyne ligands (Table 1).

Table 1

ν(C≡NR) and ν(C=N) absorptions for the alkyne complexes **9a**–**12b′** and the carbyne complexes **15**–**18** (in cm^{-1}; solvent: CH_2Cl_2)

Complex	ν(C≡NR)	ν(C≡O)	ν(C=N)
mer-$[Br(CO)(EtNC)_3Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(9a)**	2208m, 2195m,sh, 2174vs, 2148w,sh	1997s	1675s
mer-$[Br(CO)(^tBuNC)_3Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(9b)**	2186m, 2157vs, 2128w,sh	1996s	1674s
mer-$[Br(CO)(EtNC)_3W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(10a)**	2210m, 2193m,sh, 2172vs, 2141w,sh	1984s	1661s
mer-$[Br(CO)(^tBuNC)_3W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(10b)**	2189m, 2154vs	1984s	1661s
trans-$[Br(EtNC)_4Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(11a)**	2196w, 2151vs, 2102w,sh	–	1671m
trans-$[Br(^tBuNC)_4Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(11b)**	2177w, 2131vs	–	1671m
trans-$[Br(EtNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(12a)**	2198w, 2145vs, 2095w,sh	–	1657m
trans-$[Br(^tBuNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(12b)**	2177w, 2124vs, 2052w,sh	–	1656m
trans-$[Br(^tBuNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]PF_6$ **(12b′)**	2176w, 2125vs, 2061w,sh	–	1655m
$[(EtNC)_5Mo{\equiv}CNEt_2]BF_4$ **(15)**	2183m, 2154w, 2112s, 2087vs	–	1531m
$[(EtNC)_5W{\equiv}CNEt_2]BF_4$ **(16)**	2180m, 2139m,sh 2109s, 2082vs	–	1540m
$[(EtNC)_4Mo(CNEt_2)_2](BF_4)_2$ **(17)**	2201w, 2157vs	–	1550w
$[(EtNC)_4W(CNEt_2)_2](BF_4)_2$ **(18)**	2195w, 2144vs	–	1558w

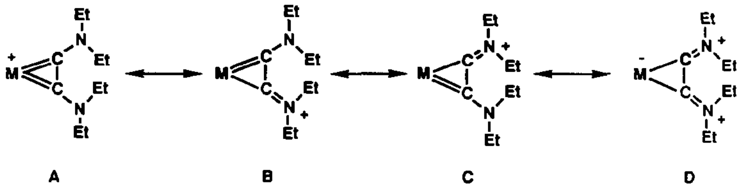


Fig. 1. Resonance forms for the metal–alkyne bonding in the diaminoacetylene complexes **9a–12b′**.

The number and relative intensities of the isocyanide stretching bands clearly indicate a *meridional* arrangement of the isocyanide ligands in the pseudo-octahedral alkyne complexes **9a–10b** and a *trans*-$M(CNR)_4$ fragment in **11a–12b′**, **17** and **18** [8c,10b,16,17].

The alkyne complexes **9a–12b′** are distinguished by an absorption at 1655–1675 cm^{-1}, which can be assigned to the (C=N) stretching vibration of the bis(diethylamino)acetylene ligand (Table 1). Similar low frequency absorptions (1600–1700 cm^{-1}) have been previously reported for other Mo^{II} and W^{II} aminoalkyne complexes [8c,9b,10b].

The ν(C=N) absorption for all bis(diethylamino)acetylene complexes is observed at higher frequency than that of the free ligand (ν(C=N) of $Et_2NC{\equiv}CNEt_2$ in CH_2Cl_2: 1632 cm^{-1}; in THF: 1645 cm^{-1}). The fairly high frequency of this vibration in **9a–12b′**, which is comparable with that of imonium cations $(R_2C{=}NR'_2)^+$ (ν(C=N) 1640–1690 cm^{-1}) [18], indicates a strong delocalization of the amino-nitrogen lone pair electrons into the alkyne π system. This delocalization is represented in valence bond terms by the resonance forms **B**, **C** and **D** (Fig. 1).

Further experimental evidence for the significant contribution of these canonical forms to the metal–alkyne bonding is provided by the temperature dependent ^1H NMR spectra of complexes **9a–12b′** and the solid-state structure of **12b′** (see ^1H NMR spectra and crystal structure of **12b′**). The bis-diethylaminocarbyne complexes **17** and **18** exhibit one characteristic low-frequency absorption, which can be assigned to the ν(C=N) vibration of the aminocarbyne ligands (Table 1). The presence of only one ν(C=N) absorption suggests a *trans* orientation of the carbyne ligands in these compounds (see also ν(C≡NEt) absorption pattern of **17** and **18**). In contrast, the IR spectrum of $[Cp^*(EtNC)W(CNEt_2)_2]BF_4$ in CH_2Cl_2 shows two ν(C=N) absorptions for the mutually *cis*-oriented diethylaminocarbyne ligands at 1610 and 1539 cm^{-1} [8d].

The ν(C=N) absorption of the bis-diethylaminocarbyne complexes **17** and **18** is observed at higher frequency (**17**: ν(C=N) 1550, **18**: ν(C=N) 1558 cm^{-1}) than that for the mono-diethylaminocarbyne precursors **15** and **16** (**15**: ν(C=N) 1531, **16**: ν(C=N) 1540 cm^{-1}) (Table 1). The fairly high frequency of this absorption points to a strong interaction of the amino nitrogen lone pair with the metal–carbon triple bond in these compounds [19]. Such an interaction is represented in valence bond terms by the 2-azavinylidene type resonance forms **E**, **F** and **G** (Fig. 2).

A "bis-carbyne" resonance form "$[M({\equiv}CNEt_2)_2]$" is not appropriate to describe the metal–carbyne bonding in **17** and **18**, although such a form emphasizes the equivalent nature of the two carbyne ligands in these compounds. This becomes evident from a simple electron count, which shows that the metal center is unable

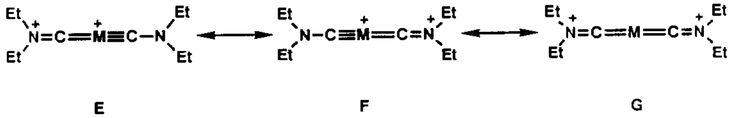


Fig. 2. Resonance forms for the metal–carbyne bonding in the bis-diethylaminocarbyne complexes **17** and **18**.

to form two metal–carbon triple bonds simultaneously in the bis-carbyne complexes **17** and **18** [20].

The ν(C=N) absorption of the bis-diethylaminocarbyne complexes **17** and **18** is observed at considerable lower frequency than that for their coupling products **11a** and **12** (Table 1). A similar effect was previously observed on going from the bis-diethylaminocarbyne complex [Cp*(EtNC)W(CNEt$_2$)$_2$]BF$_4$ (ν(C=N) 1610, 1539 cm^{-1}) to the coupling products [Cp*(EtNC)$_2$W(η^2-Et$_2$NC≡CNEt$_2$)]BF$_4$ (ν(C=N) 1629, 1579 cm^{-1}) and [Cp*(Br)$_2$(EtNC)W(η^2-Et$_2$NC≡CNEt$_2$)]BF$_4$ (ν(C=N) 1647 cm^{-1}) [8d]. This effect offers a convenient spectroscopic probe for distinguishing between bis-aminocarbyne complexes and their coupling products. An additional IR spectroscopic method of differentiating between these compounds involves the opposite metal effect on the position of the ν(C=N) absorption. For the bis-aminocarbyne complexes a shift of the ν(C=N) absorption to higher frequency is observed on going from molybdenum to tungsten (Table 1). The same effect is found for the mono-aminocarbyne precursors **15** and **16** (Table 1) and for other molybdenum and tungsten aminocarbyne complexes [21]. In contrast, the ν(C=N) absorption of the molybdenum diaminoacetylene complex **11a** occurs at higher frequency (ν(C=N) 1671 cm^{-1}) than that for the analogous tungsten compound **12a** (ν(C=N) 1657 cm^{-1}). The same effect is observed for a substantial number of Mo^{II} and W^{II} diaminoacetylene complexes (compare for example the ν(C=N) absorption of **9b** with **10b** and **11b** with **12b**) [8c].

^{1}H NMR spectra

The ^{1}H NMR spectra of the bis(diethylamino)acetylene complexes **9a–12b′** reveal that these compounds are fluxional (Table 2). The fluxionality is due to hindered rotation of the diethylamino groups around the C$_{\text{alkyne}}$–N bonds. Thus, the spectra of **9a–12b′** at the low exchange limit show two triplet resonances in a 1/1 intensity ratio for the methyl protons of the diethylamino groups. Similarly, two quartet resonances in a 1/1 intensity ratio are observed for the homotopic methylene protons of the diethylamino groups. Raising the temperature causes the methyl proton resonances to broaden and then collapse to one signal at the coalescence temperature. At the fast exchange limit only one triplet resonance is observed for these protons. Analogous temperature dependence is observed for the methylene proton signals.

The free energy of activation, $\Delta G^{\ddagger}(T_c)$, for the site exchange of the ethyl groups in the alkyne ligand can be calculated from the Eyring equation by using the Gutowsky–Holm equation to derive the rate constant for the site exchange, k_{ex}, at the coalescence temperature T_c (methylene protons) (Table 3) [22,23].

Rotational barriers for all molybdenum complexes are larger than those for the analogous tungsten compounds (compare for example $\Delta G^{\ddagger}$ values for **9a** and **10a**

Table 2

^1H NMR data for the alkyne complexes **9a–12b′** in CD_2Cl_2 (relative intensities and multiplicities in parentheses, coupling constants in Hz)

Complex	$(C\mathit{H}_3CH_2)_2N$	$C\mathit{H}_3CH_2NC$	$(C\mathit{H}_3)_3CNC$	$(CH_3C\mathit{H}_2)_2N$	$CH_3C\mathit{H}_2NC$	T (°C)
9a	1 18 (6,t) [a]; 1.37 (6,t) [b]	1.37 (6,t) [b]; 1.39 (3,t)	–	3.61 (4,q); 4.19 (4,q)	3 80 (4,q); 3 84 (2,q)	−50
9a [c]	1.33 (12,t)	1.43 (6,t); 1.45 (3,t)	–	3.89 (8,q)	3.84 (4,q); 3.90 (2,q)	+20
9b	1.19 (6,t); 1 40 (6,t)	–	1.47 (18,s); 1 50 (9,s)	3.63 (4,q); 4.17 (4,q)	–	−40
9b [c]	1.36 (12,t)	–	1.50 (18,s); 1.54 (9,s)	3.93 (8,q)	–	+20
10a	1.16 (6,t); 1.33 (6,t)	1.39 (6,t); 1.42 (3,t)	–	3.59 (4,q); 4.05 (4,q)	3.90 (4,q); 3.93 (2,q)	−50
10a	1.30 (12,t)	1.44 (6,t); 1.47 (3,t)	–	3.89 (8,br) [d]	3.94 (4,q), 3.99 (2,q)	+20
10b	1.12 (6,t); 1.30 (6,t)	–	1.43 (18,s); 1.46 (9,s)	3.55 (4,q); 3.96 (4,q)	–	−80
10b	1.28 (12,t)	–	1.51 (18,s); 1 54 (9,s)	3.85 (8,br) [d]	–	+20
11a	1.10 (6,t); 1.29 (6,t)	1.32 (12,t)	–	3 52 (4,q); 4.16 (4,q)	3.76 (8,q)	−45
11a [c]	1.23 (12,t)	1.35 (12,t)	–	3.88 (8,q)	3.78 (8,q)	+20
11b	1.10 (6,t); 1.30 (6,t)	–	1.39 (36,s)	3.51 (4,q); 4.11 (4,q)	–	−80
11b [c]	1.26 (12,t)	–	1 47 (36,s)	3.89 (8,q)	–	+20
12a	1.10 (6,t); 1.26 (6,t)	1.35 (12,t)	–	3.51 (4,q); 4.01 (4,q)	3.88 (8,q)	−70
12a	1.24 (12,t)	1.41 (12,t)	–	3.83 (8,q)	3.92 (8,q)	+20
12b	1.06 (6,t); 1.24 (6,t)	–	1.39 (36,s)	3.48 (4,q); 3.95 (4,q)	–	−80
12b	1.23 (12,t)	–	1.49 (36,s)	3.80 (8,q)	–	+20
12b′	1.24 (12,t)	–	1.50 (36,s)	3.81 (4,q)	–	+20

[a] All $^3J(HH)$ coupling constants for the ethyl groups are 7.3 Hz [b] Methyl proton resonances of the diethylamino groups and the mutually *trans* oriented ethyl isocyanide ligands are by accident coincident [c] The ^1H NMR spectra of these complexes were recorded on a Bruker WP 100 SY FT spectrometer. [d] The methylene proton resonance is broad because the fast exchange limit is not reached

Table 3

Coalescence temperature, T_c (methylene protons; 400 MHz), and activation barrier to rotation of the diethylamino groups, $\Delta G^{\ddagger}$ (T_c), in the alkyne complexes **9a–12b**

Complex	T_c (K)	$\Delta G^{\ddagger}$ (kJ mol^{-1})
9a	297	56.9
9b	293	56.2
10a	267	51.5
10b [a]	255	50.2
11a	273	51.8
11b	263	50.0
12a	247	47.2
12b	232	44.4

[a] The temperature dependant ^1H NMR spectra of this complex were recorded on a JEOL GX 270 spectrometer.

or **11b** and **12b**). An increase in the activation energy is also observed on going from the carbonyl-free to the monocarbonyl compounds (compare e.g. $\Delta G^{\ddagger}$ values for **11a** and **9a** or **12b** and **10b**). The same effect has been previously observed for the related tungsten diaminoacetylene complexes $(I)_2(CO)_n(^tBuNC)_{3-n}W[\eta^2$-$Et_2NC{\equiv}CN(H)^tBu]]I$ ($n = 1$: $\Delta G^{\ddagger} = 56.9$ kJ/mol; $n = 2$: $\Delta G^{\ddagger} = 62.3$ kJ/mol) and $[I(CO)_n(^tBuNC)_{4-n}W[\eta^2$-$Et_2NC{\equiv}CN(H)^tBu]]I$ ($n = 0$: $\Delta G^{\ddagger} = 58.2$ kJ/mol; $n = 1$: $\Delta G^{\ddagger} = 64.0$ kJ/mol) [10b]. It is also noteworthy that rotational barriers of diethylamino groups in aminoalkyne ligands are influenced by the other alkyne substituent. This is shown by a comparison of the barriers observed for the complexes $[Br(EtNC)_4W(\eta^2$-$Et_2NC{\equiv}CNEt_2)]Br$ (**12a**) ($\Delta G^{\ddagger}$ = 47.2 kJ/mol) and $[I(EtNC)_4W[\eta^2$-$Et_2NC{\equiv}CN(H)Et]]BF_4$ ($\Delta G^{\ddagger}$ = 65.3 kJ/mol) [8c] or $[Br(^tBuNC)_4W(\eta^2$-$Et_2NC{\equiv}CNEt_2)]Br$ (**12b**) ($\Delta G^{\ddagger}$ = 44.1 kJ/mol) and $[I(^tBuNC)_4W[\eta^2$-$Et_2NC{\equiv}CN(H)^tBu]]I$ ($\Delta G^{\ddagger} = 58.2$ kJ/mol) [10b].

Proton resonances of the alkyl isocyanide ligands are not temperature-dependent in the range −80 to +20°C, providing further evidence that hindered rotation of the diethylamino groups causes the observed fluxionality of **9a–12b**. In addition they indicate that the barrier to alkyne rotation around an axis connecting the metal center with the midpoint of the C≡C bond is low in **9a–12b**. Low barriers to alkyne rotation have been also found for other Mo^{II} and W^{II} aminoalkyne complexes [8c,10a,b,d].

^{13}C NMR spectra

Further support for the assigned structures to **9a–12b′** is provided by the ^{13}C NMR spectra recorded at the fast exchange limit (Table 4). Therefore all complexes display only one resonance for the methyl- and one resonance for the methylene-carbon of the diethylamino groups.

The bis(diethylamino)acetylene complexes **9a–12b′** are distinguishable by a low-field resonance for the alkyne-carbons at δ 185.6–197.7 (Table 4). Comparable chemical shifts were previously observed for the alkyne-carbons of other molybdenum(II) and tungsten(II) aminoalkyne complexes [8b–d,9a,9b,10]. The chemical shift for the bound alkyne carbons has been correlated with the extent of donation from the filled alkyne $\pi_{\perp}$ orbital to a vacant metal $d\pi$-orbital reflecting the electron-donor ability of the alkyne ligand [12,24,25]. On the basis of this correla-

Table 4

^{13}C NMR spectral data for the alkyne complexes **9a**–**12b′** (in CD_2Cl_2 at +20°C)

Complex	$(\mathit{C}H_3CH_2)_2N$	$\mathit{C}H_3CH_2NC$	Me_3CNC	$CH_3\mathit{C}H_2NC$	$(CH_3\mathit{C}H_2)_2N$	$Me_3\mathit{C}NC$	$RN\mathit{C}$	C≡C	CO
9a	14.3	14.6 [a]; 14.7	–	40.2; 40.3 [a]	51.1	–	148.6; 151.0 [a]	195.6	211.7
9b	14.6	–	30.2 [a]; 30.3	–	51.2	58.4; 58.6 [a]	148.6; 150.8 [a]	196.2	212.1
10a	14.5	15.0 [a]; 15.1	–	40.2; 40.6 [a]	50.9	–	143.1; 145.5 [a]	185.6	206.3
10b	14.6	–	30.3 [a]; 30.4	–	50.7	58.6 58.8 [a]	143.0; 145.0 [a]	186.1	206.7
11a	14.5	15.2	–	40.0	50.4	–	157.5	197.1	–
11b	14.8	–	30.6	–	50.4	57.8	157.8	197.7	–
12a	14.6	15.5	–	40.3	50.1	–	152.0	186.7	–
12b	14.7	–	30.7	–	50.0	58.0	152.4	187.4	–
12b′	14.7	–	30.7	–	50.1	58.1	152.6	187.7	–

[a] Carbon resonance of the mutually *trans* oriented isocyanide ligands.

tion the chemical shift of the alkyne-carbons of **9a**–**12b′** suggests a four electron donation from the alkyne ligand to the metal center.

The alkyne-carbon resonances of the molybdenum complexes appear at lower field than those for the analogous tungsten compounds. This is consistent with the trend in ^{13}C shielding previously observed for the Group VI metal triad [8c,26].

Crystal structure of 12b′

The molecular structure of **12b′** was confirmed by a single crystal X-ray diffraction study. Two views of the cation of **12b′** with the numbering scheme are given in Figs. 3 and 4. Selected bond lengths and angles are listed in Table 5, and fractional coordinates in Table 6.

The cation in **12b′** may be described as having a monocapped trigonal-prismatic coordination geometry, analogous to that in $[X(RNC)_4Mo[\eta^2\text{-}R(H)NC{\equiv}CN(H)R]]^+$ cations (X = Br, I, CN; R = ^tBu) [27,28], with the bromo ligand in the capping position. The capped face consists of the four isocyanide ligands, and the prism edge opposite the capped face is occupied by the acetylene ligand (Fig. 3). Alternatively, the coordination geometry of the cation in **12b′** can be viewed as distorted octahedral, with the midpoint of the C≡C bond and the bromo ligand occupying two *trans* coordination sites. The coordination sphere is completed by the four isocyanide ligands, which, as revealed by the $Br\text{-}W\text{-}C_{isocyanide}$ angles ((Br–W–C11)–(Br–W–C41) = 80.4(2)–82.9(2)°) (Table 5), are bent out of the equatorial plane towards the bromo ligand (Fig. 3). In either case, the symmetry of the $[WC_6Br]$ polyhedron is approximately C_{2v}, with the mirror planes intersecting in the W–Br bond (Fig. 4).

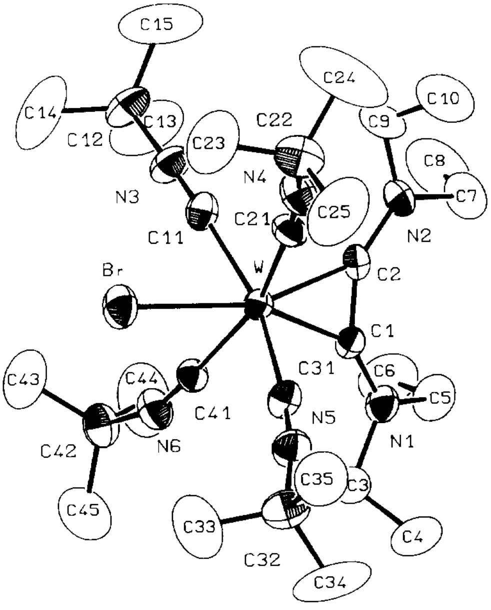


Fig. 3. ORTEP plot of the cation in **12b′** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity

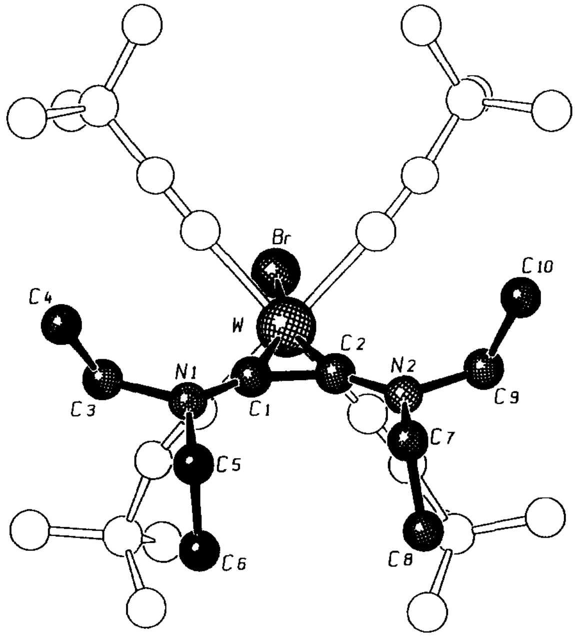


Fig. 4. Structure of the cation in **12b′** (SCHAKAL) viewed down the C_{mid}–W–Br axis.

The t-butyl isocyanide ligands show approximately linear M–C–N–C geometry, the W–C≡N and C≡N–C angles averaging 173.6 and 169.6°, respectively. The $W-C_{isocyanide}$ and C≡N bond lengths, which range from 208.6(5) to 212.1(6) pm and 113.6(7) to 115.4(7) pm, respectively, are similar to those in other Mo^{II} and W^{II} isocyanide complexes [27–29].

The W–Br bond length (265.9(1) pm) is not significantly different from that observed for other W^{II} bromo complexes such as $W(CO)_3(2,2'\text{-bipy})(Br)(GeBr_3)$ (W–Br 260.3(6) pm) [30], $W(CO)_3(dpam)(Br)_2$ (dpam = bis(diphenylarsino)-methane) ($W-Br_{av}$ 265.5 pm) [31], $NMe_4[W(CO)_4(Br)_3]$ (W–Br 263.8(4) pm) [32] and $[Br({}^tBuNC)_4W[\eta^2\text{-}PhC{\equiv}CN(H){}^tBu]]PF_6$ (W–Br 264.3 pm) [33]. It is however smaller than the length of a W–Br single bond (272 pm) estimated from the sum of the covalent radii of a single bonded tungsten and a bromine atom (r_W 158, r_{Br} 114 pm) [34,35].

Striking features of the structure involve the bonding parameters of the alkyne ligand:

(a) The $W-C_{alkyne}$ distances (W–C(1) 204.6(5), W–C(2) 203.7(5) pm) are very close to those reported for M^{II} complexes (M = Mo, W) containing four-electron donor alkyne ligands [12,27,28]. They are, however, considerably smaller than those in M^{II} complexes containing two-electron donor ligands, such as $Cp_2Mo(\eta^2\text{-}PhC{\equiv}CPh)$ ($Mo-C_{alkyne}$ 214.4(6) pm) [36] and $Cp'_2Mo(\eta^2\text{-}CF_3C{\equiv}CCF_3)$ ($Cp' = \eta^5\text{-}C_5H_4Me$; $Mo-C_{alkyne}$ 212.9(7) pm) [37].

(b) The acetylenic C–C distance of 137.7(7) pm is similar to that in other M^{II} aminoalkyne complexes such as $[I({}^tBuNC)_4Mo[\eta^2\text{-}{}^tBu(H)NC{\equiv}CN(H){}^tBu]]I$ ($(C-C)_{alkyne}$ 134.8(10) pm) [27] and $[NC({}^tBuNC)_4Mo[\eta^2\text{-}{}^tBu(H)NC{\equiv}CN(H){}^tBu]]BPh_4$ ($(C-C)_{alkyne}$ 140.2(8) pm) [28]. It is, however, larger than the corresponding

Table 5

Selected bond lengths (pm) and angles (°) in **12b'** [a]

W-Br	265.9(1)	Br-W-C(1)	159.1(1)
W-C(1)	204.6(5)	Br-W-C(2)	160.3(2)
W-C(2)	203.7(5)	Br-W-C(11)	82.9(2)
W-C(11)	211.2(6)	Br-W-C(21)	80.4(2)
W-C(21)	212.1(6)	Br-W-C(31)	81.8(1)
W-C(31)	211.4(5)	Br-W-C(41)	81.3(1)
W-C(41)	208.6(5)	C_{mid}-W-C(11)	93.7
W-C_{mid}	192.2	C_{mid}-W-C(21)	103.4
C(1)-C(2)	137.7(7)	C_{mid}-W-C(31)	101.5
C(1)-N(1)	132.5(7)	C_{mid}-W-C(41)	94.8
C(2)-N(2)	133.3(7)	N(1)-C(1)-C(2)	144.3(5)
N(1)-C(3)	149.2(7)	C(1)-C(2)-N(2)	142.7(5)
N(1)-C(5)	146.6(7)	C(1)-N(1)-C(3)	119.4(5)
N(2)-C(7)	146.5(8)	C(1)-N(1)-C(5)	124.1(5)
N(2)-C(9)	146.0(8)	C(3)-N(1)-C(5)	115.1(5)
C(11)-N(3)	113.6(7)	C(2)-N(2)-C(7)	126.3(5)
C(21)-N(4)	115.4(7)	C(2)-N(2)-C(9)	119.4(5)
C(31)-N(5)	115.1(7)	C(7)-N(2)-C(9)	114.3(5)
C(41)-N(6)	115.2(7)	W-C(11)-N(3)	175.4(5)
N(3)-C(12)	148.2(7)	W-C(21)-N(4)	171.4(5)
N(4)-C(22)	146.2(8)	W-C(31)-N(5)	173.2(5)
N(5)-C(32)	145.4(8)	W-C(41)-N(6)	174.2(5)
N(6)-C(42)	145.4(7)	C(11)-N(3)-C(12)	176.5(6)
		C(21)-N(4)-C(22)	170.5(6)
		C(31)-N(5)-C(32)	169.7(6)
		C(41)-N(6)-C(42)	161.6(6)

[a] Numbers in parentheses are estimated standard deviations in the last digit given; C_{mid} denotes the midpoint of the alkyne C-C bond

distance reported for M^{II} alkyne complexes in which the alkyne ligand does not bear heteroatom substituents, such as $[Cp(CO)(PPh_3)Mo(\eta^2\text{-}PhC{\equiv}CPh)]BF_4$ ($(C-C)_{alkyne}$ 129(2) pm) [38] and $(\eta^2\text{-}Et_2NCS_2)_2(CO)W(\eta^2\text{-}HC{\equiv}CH)$ ($(C-C)_{alkyne}$ 129(1) pm) [39].

(c) The lengths of the C_{alkyne}-N bonds (C(1)-N(1) 132.5(7), C(2)-N(2) 133.3(7) pm) are intermediate between that expected for a C(sp^2)-N(sp^2) single (144 pm) and that expected for a C(sp^2)-N(sp^2) double bond (127 pm) [40-42].

(d) The NCCN framework of the bis(diethylamino)acetylene ligand is rigidly planar, and the tungsten and bromine atoms also lie in this plane (Fig. 4). This is indicated by the maximal deviation of one of these six atoms by less than 8 pm from the least-squares plane. The amino groups are also rigidly planar. The dihedral angle between the two amino planes defined by the atoms C(1), N(1), C(3) and C(5) and C(2), N(2), C(7) and C(9) being 11° (Fig. 4). The planarity of the amino groups is reflected in the sum of the angles around N(1) and N(2) of 358.6 and 360.0°, respectively, indicating sp^2-hybridization of the nitrogen atoms. Finally, both diethylamino groups are pushed away from the metal atom. The C≡C-N angles have values (N(1)-C(1)-C(2) 144.3(5) and C(1)-C(2)-N(2) 142.7(5)°), very close to those reported for most Mo^{II} and W^{II} alkyne complexes [12].

All these features provide structural evidence that bis(diethylamino)acetylene is acting as a four-electron donor ligand in **9a-12b'**. They furthermore reveal

Table 6

Fractional atomic coordinates and their estimated standard deviations of non-hydrogen atoms in **12b′** [a]

Atom	*x*	*y*	*z*	U_{eq}
W	0.30324(1)	0.18301(1)	0.27737(1)	0.027
Br	0.22934(4)	0.19773(4)	0.42514(4)	0.046
N1	0.4218(3)	0.0668(3)	0.1685(3)	0.039
N2	0.3157(3)	0.2415(4)	0.0761(3)	0.039
N3	0.1364(3)	0.1692(4)	0.1942(3)	0.044
N4	0.3000(3)	0.4001(3)	0.3076(3)	0.044
N5	0.4417(3)	0.1932(4)	0.4162(3)	0.044
N6	0.2681(3)	−0.0276(3)	0.3079(3)	0.043
C1	0.3718(3)	0.1297(4)	0.1857(3)	0.030
C2	0.3302(3)	0.1986(4)	0.1503(3)	0.029
C3	0.4541(3)	0.0124(4)	0.2411(4)	0.046
C4	0.5372(4)	0.0270(6)	0.2491(6)	0.075
C5	0.4367(4)	0.0325(5)	0.0814(4)	0.050
C6	0.3777(4)	−0.0298(5)	0.0496(5)	0.069
C7	0.3461(4)	0.2195(5)	−0.0091(4)	0.054
C8	0.2933(6)	0.1642(6)	−0.0614(6)	0.087
C9	0.2674(4)	0.3204(5)	0.0766(5)	0.055
C10	0.3102(5)	0.4079(5)	0.0683(6)	0.084
C11	0.1946(3)	0.1779(4)	0.2229(4)	0.036
C12	0.0615(3)	0.1519(5)	0.1559(4)	0.045
C13	0.0673(5)	0.0764(6)	0.0945(7)	0.088
C14	0.0108(5)	0.135(1)	0.2289(7)	0.107
C15	0.0386(6)	0.2381(6)	0.1081(7)	0.094
C21	0.3020(3)	0.3248(4)	0.2899(4)	0.036
C22	0.2960(4)	0.4902(4)	0.3448(5)	0.051
C23	0.2339(5)	0.4878(6)	0.4097(6)	0.079
C24	0.2762(8)	0.5540(6)	0.2704(7)	0.101
C25	0.3681(5)	0.5113(6)	0.3873(7)	0.086
C31	0.3961(3)	0.1882(4)	0.3632(4)	0.033
C32	0.4884(4)	0.1973(5)	0.4939(4)	0.051
C33	0.4415(5)	0.1625(7)	0.5670(5)	0.083
C34	0.5566(5)	0.1384(6)	0.4787(7)	0.084
C35	0.5111(5)	0.2925(5)	0.5095(6)	0.072
C41	0.2838(3)	0.0470(4)	0.3003(4)	0.031
C42	0.2265(4)	−0.1113(4)	0.3041(4)	0.043
C43	0.1504(4)	−0.0930(6)	0.3411(6)	0.076
C44	0.2227(6)	−0.1395(7)	0.2096(5)	0.082
C45	0.2685(5)	−0.1810(5)	0.3573(6)	0.083
P	0.0225(1)	0.2195(2)	0.8258(1)	0.064
F1	−0.0267(4)	0.1613(4)	0.8882(4)	0.106
F2	−0.0518(4)	0.2598(5)	0.7842(4)	0.131
F3	0.0167(4)	0.2989(5)	0.8936(5)	0.130
F4	0.0212(4)	0.1451(5)	0.7557(5)	0.132
F5	0.0926(4)	0.1839(6)	0.8677(5)	0.150
F6	0.0680(4)	0.2800(5)	0.7635(5)	0.136
C_{mid}	0.3510	0.1641	0.1680	

[a] Anisotropically refined atoms are given in the form of their isotropic equivalent displacement parameter defined as $U_{eq} = (U_1 \cdot U_2 \cdot U_3)^{1/3}$, where U_1, U_2 and U_3 are the eigenvalues of the U_{ij} matrix

extensive π-electron delocalization in the ynediamine ligand, indicating, in agreement with the spectroscopic data, a strong contribution of the resonance forms **B–D** to the metal–alkyne bonding in **9a–12b′** (Fig. 1).

Experimental

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (pentane, toluene, Et_2O, DME 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 over 4 Å molecular sieves.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were recorded on a Nicolet DX 5 FT spectrophotometer ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded in dry deoxygenated methy lene-d_2 chloride on a JEOL GX 400 FT instrument unless otherwise stated Chemical shifts were referenced to residual solvent signals (CD_2Cl_2, δ_H 5.32 and δ_C 53.8 ppm). Mass spectra were obtained with a Finnigan MAT 311 A and MAT 90 spectrometer; m/z values shown refer to the ^{98}Mo, ^{184}W and ^{79}Br isotopes Conductivity measurements were carried out as described previously [43].

The complexes *fac*-$M(CO)_3(MeCN)_3$ (**3**, **4**), *fac*-$M(CO)_3(CNR)_3$ (**5a–6b**) $M(CO)_2(CNR)_3(Br)_2$ (**7a–8b**), $M(CNEt)_6$ (**13**, **14**) and $[(EtNC)_5M{\equiv}CNEt_2]BF$ (**15**, **16**) were prepared as described previously [8a] and [10d]. EtNC and ^tBuNC were made by published procedures [44,45], distilled and stored under nitrogen $Et_2NC{\equiv}CNEt_2$ was obtained by Viehe's method and $[Et_3O]BF_4$ by Meerwein' method [2b,46].

1. mer-*$[Br(CO)(EtNC)_3Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**9a**)*

To a yellow solution of 1.19 g (2.49 mmol) of **7a** in 50 ml of CH_2Cl_2 at room temperature were added 0.66 ml (2.75 mmol) of $Et_2NC{\equiv}CNEt_2$. Gas evolution immediately occurred and the solution turned to red. The mixture was stirred for 2 h until the reaction was complete (IR monitoring, disappearance of the $\nu(CO)$ absorption of **7a** in CH_2Cl_2 at 1933 cm^{-1}). The solvent was then removed *in vacuo* and the residue purified by column chromatography on silylated silica at 0°C. Elution with THF gave a green band, from which the neutral alkyne complex $(Br)_2(CO)(EtNC)_2Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)$ was obtained as a brown microcrystalline solid after evaporation of the solvent and crystallization of the residue from THF/Et_2O. Yield: 70 mg (5%).

Further elution with THF/CH_2Cl_2 (20/1) afforded a red band, from which complex **9a** was obtained as an orange, microcrystalline solid after removal of the solvent *in vacuo* and crystallization of the oily residue from $THF/CH_2Cl_2/Et_2O$. M.p. 102°C. Yield 1.23 g (80%). Found: C, 39.26; H, 5.70; Br, 25.98; Mo, 15.44; N, 11.66; O, 3.10. $C_{20}H_{35}Br_2MoN_5O$ (617.28) calc.: C, 38.92; H, 5.71; Br, 25.89; Mo, 15.54; N, 11.35; O, 2.59%.

2. mer-*$[Br(CO)(^tBuNC)_3Mo(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ (**9b**)*

A yellow solution of 590 mg (1.05 mmol) of **7b** in 40 ml of CH_2Cl_2 was treated at room temperature with 0.28 ml (1.16 mmol) of $Et_2NC{\equiv}CNEt_2$. Completion of the reaction after 2 h was revealed by IR spectroscopic monitoring (disappearance of the $\nu(CO)$ absorption of **7b** in CH_2Cl_2 at 1930 cm^{-1}). The resulting red solution was evaporated to dryness and the oily residue crystallized from CH_2Cl_2/Et_2O to give complex **9b** as an orange microcrystalline solid. M.p. 70°C (dec.). Yield: 690 mg (94%). Found: C, 44.70; H, 6.76; Br, 22.69; Mo, 13.91; N, 10.26; O, 2.89.

$C_{26}H_{47}Br_2MoN_5O$ (701.44) calc.: C, 44.52; H, 6.75; Br, 22.78; Mo, 13.68; N, 9.99; O, 2.28%.

3. mer-*[Br(CO)(EtNC)$_3$W(η^2-Et$_2$NC≡CNEt$_2$)]Br* (**10a**)

A solution of 740 mg (1.31 mmol) of **8a** in 40 ml of THF was treated with 0.35 ml (1.44 mmol) of $Et_2NC{\equiv}CNEt_2$ and the mixture then refluxed. Completion of the reaction after 45 min was revealed by IR spectroscopy (disappearance of the ν(CO) absorption of **8a** in THF at 1905 cm^{-1}). The resulting red solution was evaporated to dryness and the residue chromatographed on silylated silica at 0°C. Elution with CH_2Cl_2/Et_2O(1/20) gave a purple fraction containing 40 mg of a mixture of products of unknown composition. Further elution with THF/CH_2Cl_2 (1/1) gave a red band, from which complex **10a** was isolated as an orange, microcrystalline solid after removal of the solvent *in vacuo* and crystallization of the oily residue from $THF/CH_2Cl_2/Et_2O$. M.p. 123°C (dec.). Yield 840 mg (91%). Found: C, 34.26; H, 5.02; Br, 22.35; N, 9.97; W, 25.27. $C_{20}H_{35}Br_2N_5OW$ (705.19) calc.: C, 34.07; H, 5.00; Br, 22.66; N, 9.93; W, 26.07%.

4. mer-*[Br(CO)(^{t}BuNC)$_3$W(η^2-Et$_2$NC≡CNEt$_2$)]Br* (**10b**)

A solution of 600 mg (0.92 mmol) of **8b** in 25 ml of THF was treated with 0.34 ml (1.40 mmol) of $Et_2C{\equiv}CNEt_2$ and the mixture then refluxed. Completion of the reaction after 45 min was revealed by IR spectroscopy (disappearance of the ν(CO) absorption of **8b** in THF at 1910 cm^{-1}). The resulting red solution was worked up, as described above for the isolation of **10a**, to give complex **10b** as an orange, microcrystalline solid. M.p. 116°C (dec.). Yield 650 mg (89%). Found: C, 39.54; H, 6.01; Br, 19.82; N, 9.07; W, 23.11. $C_{26}H_{47}Br_2N_5OW$ (789.35) calc.: C, 39.56; H, 6.00; Br, 20.25; N, 8.87; W, 23.29%.

5. trans-*[Br(EtNC)$_4$Mo(η^2-Et$_2$NC≡CNEt$_2$)]Br* (**11a**)

To a suspension of 420 mg (0.68 mmol) of **9a** in 40 ml of THF were added 0.065 ml (0.88 mmol) EtNC and the mixture was refluxed for 1.5 h until the reaction was complete (disappearance of the ν(CO) absorption of **9a** in THF at 1978 cm^{-1}). The resulting slurry was evaporated *in vacuo* and the residue washed with THF/Et_2O to give complex **11a** as a green solid. M.p. 139°C. Yield 410 mg (94%). Found: C, 40.85; H, 6.28; Br, 24.54; Mo, 14.69; N, 13.09. $C_{22}H_{40}Br_2MoN_6$ (644.35) calc.: C, 41.01; H, 6.26; Br, 24.80; Mo, 14.89; N, 13.04%. FD-MS (CH_2Cl_2): m/z 565 $[K]^+$.

6. trans-*[Br(^{t}BuNC)$_4$Mo(η^2-Et$_2$NC≡CNEt$_2$)]Br* (**11b**)

A red solution of 1.00 g (1.43 mmol) of **9b** in 60 ml of THF was treated with 0.21 ml (1.86 mmol) of ^{t}BuNC and the mixture then refluxed. Completion of the reaction after 2 h was revealed by IR spectroscopy (disappearance of the ν(CO) absorption of **9b** in THF at 1979 cm^{-1}). The resulting brown slurry was evaporated to dryness and the residue washed with THF/Et_2O to give complex **11b** as a green solid. M.p. 156°C. Yield 1.03 g (96%). Found: C, 47.36; H, 7.35; Br, 20.66; Mo, 13.00; N, 10.96. $C_{30}H_{56}Br_2MoN_6$ (756.56) calc.: C, 47.63; H, 7.46; Br, 21.12; Mo, 12.68; N, 11.11%.

7. trans-*[Br(EtNC)$_4$W(η^2-Et$_2$NC≡CNEt$_2$)]Br (12a)*

To a red solution of 360 mg (0.51 mmol) of **10a** in 50 ml of DME were added 0.042 ml (0.56 mmol) of EtNC and the mixture then refluxed. Completion of the reaction after 5 h was confirmed by IR spectroscopy (disappearance of the ν(CO) absorption of **10a** in DME at 1966 cm^{-1}). The resulting slurry was evaporated to dryness and the residue washed with THF/Et_2O to give complex **12a** as a purple solid. M.p. 136°C. Yield 340 mg (91%). Found: C, 36.15; H, 5.61; Br, 21.01; N, 11.78; W, 25.13. $C_{22}H_{40}Br_2N_6W$ (732.26) calc.: C, 36.09; H, 5.50; Br, 21.82; N, 11.48; W, 25.11%. FD-MS (CH_2Cl_2): m/z 651 $[K]^+$.

8. trans-*[Br(^{t}BuNC)$_4$W(η^2-Et$_2$NC≡CNEt$_2$)]Br (12b)*

A red solution of 1.39 g (1.76 mmol) of **10b** in 50 ml of DME was treated with 0.26 ml (2.30 mmol) of ^{t}BuNC and the mixture then refluxed for 4 h until the reaction was complete (IR monitoring). The resulting purple-brown slurry was worked up as described above for **12a** to give complex **12b** as a purple solid. M.p. 150°C. Yield 1.29 g (87%). Found: C, 42.79; H, 6.79; Br, 18.61; N, 9.98; W, 21.50. $C_{30}H_{56}Br_2N_6W$ (844.47) calc.: C, 42.67; H, 6.68; Br, 18.93; N, 9.95; W, 21.77%.

9. trans-*[Br(^{t}BuNC)$_4$W(η^2-Et$_2$NC≡CNEt$_2$)]PF$_6$ (12b′)*

To a purple solution of 110 mg (0.13 mmol) of **12b** in 20 ml of CH_2Cl_2 were added 45 mg (0.13 mmol) of $TlPF_6$ and the mixture stirred at ambient temperature for 5 h. The resulting red slurry was treated with 5 ml of Et_2O and filtered through a filter cannula. The red filtrate was evaporated *in vacuo* and the residue washed with THF/Et_2O to give complex **12b′** as a purple solid. M.p. 170°C. Yield: 110 mg (93%). Found: C, 39.60; H, 6.26; Br, 8.47; N, 9.34; W, 20.25. $C_{30}H_{56}BrF_6N_6PW$ (909.53) calc.: C, 39.62; H, 6.21; Br, 8.78; N, 9.24; W, 20.21%.

10. Synthesis of trans-*[Br(EtNC)$_4$Mo(η^2-Et$_2$NC≡CNEt$_2$)]Br (11a) starting from [(EtNC)$_5$Mo≡CNEt$_2$]BF$_4$ (15)*

To a purple solution of 200 mg (0.37 mmol) of **15** in 40 ml CH_2Cl_2 at −30°C were added 70 mg (0.37 mmol) of $[Et_3O]BF_4$. The mixture was then warmed to room temperature and stirred for 12 h. Completion of the reaction was confirmed by IR spectroscopy (disappearance of the strong ν(C≡NEt) vibration of **15** in CH_2Cl_2 at 2087 cm^{-1}). The resulting black solution of the bis-diethylaminocarbyne complex **17** was subsequently treated with 220 mg (1.05 mmol) of $[NEt_4]Br$ and stirred for 12 h at ambient temperature. Completion of the reaction was indicated by disappearance of the ν(C=N) absorption of **17** in CH_2Cl_2 at 1550 cm^{-1}. The reaction mixture was then evaporated to dryness and the residue twice subjected to column chromatography on silylated silica at 0°C with THF/CH_2Cl_2 (5/1) to give a red eluate containing complex **11a**. After removal of the solvent from the eluate, the residue was slurried with a mixture of CH_2Cl_2/Et_2O (1/1), the slurry freed from $[NEt_4]X$ salts by filtration through a cannula and the filtrate evaporated to dryness *in vacuo*. The residue was washed with THF/Et_2O to give complex **11a** as a green solid. Yield 90 mg (38%). The product was characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy.

11. Synthesis of trans-*[Br(EtNC)$_4$W(η^2-Et$_2$NC≡CNEt$_2$)]Br (12a) starting from [(EtNC)$_5$W≡CNEt$_2$]BF$_4$ (16)*

To a purple solution of 230 mg (0.36 mmol) of **16** in 40 ml CH_2Cl_2 were added at −30°C 70 mg (0.37 mmol) of $[Et_3O]BF_4$. The mixture was warmed to room temperature and stirred for 12 h. Completion of the reaction was confirmed by IR spectroscopy (disappearance of the strong ν(C≡NEt) vibration of **16** in CH_2Cl_2 at 2082 cm^{-1}). The resulting black solution of the bis-diethylaminocarbyne complex **18** was treated with 200 mg (0.95 mmol) of $[NEt_4]Br$ and stirred for 8 h at ambient temperature. Completion of the reaction was indicated by disappearance of the ν(C=N) absorption of **18** in CH_2Cl_2 at 1558 cm^{-1}. The reaction mixture was then worked up as described under *10* to give complex **12a** as a purple solid. Yield: 95 mg (36%). The product was characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy.

12. Structure determination of 12b′

Suitable crystals were obtained as purple blocks upon cooling a saturated CH_2Cl_2/pentane solution of **12b′** from room temperature to −78°C. Complex **12b′** crystallizes in the monoclinic space group $P2_1/a$ (non-standard Inter. Tables. No.: 14). Unit cell constants were obtained by centering, and least-squares refinement of 15 reflections at high θ values (a 1791.8(2), b 1489.3(2), c 1542.0(2) pm, β 90.71(1)°; V 4115 × 10^6 pm^3, $Z = 4$, ρ_{calc} 1.47 g cm^{-3}).

Data collection was performed on a Syntex $P2_1$ four circle diffractometer with graphite monochromated Mo-K_α radiation (λ 71.073 pm) at -50 ± 3°C. Intensity data for 7787 reflections in the range $1.0° \leq \theta \leq 25.0°$ (h, k, $\pm l$) were collected by ω-scan with a scan range of 0.8° and a stationary background determination at 0.6° from each reflection. Scan speed ranged from 0.8 to 29.3°/ min. The intensity data were corrected for Lorentz and polarization effects and for absorption (empirical correction, 9 reflections, μ 37.1 cm^{-1}). During data collection no decay was observed. After merging, 6428 of 7235 unique reflections ($I > 2.0$) were used in the refinement. The structure was solved by the Patterson method and subsequent least-squares refinement cycles and difference Fourier syntheses.

All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions (C–H = 95 pm) and were included in the structure factor calculation but not refined (467 parameters). Refinement minimized the function $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2$ and converged yielding R-values of $R = 0.042$ and $R_w = 0.041$. Residual electron density maxima and minima were 0.94 and −0.70 $e^-/Å^3$. Atomic scattering parameters were taken from ref. 47. Anomalous dispersion effects were included for all non-hydrogen atoms [48]. All calculations were performed on a MicroVAX 3100 computer using standard programs [49–53]. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD-55623, the names of the authors, and the journal citation.

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References

1 (a) H.G Viehe, Angew. Chem., 79 (1967) 744, Angew. Chem., Int. Ed Engl., 6 (1967) 767; (b) S.R. Sandler and W. Karo, Organic Functional Group Preparations, Academic Press, New York, 1971, p. 119; (c) J. Ficini, Tetrahedron, 32 (1976) 1449

2 (a) H.G. Viehe and M. Reinstein, Angew. Chem., 76 (1964) 537; Angew. Chem., Int. Ed. Engl., 3 (1964) 581; (b) S.Y Delavarenne and H G. Viehe, Chem. Ber., 103 (1970) 1209; (c) C. Wilcox and R. Breslow, Tetrahedron Lett , 21 (1980) 3241, (d) L. Rene, Z. Janousek and H G. Viehe, Synthesis, (1982) 645.

3 (a) A. Krebs, A. Güntner, A. Senning, E.K. Moltzen, K.J. Klabunde and M.P. Kramer, Angew. Chem., 96 (1984) 691; Angew. Chem., Int. Ed. Engl., 23 (1984) 729; (b) A. Krebs, A. Güntner, S Versteylen and S. Schulz, Tetrahedron Lett., 25 (1984) 2333; (c) H. Gotthardt and T. Lohr, Lieb Ann Chem., (1987) 189; (d) H. Gotthardt, T. Lohr and D J. Brauer, Chem. Ber., 120 (1987) 751; (e) H. Gotthardt and J. Blum, ibid., 118 (1985) 2079, (f) H. Gotthardt and J. Blum, ibid., 118 (1985) 4578; (g) H. Gotthardt, J. Blum and K. Schenk, ibid., 119 (1986) 1315.

4 R.B. King and C.A. Harmon, Inorg. Chem , 15 (1976) 879.

5 (a) K.H. Dötz and C.G. Kreiter, Chem. Ber., 109 (1976) 2026; (b) K.H. Dötz and D. Neugebauer, Angew. Chem., 90 (1978) 898; Angew. Chem., Int. Ed. Engl., 17 (1978) 851

6 (a) H. Fischer, J. Hofmann, U Gerbing and A. Tiriliomis, J. Organomet. Chem., 358 (1988) 229, (b) H. Fischer and I. Pashalidis, ibid , 348 (1988) C1; (c) H. Fischer, K. Treier and J Hofmann, ibid , 384 (1990) 305.

7 M.L Listemann and R.R. Schrock, Organometallics, 4 (1985) 74.

8 (a) A.C. Filippou and W. Grünleitner, J. Organomet. Chem., 398 (1990) 99; (b) A.C. Filippou and W. Grünleitner, ibid., 393 (1990) C10; (c) A.C. Filippou and W. Grunleitner, Z Naturforsch., Teil B, 46 (1991) 216; (d) A.C. Filippou, W. Grunleitner, C. Völkl and P. Kiprof, Angew. Chem., 103 (1991) 1188; Angew. Chem., Int. Ed Engl., 30 (1991) 1167.

9 (a) C.T Lam, P.W.R. Corfield and S.J. Lippard, J Am. Chem. Soc , 99 (1977) 617; (b) C.M. Giandomenico, C.T. Lam and S.J. Lippard, ibid., 104 (1982) 1263; (c) R. Hoffmann, C N. Wilker, S.J. Lippard, J.L Templeton and D.C. Brower, ibid., 105 (1983) 146; (d) R.N Vrtis and S.J. Lippard, Isr. J. Chem., 30 (1990) 331; (e) E.M. Carnahan and S.J. Lippard, J. Chem. Soc., Dalton Trans., (1991) 699.

10 (a) A.C. Filippou and W. Grunleitner, Z. Naturforsch., Teil B, 44 (1989) 1023; (b) A.C. Filippou, Polyhedron, 9 (1990) 727; (c) A.C. Filippou, C. Völkl, W Grünleitner and P. Kiprof, Angew. Chem., 102 (1990) 224; Angew. Chem., Int. Ed. Engl., 29 (1990) 207, (d) A.C. Filippou, C. Volkl, W Grünleitner and P. Kiprof, Z. Naturforsch , Teil B, 45 (1990) 351; (e) A. Mayr and C M Bastos, J Am. Chem. Soc., 112 (1990) 7797.

11 C. Völkl, Diplomarbeit, Technische Universitat München, 1989.

12 J.L Templeton, Adv. Organomet. Chem., 29 (1989) 1.

13 J.J Lingane, Electroanalytical Chemistry, Interscience, New York, 1958.

14 W.J. Geary, Coord. Chem Rev., 7 (1971) 81.

15 (a) M.R. Churchill, H.J. Wasserman, S J Holmes and R.R. Schrock, Organometallics, 1 (1982) 766; (b) W J Sieber, K Eberl, M. Wolfgruber and F.R. Kreißl, Z. Naturforsch., Teil B, 38 (1983) 1159; (c) F.R. Kreißl, W.J. Sieber and M. Wolfgruber, ibid., 38 (1983) 1419; (d) J.A.K. Howard, J.C. Jeffery, J C V Laurie, I Moore, F.G A Stone and A. Stringer, Inorg. Chim Acta, 100 (1985) 23; (e) K R. Birdwhistell, T L. Tonker and J.L. Templeton, J. Am. Chem Soc., 107 (1985) 4474; (f) A P James and F G.A. Stone, J. Organomet Chem., 310 (1986) 47; (g) H.P. Kim, S. Kim, R.A. Jacobson and R J Angelici, Organometallics, 5 (1986) 2481, (h) J.B. Sheridan, G.L. Geoffroy and A.L. Rheingold, ibid., 5 (1986) 1514, (i) A. Mayr, G.A. McDermott, A M. Dorries and D. Van Engen, ibid., 6 (1987) 1503.

16 F.A Cotton, Inorg. Chem., 3 (1964) 702.

17 F.A. Cotton and C.S. Kraihanzel, J. Am. Chem. Soc., 84 (1962) 4432.

18 C. Sandorfy, in S Patai (Ed.), The Chemistry of the Carbon-Nitrogen Double Bond, Interscience Publishers, London, 1970.

19 A.C. Filippou and W. Grünleitner, J. Organomet. Chem., 407 (1991) 61.

20 H. Fischer, P. Hofmann, F R Kreißl, R.R. Schrock, U Schubert and K. Weiss, Carbyne Complexes, VCH, Weinheim, 1988.

21 (a) A.C. Filippou, E.O. Fischer and W. Grünleitner, J. Organomet. Chem., 386 (1990) 333; (b) A.C. Filippou, W. Grünleitner, E.O. Fischer, W. Imhof and G. Huttner, ibid., 413 (1991) 165.

22 H.S. Gutowsky and C.H Holm, J. Chem. Phys., 25 (1956) 1228.

23 H. Kessler, Angew. Chem., 82 (1970) 237; Angew Chem., Int. Ed Engl., 9 (1970) 219.

24 B.C. Ward and J.L. Templeton, J. Am. Chem Soc., 102 (1980) 1532.

25 J.L. Templeton and B.C. Ward, J Am. Chem. Soc., 102 (1980) 3288.

26 L J. Todd and J.R. Wilkinson, J. Organomet. Chem , 77 (1974) 1.

27 P.W R. Corfield, L.M. Baltusis and S.J. Lippard, Inorg. Chem., 20 (1981) 922.

28 J.C. Dewan, C.M. Giandomenico and S.J. Lippard, Inorg. Chem., 20 (1981) 4069.

29 (a) D.F. Lewis and S J. Lippard, Inorg. Chem., 11 (1972) 621, (b) C.T. Lam, M Novotny, D.L. Lewis and S.J. Lippard, ibid., 17 (1978) 2127; (c) E.B. Dreyer, C T. Lam and S J Lippard, ibid , 18 (1979) 1904, (d) W.A. LaRue, A.T Liu and J.S. Filippo Jr , ibid., 19 (1980) 315; (e) D.L. Lewis and S.J. Lippard, J. Am. Chem. Soc., 97 (1975) 2697; (f) P. Brant, F.A Cotton, J.C. Sekutowski, T.E. Wood and R.A. Walton, ibid., 101 (1979) 6588; (g) C.M. Giandomenico, J.C. Dewan and S.J. Lippard, ibid , 103 (1981) 1407.

30 E.M. Cradwick and D. Hall, J Organomet. Chem., 25 (1970) 91.

31 M.G.B. Drew, A.W. Johans, A.P. Wolters and I.B. Tomkins, Chem. Commun., (1971) 819.

32 M G B Drew and A.P. Wolters, J. Chem. Soc., Chem Commun., (1972) 457.

33 A.C. Filippou, C. Völkl and P Kiprof, unpublished results.

34 V A. Semion, Y.A. Chapovskii, Y.T. Struchkov and A.N. Nesmeyanov, Chem. Commun , (1968) 666.

35 A.G. Sharpe in V. Gutmann (Ed.), Halogen Chemistry, Academic Press, London, 1967, p. 2

36 A. DeCian, J. Colin, M. Schappacher, L. Ricard and R. Weiss, J. Am. Chem. Soc., 103 (1981) 1850.

37 J.L. Petersen and J.W. Egan Jr., Inorg. Chem., 20 (1981) 2883.

38 K. Sunkel, U. Nagel and W. Beck, J. Organomet Chem., 222 (1981) 251.

39 L. Ricard, R. Weiss, W.E. Newton, G.J.-J Chen and J.W McDonald, J. Am Chem. Soc , 100 (1978) 1318.

40 R. Allman, in S Patai (Ed.), The Chemistry of the Hydrazo, Azo and Azoxy Groups, Interscience, London, 1975, pp. 27–28.

41 M. Burke-Laing and M Laing, Acta Crystallogr., Sect. B, 32 (1976) 3216.

42 I. Hargittai and R. Seip, Acta Chem. Scand , Ser. A, 30 (1976) 540.

43 A.C. Filippou, E O Fischer and R. Paciello, 347 (1988) 127

44 J. Casanova Jr., R E. Schuster and N D. Werner, J. Chem. Soc., (1963) 4280.

45 R.E. Schuster, J.E. Scott and J. Casanova Jr., Org Synth., 46 (1966) 75.

46 H. Meerwein, G Hinz, P. Hofmann, E. Kroning and E. Pfeil, J. Prakt. Chem., 147 (1937) 257.

47 D.T. Cromer and J.B Mann, Acta Crystallogr., Sect. A, 24 (1968) 321

48 D.T. Cromer and D Liberman, J. Chem. Phys., 53 (1970) 1891.

49 R.E. Schmidt, M Birkhahn, W. Massa, P. Kiprof and E. Herdtweck, STRUX-III, Programmsystem zur Verarbeitung von Rontgendaten, Universitat Marburg 1980, TU München 1985–1989, Deutschland.

50 G.M. Sheldrick, SHELXS-86, Universitat Göttingen, Germany, 1986

51 G.M. Sheldrick, SHELX-76 A Program for Crystal Structure Determination, University Chemical Laboratory, Cambridge, England, 1976

52 C.K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Oak Ridge National Laboratory, Tennessee, USA, 1965.

53 E. Keller, SCHAKAL, ein Programm zur Darstellung von Molekulen, Universität Freiburg, Deutschland, 1990.