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Metal–carbon multiple bonds: novel syntheses and reactions of aminocarbyne complexes of tungsten

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Abstract

Syntheses and reactions of low and high valence tungsten aminocarbyne complexes are reported. The addition of LiN^iPr_2 to $W(CO)_6$ in Et_2O affords the imidoyl complex $Li[(CO)_5WC(O)N^iPr_2]$, which is converted to the aminocarbyne complexes *trans*-$X(CO)_4W{\equiv}CN^iPr_2$ (X = Cl (**1a**) or Br (**1b**)) after treatment with $C_2O_2X_2$. Complexes **1a** and **1b** react with γ-picoline (pic), 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) to yield the CO substitution products $X(CO)_2L_2W{\equiv}CN^iPr_2$ (**3a**, **3b**, **5a** and **6a**) (L = pic (**3**); L_2 = bpy (**5**); or phen (**6**)). Analogous reactions are also observed for the dicyclohexylaminocarbyne complexes *trans*-$X(CO)_4W{\equiv}CNCy_2$ (X = Cl (**2a**) or Br (**2b**)), affording the compounds $X(CO)_2L_2W{\equiv}CNCy_2$ (**4a**, **7b** and **8b**) (L = pic (**4**); L_2 = bpy (**7**) or phen (**8**)). Complexes **1a–8b** are useful starting materials for the synthesis of a variety of low and high valence tungsten aminocarbyne complexes. Thus treatment of **1a** and **1b** or **3a** and **3b** with ^{t}BuNC results in the formation of the isocyanide derivatives $X(CO)_2(^t BuNC)_2W{\equiv}CN^iPr_2$ (X = Cl (**9a**) or Br (**9b**)). Complex **9a** is converted to the monocarbonyl complex $Cl(CO)(^t BuNC)_3W{\equiv}CN^iPr_2$ (**10a**), when it is treated with ^{t}BuNC in refluxing toluene. Complexes **3b** and **4a** react with NaCp and KCp^* ($Cp^* = C_5Me_5$) to give the half-sandwich aminocarbyne complexes $Cp(CO)_2W{\equiv}CNR_2$ (R = ^{i}Pr (**11**) or Cy (**12**)) and $Cp^*(CO)_2W{\equiv}CN^iPr_2$ (**13**) respectively. Similarly, **7b** or **8b** are converted to the dinuclear aminocarbyne complex $NEt_4[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNCy_2]$ (**14b**), when they are treated with $K_2[cis\text{-}Mo(CO)_4(PPh_2)_2]$ and $[NEt_4]Br$. No carbyne–carbonyl coupling is observed in these reactions. Oxidation of **1a** with $PhICl_2$ and **1b** with Br_2 in 1,2-dimethoxyethane (DME) affords after elimination of all CO ligands the 16-electron aminocarbyne complexes *mer*-$X_3(DME)W{\equiv}CN^iPr_2$ (X = Cl (**15a**) or Br (**15b**)). In comparison, oxidation of **11–13** with $PhICl_2$ yields the 18-electron aminocarbyne complexes $Cp(Cl)_2(CO)W{\equiv}CNR_2$ (R = ^{i}Pr (**16**) or Cy (**17**)) and $Cp^*(Cl)_2(CO)W{\equiv}CN^iPr_2$ (**18**) respectively. Restricted rotation of the amino group about the $C_{carbyne}$–N bond is observed for the first time in the complexes **16** and **17** originating from the competition of the carbyne and the carbonyl ligand for metal–ligand back bonding in these compounds.

Keywords: Tungsten; Aminocarbyne complexes; Multiple bonds; Oxidation

1. Introduction

Carbyne ligands (CR) provide for bonding to transition metals one donor orbital of σ symmetry and two orthogonal low-lying acceptor molecular orbitals (MOs) of π symmetry [1]. Degeneracy of the two acceptor orbitals is lifted when the substituent R has no rotational symmetry [1c]. The resulting difference in energy between the two acceptor MOs is for alkylcarbyne and arylcarbyne ligands low, and therefore two nearly equivalent π interactions can develop with the metal center. In comparison, in aminocarbyne ligands (CNR_2) a strong interaction of the p-type lone pair of the amino-nitrogen with one of the two acceptor atomic orbitals of the carbyne–carbon occurs, leading to a large energy gap between the two acceptor levels [2]. Consequently, aminocarbyne ligands have only one acceptor MO comparable in energy with those of the alkylcarbyne or arylcarbyne ligands and are closely related to vinylidene ligands [3]. This electronic difference is reflected in the physical properties, the spectroscopic data, the structures and the reactions of aminocarbyne complexes [1a,4,5]. In this work we present several reactions of low valence tungsten diisopropylaminocarbyne and dicyclohexylaminocarbyne complexes, emphasizing the electronic effect of the amino substituent on the reactivity of compounds with metal–carbon triple bonds.

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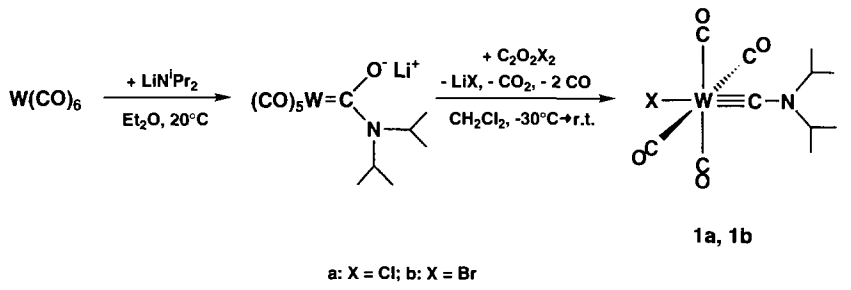
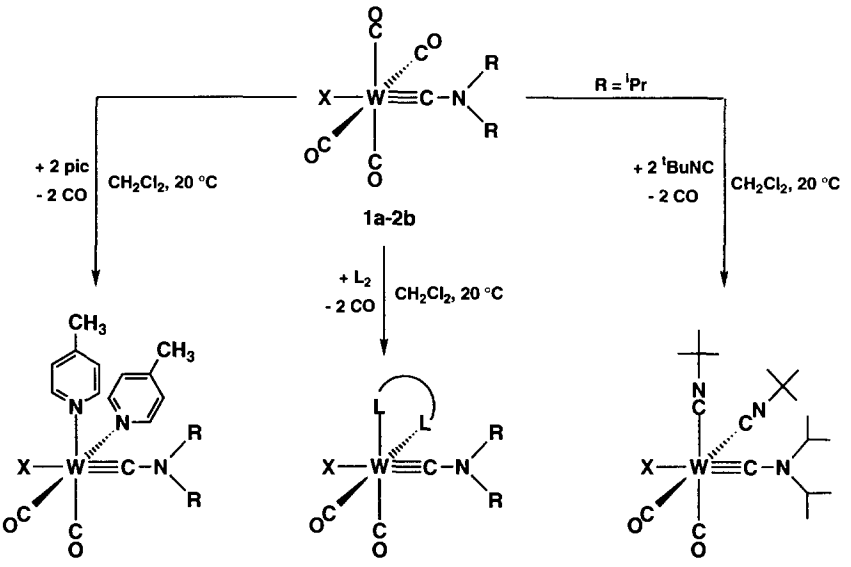


Scheme 1.

2. Results and discussion

We have recently reported an efficient method for the synthesis of chromium aminocarbyne complexes of the type $X(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (X = Cl or Br; pic = γ-picoline) and have further demonstrated these complexes to be suitable starting materials for the preparation of various low and high valence chromium aminocarbyne complexes [6]. The three-step procedure leading to the bis(γ-picoline) complexes involves in the first step a nucleophilic addition of LiN^iPr_2 to $Cr(CO)_6$ to afford the imidoyl complex $Li[(CO)_5CrC(O)N^iPr_2]$. This is followed by the reaction of the imidoyl complex with oxalyl chloride or bromide to give the aminocarbyne complexes *trans*-$X(CO)_4Cr{\equiv}CN^iPr_2$. In the last step, decarbonylation of the tetracarbonyl complexes with γ-picoline yields the desired compounds. Extension of this method to the synthesis of analogous tungsten complexes was restricted by the low product selectivity in the first step. Thus the reaction of $W(CO)_6$ with LiN^iPr_2 in tetrahydrofuran (THF) has been previously reported to afford not only the desired mono adduct $Li[(CO)_5WC(O)N^iPr_2]$, but also the bis adduct $Li_2[cis\text{-}(CO)_4W\{C(O)N^iPr_2\}_2]$, even when the reaction was carried out in the presence of excess $W(CO)_6$ [7]. Assuming that the formation of the bis adduct could be circumvented, if the nucleophilicity of LiN^iPr_2 would be reduced, we examined the course of this reaction in a



	X	R
3a	Cl	^{i}Pr
3b	Br	^{i}Pr
4a	Cl	Cy

	X	R	L$_2$
5a	Cl	^{i}Pr	bpy
6a	Cl	^{i}Pr	phen
7b	Br	Cy	bpy
8b	Br	Cy	phen

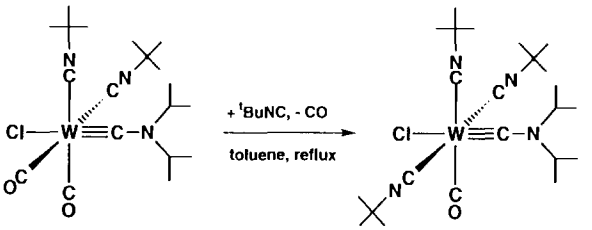
Scheme 2.

less-coordinating solvent such as Et_2O. In fact, when a suspension of $W(CO)_6$ in Et_2O was treated with a slight excess of LiN^iPr_2 at ambient temperature, the carbonyl complex rapidly dissolved to give an orange–brown solution, from which the imidoyl complex $Li[(CO)_5WC(O)N^iPr_2]$ precipitated out as an intense-yellow solid (Scheme 1). Evidence of the selective formation of the mono adduct was provided by the IR spectrum of the solution, which revealed that the ν(CO) absorption of $W(CO)_6$ at 1980 cm^{-1} had been replaced at the end of the reaction by four new ν(CO) absorptions at 2048, 1946, 1914 and 1883 cm^{-1}, tentatively assigned to the $A_1^{(2)}$, B_1, E and $A_1^{(1)}$ CO stretching modes of the product $Li[(CO)_5WC(O)N^iPr_2]$ [6a]. After evaporation of the solvent the lithium salt was isolated in essentially quantitative yield as an intense-yellow solid, which is easily hydrolyzed to give $W(CO)_6$. Treatment of $Li[(CO)_5WC(O)N^iPr_2]$ with an equivalent amount of oxalyl chloride or bromide in CH_2Cl_2 at -30 °C and subsequent warming of the reaction solutions to room temperature afforded the aminocarbyne complexes *trans*-$X(CO)_4W{\equiv}CN^iPr_2$ (X = Cl (**1a**) or Br (**1b**)) (Scheme 1). This transformation corresponds formally to an abstraction of an oxygen atom from an acyl ligand and has been first devised by Fischer and Fischer [8a] and Mayr and coworkers [8b,c] for the preparation of analogous alkylcarbyne and arylcarbyne complexes of Group 6 transition metals. Following a similar procedure, Hill and coworkers [9] have recently reported the synthesis of *mer*-$X(CO)_3(PPh_3)W{\equiv}CN^iPr_2$ (X = Cl, Br or CF_3CO_2).

Complexes **1a** and **1b** were purified by column chromatography on silylated silica at -10 °C and isolated as yellow solids, which are soluble in CH_2Cl_2, moderately soluble in Et_2O but insoluble in *n*-pentane. They are, like other *trans*-halo(tetracarbonyl)aminocarbyne complexes of tungsten, thermolabile compounds decomposing slowly in solution at room temperature by loss of CO ligands [10]. When this thermal decarbonylation was carried out in the presence of an excess of 4-methylpyridine (γ-picoline), the thermally stable CO substitution products $X(CO)_2(pic)_2W{\equiv}CN^iPr_2$ (X = Cl (**3a**) or Br (**3b**)) were selectively formed (Scheme 2). Similarly, reaction of *trans*-$Cl(CO)_4W{\equiv}CNCy_2$ (**2a**) with γ-picoline in refluxing CH_2Cl_2 gave the analogous dicyclohexylaminocarbyne complex $Cl(CO)_2(pic)_2W{\equiv}CNCy_2$ (**4a**) (Scheme 2).

Complexes **3a–4a** were isolated as yellow solids in essentially quantitative yield after removal of the solvent and washing away the excess γ-picoline. They are soluble in CH_2Cl_2, sparingly soluble in Et_2O and decompose, when heated in a sealed capillary under nitrogen, at 108 °C, 98 °C and 166 °C respectively.

Analogous reactions occurred when the complexes *trans*-$X(CO)_4W{\equiv}CNR_2$ (**1a–2b**) were treated with chelating nitrogen-based ligands, such as 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen), affording the dicarbonyl complexes $X(CO)_2L_2W{\equiv}CNR_2$ (**5a–8b**) (L_2 = bpy or phen) (Scheme 2). IR monitoring of these reactions revealed clean conversion of the starting materials to the products, which were isolated with an essentially quantitative yield as purple solids, that are soluble in *N,N*-dimethylformamide (DMF) but sparingly soluble in CH_2Cl_2 and insoluble in Et_2O. Similarly, treatment of *trans*-$X(CO)_4W{\equiv}CN^iPr_2$ (**1a** and **1b**) or the γ-picoline derivatives $X(CO)_2(pic)_2W{\equiv}CN^iPr_2$ (**3a** and **3b**) with slightly more than two equivalents of *tert*-butyl isocyanide in CH_2Cl_2 at ambient temperature gave the aminocarbyne complexes $X(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$ (X = Cl (**9a**) or Br (**9b**)) (Scheme 2). These were purified by column chromatography on silylated silica at -20 °C and isolated as yellow solids, that are soluble in CH_2Cl_2 and Et_2O and melt without decomposition at 106 °C and 83 °C respectively. Reaction of **9a** with a slight excess of ^{t}BuNC in refluxing toluene led to the clean formation of the monocarbonyl complex $Cl(CO)(^tBuNC)_3W{\equiv}CN^iPr_2$ (**10a**):

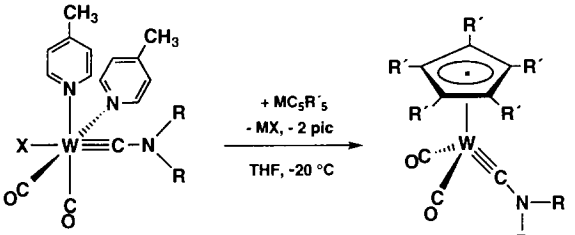


9a **10a**

This was isolated with an 80% yield as a yellow solid, which is soluble in CH_2Cl_2 and Et_2O, but sparingly soluble in *n*-pentane. Similar reactions to those yielding **3a–10a** have been observed earlier for alkylcarbyne, arylcarbyne and diethylaminocarbyne complexes of the type *trans*-$X(CO)_4M{\equiv}CR$ (X = Cl, Br or I; M = Cr, Mo or W; R = Me, Ph or NEt_2) [1,8b,8c,11].

Compounds **3a–4a** were found like other bis-picoline-substituted carbyne complexes to be useful starting materials for the synthesis of half-sandwich carbyne complexes bearing cyclopentadienyl ligands [5a,6a,12]. This property can be ascribed to the presence of the γ-picoline ligands, which not only are coordinatively labile but also enhance the electron density at the metal center, thereby preventing undesirable redox reactions of **3a–4a** with nucleophiles, which might act as reducing agents such as alkali metal cyclopentadienyls. Thus treatment of **3b** and **4a** with NaCp in THF at -60 °C and warming of the reaction solutions to -20 °C afforded the aminocarbyne complexes $Cp(CO)_2W{\equiv}$

CNR_2 (R = ^{i}Pr (**11**) or Cy (**12**)) with 78% and 77% yields respectively:

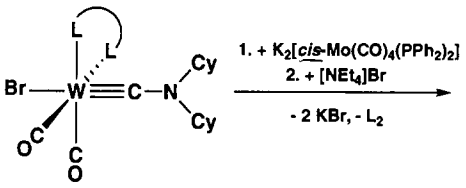


3b, 4a **11-13**

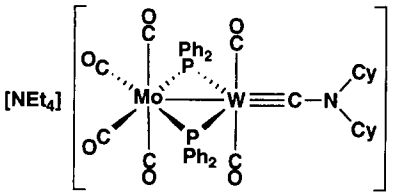
	R	R'
11	^{i}Pr	H
12	Cy	H
13	^{i}Pr	Me

Likewise, the reaction of **3b** with KCp^* ($Cp^* = C_5Me_5$) in THF gave the aminocarbyne complex $Cp^*(CO)_2W{\equiv}CN^iPr_2$ (**13**), which was obtained as an intense-yellow solid with 75% yield. Complexes **11–13** were purified by column chromatography on silica at −20 °C and isolated as yellow solids, which are soluble in all common organic solvents and melt without decomposition at 64 °C, 139 °C and 113 °C respectively.

Not only the coordinatively labile γ-picoline ligands in **3a–4a** but also the chelating ligands bpy and phen in **5a–8b** can be easily displaced from the coordination sphere by strong chelating nucleophiles. Thus reaction of **7b** or **8b** with $K_2[cis\text{-}Mo(CO)_4(PPh_2)_2]$, which was prepared in situ from $cis\text{-}Mo(CO)_4(PPh_2H)_2$ (**14a**) and KH, gave the dinuclear complex $K[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNCy_2]$, bearing a terminal aminocarbyne ligand:



7b, 8b



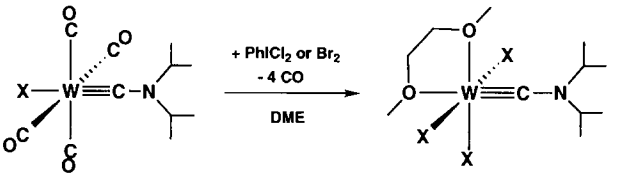
14b

This was converted to the tetraethylammonium salt **14b** by treatment with $[NEt_4]Br$ and isolated with 45% yield as a yellow air-sensitive solid that is soluble in DMF, CH_2Cl_2 and THF.

No carbyne–carbonyl coupling was observed in this reaction. In contrast, the addition of cyanide or dithiocarbamates to analogous alkylcarbyne or arylcarbyne complexes of the general formula $X(CO)_2L_2W{\equiv}CR$ (X = Cl, Br or BF_4; L_2 = bpy, phen or 1,2-bis-diphenylphosphino)ethane (dppe); R = Me, Ph, CH_2Ph or $CHMe_2$) has been previously shown to induce coupling of the carbyne ligand with one carbonyl ligand to afford anionic η^2-ketenyl complexes [13]. The transformation of **7b** or **8b** to **14b** supports therefore earlier observations that the presence of a π donor substituent at the carbyne–carbon prevents the well-known nucleophile-induced carbyne–carbonyl coupling reaction of low valence metal (Fischer-type) carbyne complexes, allowing the synthesis of anionic aminocarbyne complexes [14,15].

Attempts to add CO_2 across the metal–carbon triple bond of **14b** were unsuccessful. This can be ascribed to the steric bulk of the dicyclohexylamino group, since the analogous diethylaminocarbyne complex $[NEt_4][(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNEt_2]$ has been previously shown to undergo a fast 2 + 2 cycloaddition reaction with CO_2 to give an oxatungstacyclobutenone complex [15a].

Oxidation of the aminocarbyne complexes **1a** and **1b** with one equivalent of $PhICl_2$, acting as a selective chlorinating reagent, or Br_2 in DME afforded after elimination of all CO ligands the octahedral, 16-electron aminocarbyne complexes *mer*-$X_3(DME)W{\equiv}CN^iPr_2$ (X = Cl (**15a**) or Br (**15b**)):



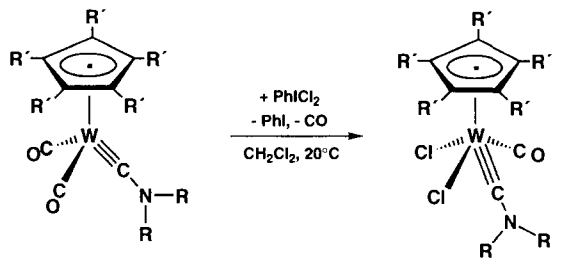
1a, 1b **15a, 15b**

a: X = Cl; b: X = Br

IR monitoring of these reactions revealed a clean conversion of the starting materials to the products **15a** and **15b**, which were isolated as green water-sensitive solids with 84% and 82% yields respectively. They are soluble in CH_2Cl_2 and DME but insoluble in Et_2O and decompose according to a thermogravimetry (TG)–mass spectrometry (MS) analysis at 95 °C and 93 °C (extrapolated onset) respectively (Fig. 1). A similar bromination reaction with that of **1b** has been previously reported for alkylcarbyne and arylcarbyne complexes of

tungsten [16]. High valence metal (Schrock-type) 16-electron aminocarbyne complexes such as **15a** and **15b** are rare, other known compounds of this type being $(^iPrO)_3(py)_2W{\equiv}CNR_2$ (R = Me or Et; py = pyridine) and $Tp'(X)_2W{\equiv}CN(R)Et$ (Tp' = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = Br or I; R = Me or Et) [5f,17].

In comparison, oxidation of the half-sandwich aminocarbyne complexes **11–13** with one equivalent of $PhICl_2$ resulted in the formation of the seven-coordinated 18-electron aminocarbyne complexes $(\eta^5\text{-}C_5R'_5)(Cl)_2(CO)W{\equiv}CNR_2$ **(16–18)** (the C_5R_5 is considered here to occupy three coordination sites):



11-13 16-18

	R	R'
16	^{i}Pr	H
17	Cy	H
18	^{i}Pr	Me

Analogous reactions have been previously observed for several other low valence Group 6 metal aminocarbyne complexes [5a,5b,6c,11e,12,18]. Compounds **16–18**, which were isolated as purple solids with a high yield, combine features of both Fischer-type aminocarbyne complexes such as **1a–13**, containing a π acceptor ligand (CO), and Schrock-type aminocarbyne complexes such as **15a** and **15b**, bearing a high valence metal centre [1]. They are soluble in CH_2Cl_2, but sparingly soluble in Et_2O and decompose, when heated in a sealed capillary under nitrogen, at 133 °C, 155 °C and 185 °C respectively. Their stability is remarkable, especially in view of earlier studies, which have shown that related aminocarbyne complexes of the type $(^iPrO)_3(py)_2W{\equiv}CNR_2$ (R = Me or Et) react with CO to give various types of carbyne-ligand coupling product [17]. This stability can be attributed to the special electronic properties of an aminocarbyne ligand. Thus aminocarbyne ligands bear only one π acceptor orbital of low energy (see Section 1). Therefore only one filled metal-localized MO of π symmetry is primarily used for the metal–carbyne back bonding in **16–18**. The other π acceptor orbital of an aminocarbyne ligand has a considerable higher energy, owing to a strong interaction with the p-type lone pair of the amino-nitrogen. In **16–18**, this orbital competes with the π* acceptor orbitals of the CO ligand for back bonding from the second filled metal-localized MO of π symmetry (**16–18** are considered here to have formally a d^4 metal electron configuration counting the carbyne ligand as a monocationic two-electron donor ligand). This electronic situation is the origin for the observed fluxionality of **16–18** (see ^1H NMR spectra) and the unusual reactivity of these compounds. The latter is demonstrated for example by the oxidative decarbonylation reaction of **16** with one equivalent of $PhICl_2$ to give the 2-azoniavinylidene complex $Cp(Cl)_4WCN^iPr_2$ [19].

3. Spectroscopic investigations

3.1. IR, ^1H NMR and ^{13}C NMR spectra

The solution IR spectra of **1a–18** reveal in the region 2200–1500 cm^{-1} characteristic $\nu(C{\equiv}N^tBu)$, $\nu(CO)$ and $\nu(C_{carbyne}{\cdots}N)$ absorptions of the coordinated tert-butyl isocyanide, carbonyl and aminocarbyne ligands respectively (Table 1). The number and relative intensities of the $\nu(C{\equiv}N^tBu)$ and $\nu(CO)$ absorptions indicate the spatial arrangement of the isocyanide and carbonyl ligands in the coordination sphere. Thus three $\nu(CO)$ absorptions are observed in the IR spectra of the tetracarbonyl complexes **1a–2b**, indicating a *trans* orientation of the halo and the aminocarbyne ligand [10,20]. In comparison, two strong $\nu(CO)$ absorptions of almost equal intensity are found in the IR spectra of the octahedral complexes **3a–9b** and **11–13** indicating a *cis* arrangement of the carbonyl ligands. Similarly, the two *cis*-oriented tert-butyl isocyanide ligands in **9a** and **9b** give rise to two $\nu(C{\equiv}N^tBu)$ absorptions. The higher frequency absorption is assigned to the symmetric A_1 mode and the lower frequency absorption to the antisymmetric B_1 mode [20]. In comparison, the octahedral

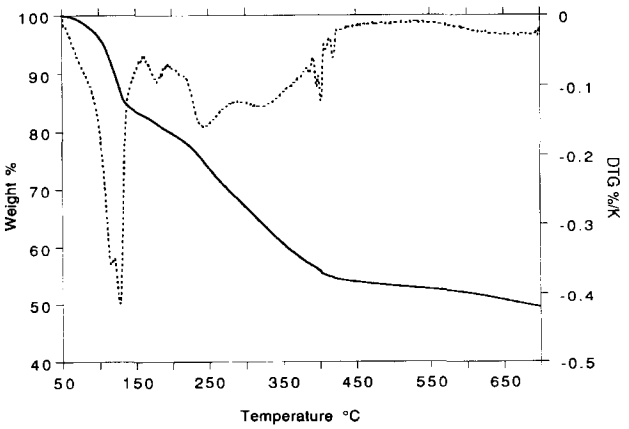


Fig. 1. TG and differential TG curves of *mer*-$Cl_3(DME)W{\equiv}CN^iPr_2$ **(15a)**.

complex **10a** shows three $\nu(C{\equiv}N^tBu)$ absorptions as expected on the basis of group theory for an $M(CN^tBu)_3$ fragment of local C_{2v} symmetry [21]. The position of the $\nu(C{\equiv}N^tBu)$ and $\nu(CO)$ absorptions depends strongly on the polarity of the solvent. This is demonstrated by the IR spectra of **5a–8b**, **9a**, **10a** or **11–13**, which reveal that the $\nu(C{\equiv}N^tBu)$ absorptions are shifted to higher frequency and the $\nu(CO)$ absorptions to lower frequency as the polarity of the solvent is increased (Table 1).

The γ-picoline complexes **3a–4a** exhibit a characteristic absorption at 1621 cm^{-1}, which is tentatively assigned to the $\nu(C{=}N)$ vibration of the γ-picoline ligands. This absorption appears at higher frequency than that of uncoordinated γ-picoline ($\nu(C{=}N)$ in CH_2Cl_2 at 1606 cm^{-1}), indicating extensive electron transfer from the ligand to the metal centre in **3a–4a**.

All aminocarbyne complexes are distinguished by an absorption in the range 1510–1610 cm^{-1}, which is assigned to the $\nu(C_{carbyne}{=}N)$ vibration. The fairly high frequency of this vibration reveals a strong π conjugation of the amino group with the metal–carbon triple bond [5,6,12]. A comparison of the aminocarbyne complexes **1a–2b** with **3a–4a**, or **9a** and **9b** with **10a** and

Table 1
$\nu(C{\equiv}N^tBu)$, $\nu(CO)$ and $\nu(C{-}N)$ absorptions of **1a–18** in various solvents

Complex	$\nu(C{\equiv}N^tBu)$ (cm^{-1})	$\nu(CO)$ (cm^{-1})	$\nu(C{=}N)_{ring}$ (cm^{-1})	$\nu(C_{carbyne}{=}N)$ (cm^{-1})	Solvent
trans-$Cl(CO)_4W{\equiv}CN^iPr_2$ (**1a**)	–	2105 w, 2019 s,sh, 1981 vs	–	1570 m	CH_2Cl_2
	–	2103 w, 2020 s,sh, 1981 vs	–	1561 m	THF
trans-$Br(CO)_4W{\equiv}CN^iPr_2$ (**1b**)	–	2104 w, 2019 s, 1982 vs	–	1570 m	CH_2Cl_2
	–	2102 w, 2016 s,sh, 1984 vs	–	1562 m	Et_2O
trans-$Cl(CO)_4W{\equiv}CNCy_2$ (**2a**)	–	2103 w, 2019 s,sh, 1980 vs	–	1564 m	CH_2Cl_2
trans-$Br(CO)_4W{\equiv}CNCy_2$ (**2b**)	–	2104 w, 2020 s,sh, 1980 vs	–	– [a]	CH_2Cl_2
$Cl(CO)_2(pic)_2W{\equiv}CN^iPr_2$ (**3a**)	–	1944 s, 1842 s	1621 m	1521 m	CH_2Cl_2
$Br(CO)_2(pic)_2W{\equiv}CN^iPr_2$ (**3b**)	–	1947 s, 1845 s	1621 m	1518 m	CH_2Cl_2
$Cl(CO)_2(pic)_2W{\equiv}CNCy_2$ (**4a**)	–	1947 s, 1843 s	1621 m	1512 m	CH_2Cl_2
$Cl(CO)_2(bpy)W{\equiv}CN^iPr_2$ (**5a**)	–	1946 s, 1848 s	– [a]	– [a]	CH_2Cl_2
	–	1937 s, 1842 s	– [a]	– [a]	DMF
$Cl(CO)_2(phen)W{\equiv}CN^iPr_2$ (**6a**)	–	1946 s, 1850 s	– [a]	– [a]	CH_2Cl_2
	–	1941 s, 1843 s	– [a]	– [a]	DMF
$Br(CO)_2(bpy)W{\equiv}CNCy_2$ (**7b**)	–	1945 s, 1849 s	– [a]	– [a]	CH_2Cl_2
	–	1936 s, 1841 s	– [a]	– [a]	DMF
$Br(CO)_2(phen)W{\equiv}CNCy_2$ (**8b**)	–	1946 s, 1848 s	– [a]	– [a]	CH_2Cl_2
	–	1938 s, 1842 s	– [a]	– [a]	DMF
$Cl(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$ (**9a**)	2171 m, 2143 m	1978 s, 1905 s	–	1538 m	CH_2Cl_2
	2166 m, 2135 m	1981 s, 1916 s	–	1527 m	Toluene
$Br(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$ (**9b**)	2171 s, 2142 s	1978 s, 1907 s	–	1539 m	CH_2Cl_2
$Cl(CO)(^tBuNC)_3W{\equiv}CN^iPr_2$ (**10a**)	2152 m, 2111 vs, 2067 m	1874 vs	–	1527 m	CH_2Cl_2
	2144 m, 2105 vs, 2067 m	1889 vs	–	1517 m	Toluene
$Cp(CO)_2W{\equiv}CN^iPr_2$ (**11**)	–	1939 s, 1851 s	–	1561 m	CH_2Cl_2
	–	1951 s, 1871 s	–	1554 m	Et_2O
	–	1944 s, 1862 s	–	1556 m	THF
$Cp(CO)_2W{\equiv}CNCy_2$ (**12**)	–	1938 s, 1850 s	–	1557 m	CH_2Cl_2
	–	1942 s, 1861 s	–	1554 m	THF
	–	1956 s, 1880 s	–	1547 m	*n*-pentane
$Cp^*(CO)_2W{\equiv}CN^iPr_2$ (**13**)	–	1926 s, 1839 s	–	1549 m	CH_2Cl_2
	–	1932 s, 1851 s	–	1546 m	THF
cis-$Mo(CO)_4(PPh_2H)_2$ (**14a**)	–	2025 m, 1926 m,sh, 1916 vs, 1894 s	–	–	THF
		2028 m, 1938 m, 1920 vs, 1914 s	–	–	*n*-pentane
$NEt_4[(CO)_4Mo(\mu\text{-}PPh_2)_2\text{-}W(CO)_2CNCy_2]$ (**14b**)	–	2000 m, 1907 vs, 1880 s, 1850 s, 1832 s	–	– [a]	CH_2Cl_2
mer-$Cl_3(DME)W{\equiv}CN^iPr_2$ (**15a**)	–	–	–	1542 m	CH_2Cl_2
mer-$Br_3(DME)W{\equiv}CN^iPr_2$ (**15b**)	–	–	–	1540 m	CH_2Cl_2
$Cp(CO)(Cl)_2W{\equiv}CN^iPr_2$ (**16**)	–	2014 s	–	1601 m	CH_2Cl_2
$Cp(CO)(Cl)_2W{\equiv}CNCy_2$ (**17**)	–	2014 s	–	1602 m	CH_2Cl_2
$Cp^*(CO)(Cl)_2W{\equiv}CN^iPr_2$ (**18**)	–	1984 s	–	1582 m	CH_2Cl_2

[a] The $\nu(C{=}N)_{ring}$ and $\nu(C_{carbyne}{=}N)$ absorptions of these compounds were not recorded.

16–18 with **11–13** shows a decrease in the $\nu(C_{carbyne}\equiv N)$ frequency upon replacement of the carbonyl ligands by the weaker π acceptor ligands γ-picoline and tert-butyl isocyanide, or upon reduction of the metal centre. This decrease is the consequence of the higher electron density at the metal centre, which results in a stronger metal–carbyne back bonding [5a,5b,6b,6c,11e]. For the same reason, the $\nu(C_{carbyne}\equiv N)$ absorption of the high valence tungsten aminocarbyne complexes **15a** and **15b**, bearing a good π donor ligand such as DME, appears at much lower frequency than that of the high valence tungsten aminocarbyne complexes **16–18**, bearing a strong π acceptor ligand such as CO (Table 1).

Further support for the structures assigned to **1a–18** is given by the ^{1}H NMR spectra (Table 2). Thus one doublet resonance and one septet resonance are observed for the methyl and methine protons of the diisopropylaminocarbyne ligand of **1a–3b**, **5a**, **6a**, **9a–11**, **13**, **15a** and **15b** in the temperature range from −80 to +20 °C, indicating pseudo-C_s molecular symmetry and rapid rotation of the amino group about the $C_{carbyne}$–N bond. In contrast, the ^{1}H NMR spectra of the aminocarbyne complexes **16** and **18** show, at room temperature, two doublet resonances for the diastereotopic methyl protons of the equivalent isopropyl groups in the ratio 1:1, indicating a *cis* orientation of the chloro ligands and the presence of a chiral metal centre in these compounds (C_1 molecular symmetry).

The ^{1}H NMR spectra of **3a–4a** show two doublet resonances for the α-H and β-H protons of the equivalent γ-picoline ligands, and those of **9a** and **9b** a singlet resonance for the tert-butyl protons of the equivalent isocyanide ligands. Similarly, a singlet set of four resonances is observed for the aromatic protons of bpy and phen, indicating a symmetric coordination of these bidentate ligands in **5a–8b**. These data show, in connection with the IR and ^{13}C NMR data, unequivocally the *trans* orientation of the halo and the aminocarbyne ligand in **3a–9b**. The ^{1}H NMR spectrum of **10a** displays two singlet resonances for the *tert*-butyl isocyanide ligands in the ratio 1:2, suggesting in agreement with the IR data a meridional arrangement of these ligands. Furthermore, two singlet resonances are observed for the methyl protons and two multiplet resonances for the methylene protons of the DME ligand in **15a** and **15b**, indicating in full agreement with the ^{13}C NMR spectra an asymmetric coordination of the chelating ligand in these compounds and the presence of the *mer* isomer.

The variable-temperature ^{1}H NMR spectra (300 MHz) of **16** and **17** reveal a fluxional process in these compounds, which can be ascribed to the restricted rotation of the amino group about the $C_{carbyne}$–N bond. This causes the two N-bonded alkyl groups of the carbyne ligand to become inequivalent in the low exchange limit spectra. Therefore, three doublets at δ = 1.24, 1.28 and 1.35 ppm are observed for the methyl protons of **16** at T = 208 K. The doublets at δ = 1.28 and 1.35 ppm are assigned to the diastereotopic methyl protons of the one isopropyl group and the doublet at δ = 1.24 ppm to the diasterotopic methyl protons of the other isopropyl group, which have by accident the same chemical shift. As the temperature is raised, the two doublets at δ = 1.28 and 1.35 ppm broaden, coalesce at T = 241 K and appear in the fast exchange limit spectrum of **16** at T = 293 K as a doublet at δ = 1.38 ppm (Table 2). In contrast, the third doublet resonance at δ = 1.24 ppm is only slightly shifted to a lower field (δ = 1.32 ppm), as the temperature is raised to 293 K (Table 2). In addition, two overlapping septet resonances at $\delta \approx 3.62$ ppm are observed for the methine protons of the aminocarbyne ligand in the low exchange limit spectrum of **16** (T = 208 K), which upon warming of the NMR sample broaden to one signal at δ = 3.63 ppm (T = 236 K) and appear in the high limit exchange spectrum of **16** (T = 293 K) as a well resolved septet at δ = 3.66 ppm. A similar temperature dependence is observed for the methine proton signals of the cyclohexyl groups in **17** and the alkyl protons of the analogous diethylaminocarbyne complexes $(\eta^5\text{-}C_5R_5)(Cl)_2(CO)M{\equiv}CNEt_2$ (R = H or Me; M = Mo or W) [19]. Additional evidence for the presence of two inequivalent N-bonded alkyl groups at low temperatures is given by the ^{13}C NMR spectrum of **17** at −20 °C, which shows two resonances for the α- and γ-carbon atoms of the cyclohexyl groups (Table 3). The free energy of activation for the site exchange of the alkyl groups in **16** was calculated with 50.5 kJ mol^{-1}. This correlates well with extended Hückel MO calculations on the model compound $Cp(Br)_2(CO)M{\equiv}CNH_2$, which show, that the conformer **A**, in which the amino plane is perpendicular to the Cp plane, is by about 42 kJ mol^{-1} more stable than the conformer **B**, which results from **A** by a 90° rotation of the amino plane about the $C_{carbyne}$–N bond (Fig. 2) [19]. Experimental support for the energy preference of conformer **A** is given by the X-ray structure of the complex $(\eta^5\text{-}C_5Me_4Et)(Br)_2(CO)W{\equiv}CNEt_2$ [19].

The $^{13}C\{^1H\}$ NMR spectra also support the structures proposed for **1a–18** (Table 3). Thus only one resonance is observed for the equivalent carbonyl ligands of **1a** and **1b**, indicating a *trans* geometry for these complexes. Similarly, only one resonance is found for the two equivalent *cis*-oriented carbonyl ligands in **3a–9b**. A considerable downfield shift is observed on going from the tetracarbonyl complexes **1a** and **1b** to the more electron-rich dicarbonyl derivatives **9a**, **9b** and **3a–8b**. This trend is consistent with earlier NMR studies on carbonyl complexes of Group 6 transition metals, which have shown that a stronger metal–carbonyl back bonding causes a deshielding of the carbonyl carbon atom [5a,5b,6,11f,g,22]. In addition, the carbonyl carbon res-

Table 2
^{1}H NMR data for **1a–18** where the relative intensities, multiplicities and coupling constants are given in parentheses

Complex	δ (ppm)						Solvent; T (°C)
	$N(CHMe_2)_2$; $N[CH(CH_2)_5]_2$; $[N(CH_2CH_3)_4]^+$	Me_3CNC; C_5Me_5	NC_5H_4Me; OCH_3; OCH_2; $[N(CH_2CH_3)_4]^+$	$N(CHMe_2)_2$; $N[CH(CH_2)_5]_2$	C_5H_5; PPh_2H	NC_5H_4Me; bpy; phen; PPh_2	
1a	1.31 (12, d, ^3J(HH) = 6.7 Hz)	–	–	3.22 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; −20
1b	1.46 (12, d, ^3J(HH) = 6.7 Hz)	–	–	3.58 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	acetone-d_6; +20
3a	1.24 (12, d, ^3J(HH) = 6.6 Hz)	–	2.36 (6, s)	3.36 (2, sept, ^3J(HH) = 6.6 Hz)	–	7.09 (4, d, ^3J(HH) = 5.9 Hz) [a] 8.66 (4, d, ^3J(HH) = 5.9 Hz) [b]	CD_2Cl_2; +20
3b	1.23 (12, d, ^3J(HH) = 6.6 Hz)	–	2.37 (6, s)	3.35 (2, sept, ^3J(HH) = 6.6 Hz)	–	7.09 (4, d, ^3J(HH) = 6.0 Hz) [a] 8.69 (4, d, ^3J(HH) = 6.0 Hz) [b]	CD_2Cl_2; +20
4a	0.9–1.9 (20, m)	–	2.36 (6, s)	2.86 (2, tt, ^3J(HH) = 3.8 Hz, ^3J(HH) = 12.0 Hz)	–	7.09 (4, d, ^3J(HH) = 6.0 Hz) [a] 8.67 (4, d, ^3J(HH) = 6.0 Hz) [b]	CD_2Cl_2; +20
5a	1.11 (12, d, ^3J(HH) = 6.5 Hz)	–	–	3.14 (2, sept, ^3J(HH) = 6.5 Hz)	–	7.80 (2, m) [c]; 8.35 (2, m) [d]; 8.89 (2, d, ^3J(HH) = 8.1 Hz) [e]; 9.09 (2, d, ^3J(HH) = 5.2 Hz) [f]	DMF-d_7 0
6a	1.07 (12, d, ^3J(HH) = 6.4 Hz)	–	–	3.09 (2, sept, ^3J(HH) = 6.4 Hz)	–	8.18 (2, dd, ^3J(HH) = 4.9 Hz, ^3J(HH) = 8.3 Hz) [g]; 8.38 (2, s) [h]; 9.03 (2, dd, ^3J(HH) = 8.3 Hz, ^4J(HH) = 1.5 Hz) [i]; 9.50 (2, dd, ^3J(HH) = 4.9 Hz, ^4J(HH) = 1.5 Hz) [j]	DMF-d_7; 0
7b	0.9–1.8 (20, m)	–	–	– [k]	–	7.82 (2, m) [c]; 8.36 (2, m) [d]; 8.92 (2, d, ^3J(HH) = 8.2 Hz) [e]; 9.14 (2, d, ^3J(HH) = 4.9 Hz) [f]	DMF-d_7; 0
8b	0.9–1.8 (20, m)	–	–	– [k]	–	8.20 (2, dd, ^3J(HH) = 4.9 Hz, ^3J(HH) = 8.3 Hz) [g]; 8.38 (2, s) [h]; 9.03 (2, dd, ^3J(HH) = 8.3 Hz, ^4J(HH) = 1.5 Hz) [i]; 9.55 (2, dd, ^3J(HH) = 4.9 Hz, ^4J(HH) = 1.5 Hz) [j]	DMF-d_7; 0

9a	1.28 (12, d, ^3J(HH) = 6.7 Hz)	1.52 (18, s)	–	3.09 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; +20
9b	1.28 (12, d, ^3J(HH) = 6.6 Hz)	1.51 (18, s)	–	3.10 (2, sept, ^3J(HH) = 6.6 Hz)	–	–	CD_2Cl_2; +20
10a	1.27 (12, d, ^3J(HH) = 6.6 Hz)	1.49 (9, s) 1.50 (18, s)	–	3.02 (2, sept, ^3J(HH) = 6.6 Hz)	–	–	CD_2Cl_2; +20
11	1.28 (12, d, ^3J(HH) = 6.6 Hz)	–	–	3.22 (2, sept, ^3J(HH) = 6.6 Hz)	5.53 (5, s)	–	CD_2Cl_2; +20
12	1.1–1.8 (20, m)	–	–	2.75 (2, tt, ^3J(HH) = 3.8 Hz, ^3J(HH) = 12.0 Hz)	5.52 (5, s)		CD_2Cl_2; +20
13	1.26 (12, d, ^3J(HH) = 6.7 Hz)	2.13 (15, s)	–	3.18 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; +20
14a	–	–	–		6.10 (2, d, ^1J(PH) = 335.4 Hz)	7.25–7.76 (20, m)	CD_2Cl_2; −20
14b	1.03 (12, t, ^3J(HH) = 7.3 Hz); 1.31–2.06 (20, m)	–	2.84 (8, q, ^3J(HH) = 7.3 Hz) [i]	–	–	7.16–8.09 (20, m)	CD_2Cl_2; 0
15a	1.31 (12, d, ^3J(HH) = 6.7 Hz)	–	3.58 (3, s); 3.78 (2, m); 4.30 (2 m); 4.94 (3, s)	4.15 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; −20
15b	1.41 (12, d, ^3J(HH) = 6.7 Hz)	–	3.89 (3, s); 4.01 (2, m); 4.36 (2, m); 4.87 (3, s)	4.54 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; +20
16	1.32 (6, d, ^3J(HH) = 6.6 Hz); 1.38 (6, d, ^3J(HH) = 6.6 Hz)	–	–	3.66 (2, sept, ^3J(HH) = 6.6 Hz)	5.71 (5, s)	–	CD_2Cl_2; +20
17	1.0–2.1 (20, m)			3.20 (2, br)	5.70 (5, s)	–	CD_2Cl_2; −20
18	1.33 (6, d, ^3J(HH) = 6.7 Hz); 1.34 (6, d, ^3J(HH) = 6.7 Hz)	2.04 (15, s)	–	3.65 (2, sept, ^3J(HH) = 6.7 Hz)	–	–	CD_2Cl_2; +20

[a,b] β- and α-H resonances of the γ-picoline ligand respectively

[c,d,e,f] H(5), H(4), H(3) and H(6) resonances of the bpy ligand respectively.

[g,h,i,j] H(3/8), H(5/6), H(4/7) and H(2/9) resonances of the phen ligand respectively.

[k] The α-H resonance of the cyclohexyl groups and the residual proton resonances of the deuterated solvent are probably superimposed.

[l] The methylene proton resonance of the $[NEt_4]$ cation and the α-H resonance of the cyclohexyl groups are superimposed.

Table 3
^{13}C NMR data for the complexes **1a–18**

Complex	δ (ppm)										Solvent; T (°C)
	C_5Me_5; NC_5H_4Me $N(CH_2Me)_4$	$N(CHMe_2)_2$; NCy_2	Me_3CNC;	$N(CHMe_2)_2$; $N(CH_2Me)_4$	Me_3CNC; OMe	C_5H_5; C_5Me_5 OCH_2	NC_5H_4Me bipy, ophen PPh_2	Me_3CNC	CO	W≡C	
1a	–	22.5	–	53.5	–	–	–	–	196.1 ($^1J_{WC}$ = 127.0 Hz)	235.9 ($^1J_{WC}$ = 190.4 Hz)	CD_2Cl_2; −20
1b	–	22.3	–	54.5	–	–	–	–	195.1	244.6	CD_2Cl_2; −20
2h	–	24.7 [a]; 25.3 [b]; 32.9 [c]; 61.6 [d]	–	–	–	–	–	–	194.9	245.1	CD_2Cl_2; −20
3a	21.2	23.3	–	51.4	–	–	125.8 [e]; 150.3 [f]; 152.8 [g]	–	225.6 ($^1J_{WC}$ = 172.1 Hz)	239.5	CD_2Cl_2; +20
3b	21.2	23.3	–	51.4	–	–	125.9 [e]; 150.3 [f]; 153.5 [g]	–	225.0 ($^1J_{WC}$ = 172.1 Hz)	239.1	CD_2Cl_2; +20
4a	21.2	25.7 [a]; 26.3 [b]; 34.0 [c]; 60.1 [d]	–	–	–		125.7 [e]; 150.2 [f]; 152.5 [g]	–	225.6 ($^1J_{WC}$ = 173.4 Hz)	240.1 ($^1J_{WC}$ = 223.3 Hz)	CD_2Cl_2; +20
5a	–	23.6	–	53.3	–	–	124.4; 127.6; 140.0; 153.3; 156.0	–	229.4	240.4	DMF-d_7; −25
6a	–	23.6	–	53.3	–	–	126.6; 128.5; 131.3; 139.0; 146.9, 153.4	–	229.0	240.4	DMF-d_7; −20
7b	–	26.0 [a]; 26.2 [b]; 34.4 [c]; 61.0 [d]	–	–	–	–	124.3; 127.4; 139.9; 153.4; 156.1	–	228.7	– [h]	DMF-d_7; 0
8b	–	25.9 [a]; 26.2 [b]; 34.5 [c]; 60.9 [d]	–	–	–	–	126.4; 128.3; 131.3; 138.8; 146.9; 153.5	–	228.2	239.8	DMF-d_7; 0
9a	–	22.9	30.8	52.5	57.1	–	–	150.7 ($^1J_{CN}$ = 14.0 Hz)	210.9 ($^1J_{WC}$ = 140.4 Hz)	235.2 ($^1J_{WC}$ = 203.9 Hz)	CD_2Cl_2; +20
9b	–	22.8	30.8	52.3	57.0	–	–	149.0 ($^1J_{CN}$ = 16.1 Hz)	210.0 ($^1J_{WC}$ = 139.7 Hz)	235.0 ($^1J_{WC}$ = 209.5 Hz)	CD_2Cl_2; +20

10a	–	23.0	31.0 [i]; 31.3	52.4	56.0; 56.9 [i]	–	–	156.4; 160.7 [i]	212.4 ($^1J_{WC}$ = 147.1 Hz)	235.5 ($^1J_{WC}$ = 209.4 Hz)	CD_2Cl_2; +20
11	–	22.8	–	52.6	–	90.9	–	–	227.3 ($^1J_{WC}$ = 189.7 Hz)	263.4 ($^1J_{WC}$ = 239.2 Hz)	CD_2Cl_2; +20
12	–	25.6 [a]; 26.2 [b]; 33.6 [c]; 60.9 [d]	–	–	–	91.0	–	–	227.5 ($^1J_{WC}$ = 187.2 Hz)	264.5 ($^1J_{WC}$ = 231.9 Hz)	CD_2Cl_2; +20
13	11.6	23.0	–	52.9	–	104.4	–	–	231.5	265.3	CD_2Cl_2; +20
14a	–	–	–	–	–	–	128.9; 130.0; 132.5; 134.5	–	208.9 ($^2J_{CP}$ = 9.4 Hz) 215.2 ($^2J_{CP}$ = 6.8 Hz)	–	CD_2Cl_2; −20
14b	7.5	26.0 [a]; 26.3 [b]; 33.5 [c]; 61.8 [d]	–	52.5	–	–	126.7–149.5	–	207.4; 212.2 (t, $^2J_{CP}$ = 4.9 Hz); 220.7	285.6 (t, $^2J_{CP}$ = 14.1 Hz)	CD_2Cl_2; 0
15a	–	28.5	–	53.3	59.4 [j]; 80.9 [j]	71.5 [j]; 82.0 [j]	–	–	–	267.9 ($^1J_{WC}$ = 267.3 Hz)	CD_2Cl_2; −20
15b	–	31.2	–	50.1	60.6 [j]; 84.3 [j]	71.4 [j]; 83.6 [j]	–	–	–	272.9	CD_2Cl_2; −10
16	–	22.9; 23.3	–	60.1	–	98.8	–	–	221.5 ($^1J_{WC}$ = 129.2 Hz)	310.0 ($^1J_{WC}$ = 205.6 Hz)	CD_2Cl_2; +20
17	–	25.1 [a]; 25.6 [b]; 25.7 [b]; 33.6 [c]; 66.7 [d]; 68.6 [d]	–	–	–	98.4	–	–	221.7 ($^1J_{WC}$ = 129.7 Hz)	310.6	CD_2Cl_2; −20
18	11.7	22.8 23.3	–	57.1	–	108.9	–	–	229.5 ($^1J_{WC}$ = 136.7 Hz)	306.2 ($^1J_{WC}$ = 210.6 Hz)	CD_2Cl_2; +20

[a,b,c,d] δ-, γ-, β- and α-carbon resonances of the cyclohexyl groups respectively.

[e,f,g] β-, γ- and α-carbon resonances of the γ-picoline ligand respectively.

[h] This carbon resonance was not observed.

[i] Resonance of the two mutually *trans*-oriented isocyanide ligands.

[j] The methyl and methylene carbon resonances of the DME ligand were assigned on the basis of the ^{1}H-coupled ^{13}C NMR spectra.

onances display satellites owing to coupling with the ^{183}W nucleus. The $^{1}J_{WC}$ coupling constants of **3a–4a** (172.1–173.4 Hz) are larger than those of **10a** (147.1 Hz), **9a** (140.4 Hz) and **1a** (127.0 Hz), giving additional evidence for a weakening of the metal–carbonyl back bonding in the series **3a–4a** > **10a** > **9a** > **1a**. The same relation is observed between the chemical shift of the metal-bound isocyanide carbon atoms and the metal–ligand back bonding as demonstrated by the NMR spectra of **9a**, **9b** and **10a**. This allows an equivocal assignment of the isocyanide carbon resonances of **10a** at $\delta = 156.4$ and 160.7 ppm (i.e. the metal-bound carbon atom of the isocyanide ligand, which is *trans* oriented to the weakest π acceptor ligand, is the most deshielded) (Table 3) [5a,5b,6,11f,g,23].

All aminocarbyne complexes are distinguished by a low field resonance for the carbyne–carbon at $\delta =$ 235.9–310.6 ppm. This resonance appears at higher field than that of analogous chromium compounds, as is expected on the basis of the Group 6 transition metal ^{13}C shielding trend [22]. Moreover, the carbyne–carbon resonance of the low valence tungsten aminocarbyne complexes **1a**, **1b** and **11–13** appears at a higher field than that of the high valence tungsten aminocarbyne complexes **15a**, **15b** and **16–18** respectively. The same trend has been previously observed for other Group 6 transition metal carbyne complexes [5a,5b,11e,12]. In addition, the carbyne carbon resonances of **1a–18** display tungsten satellites due to $^{13}C–^{183}W$ coupling. The $^{1}J_{WC}$ coupling constants of **11–13** and **16–18** are comparable with those of other low and high valence tungsten aminocarbyne complexes bearing a Cp ligand (e.g. $Cp^{*}(Br)_2(CO)W{\equiv}CNEt_2$, $^{1}J_{WC} = 206.3$ Hz; $Cp^{*}(CO)_2W{\equiv}CN(Et)CH_2SiMe_3$, $^{1}J_{WC} = 235.6$ Hz).

Additional structural information is given finally by the mass spectra (see Section 5) and by the ^{31}P NMR spectra of **14a** and **14b** revealing a singlet resonance at $\delta = 17.4$ and 157.1 ppm respectively. The ^{31}P signal of **14b** shows tungsten satellites, the $^{1}J_{PW}$ coupling constant being 341.8 Hz.

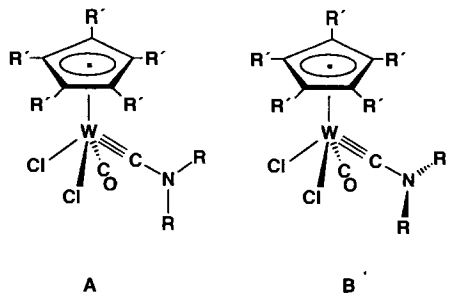


Fig. 2. Conformers **A** and **B** for the complexes $(\eta^5\text{-}C_5R'_5)(Cl)_2(CO)W{\equiv}CNR_2$ (**16–18**).

4. Conclusion

Convenient syntheses of a variety of Fischer-type aminocarbyne complexes of the type $X(CO)_2L_2W{\equiv}CNR_2$ (X = Cl or Br; L = CO, pic or ^{t}BuNC; L_2 = bpy or phen; R = ^{i}Pr or Cy) and $(\eta^5\text{-}C_5R'_5)(CO)_2W{\equiv}CNR_2$ (R' = H or Me; R = ^{i}Pr or Cy) have been developed starting from $W(CO)_6$. Reaction of $Br(CO)_2L_2W{\equiv}CNCy_2$ (L_2 = bpy or phen) with $K_2[cis\text{-}Mo(CO)_4(PPh_2)_2]$ and NEt_4Br affords the binuclear aminocarbyne complex $NEt_4[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNCy_2]$, indicating that the presence of a π donor substituent at the carbyne carbon atom prevents the nucleophile-induced carbyne–carbonyl coupling reaction, which is oftenly observed for Fischer-type carbyne complexes. Oxidation of Fischer-type aminocarbyne complexes with halogens is a very efficient method for the synthesis of Schrock-type aminocarbyne complexes, as demonstrated by the halogenation of the tetracarbonyl complexes *trans*-$X(CO)_4W{\equiv}CN^{i}Pr_2$ to give the 16-electron aminocarbyne complexes *mer*-$X_3(DME)W{\equiv}CN^{i}Pr_2$, or the reaction of $(\eta^5\text{-}C_5R'_5)(CO)_2W{\equiv}CNR_2$ with $PhICl_2$ to afford the 18-electron aminocarbyne complexes $(\eta^5\text{-}C_5R'_5)(Cl)_2(CO)W{\equiv}CNR_2$. In the latter compounds, competition of the carbyne and the CO ligand occurs for back bonding from the metal center, resulting in a restricted rotation of the amino group about the $C_{carbyne}–N$ bond, as evidenced by the variable-temperature ^{1}H NMR spectra. Studies are currently in progress to explore the reactions of these compounds, which combine reactivity patterns of both Fischer- and Schrock-type carbyne complexes, as demonstrated by their oxidation to give the 2-azoniavinylidene complexes $(\eta^5\text{-}C_5R'_5)(Cl)_4WCNR_2$ or their reduction to give aminocarbyne complexes of the type $(\eta^5\text{-}C_5R'_5)(CO)_nL_{2-n}W{\equiv}CNR_2$ (n = 0, 1; L = two-electron donor ligand).

5. Experimental details

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane, Et_2O, THF, DME and toluene over Na–benzophenone; CH_2Cl_2 over P_2O_5 and Na–Pb alloy), distilled under nitrogen and stored over 4 Å molecular sieves prior to use. All column chromatography was carried out in a thermostatted column of 20 cm length and 2.0 cm diameter. The stationary phases were silica (Merck; 0.063–0.2 mm) and silylated silica (Merck; 0.063–0.2 mm), which were degassed, dried in vacuo at room temperature and about 150 °C respectively and saturated with nitrogen.

Elemental analyses were performed by the Microanalytical Laboratory of the Inorganic Chemistry Depart-

ment of Technische Universität München and of Humboldt Universität Berlin. IR spectra were recorded on a Bruker IFS 25 and a Perkin Elmer 1650 FT spectrophotometer. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in dry deoxygenated methylene-d_2-chloride, acetone-d_6 and *N,N*-dimethylformamide-d_7 on a JEOL-GX 400 (**1a–3b**, **9a–11**, **13**, **15a–16** and **18**), JEOL-FX 90Q (**5a–8b**, **14a** and **14b**) or a Bruker AM-300 spectrometer (**4a**, **12** and **17**). Chemical shifts were referenced to residual solvent signals (methylene-d_2-chloride, δ_H = 5.32 ppm and δ_C = 53.8 ppm; acetone-d_6, δ_H = 2.04 ppm and δ_C = 29.8 ppm; *N,N*-dimethylformamide-d_7, δ_H = 2.74 ppm and δ_C = 30.1 ppm). The ^{31}P NMR spectra of **14a** and **14b** were recorded on a JEOL-FX 90Q spectrometer in CD_2Cl_2 at −20 °C and −30 °C respectively. The chemical shifts are referenced to 85% H_3PO_4 in water. Mass spectra were obtained with a Varian MAT 311A, a Varian MAT 90A or a HP 5995A spectrometer; *m/z* values are relative to the ^{184}W, ^{35}Cl and ^{79}Br isotopes. TG–MS analyses of **15a** and **15b** were performed by virtue of TG analysis thermobalance (Perkin–Elmer) and a QMG 420 mass spectrometer (Balzers), which were coupled by a capillary system heated to 280 °C. Samples of 1–4 mg mass were heated in a dynamic He atmosphere (purity, 5.0; flow, 45 standard cm^3 min^{-1}). A temperature programme was used between 50 and 700 °C with a heating rate of 10 K min^{-1}.

Oxalyl chloride, oxalyl bromide and γ-picoline were supplied from Aldrich and distilled before use. Tert-butyl isocyanide, NaCp and $PhICl_2$ were prepared according to published procedures [24–26]. KH was supplied from Aldrich, washed repeatedly with *n*-pentane and stored under argon. KCp^* was obtained from KH and C_5Me_5H [27]. *cis*-$Mo(CO)_4(PPh_2H)_2$ (**14a**) was obtained from *cis*-$Mo(CO)_4(HNC_5H_{10})_2$ and PPh_2H [28] following the procedure of Darensbourg and Kump [29].

5.1. *trans-Cl(CO)$_4$W≡CN^{i}Pr$_2$ (1a)*

To a suspension of 3.36 g (9.55 mmol) of $W(CO)_6$ in 70 ml of Et_2O was added dropwise at room temperature a solution of 1.33 g (12.42 mmol) of LiN^iPr_2 in 100 ml of Et_2O. The mixture was stirred for 2 h. Completion of the reaction was revealed by IR spectroscopy (replacement of the ν(CO) absorption of the starting material at 1980 cm^{-1} by the ν(CO) absorptions of $Li[(CO)_5WC(O)N^iPr_2]$ at 2048, 1946, 1914 and 1883 cm^{-1}). The resulting yellow suspension was evaporated to dryness, the oily residue washed once with a cold *n*-pentane–Et_2O mixture (5:1) (−30 °C) to remove traces of $W(CO)_6$ and excess LiN^iPr_2, frozen in liquid nitrogen, pulverized and then dried in vacuo at −20 °C. The resulting yellow powder of the metallate $Li[(CO)_5WC(O)N^iPr_2]$ was suspended in 50 ml of CH_2Cl_2 and treated at −30 °C with a solution of 0.82 ml (9.40 mmol) of $C_2O_2Cl_2$ in 20 ml of CH_2Cl_2. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h; the resulting brown suspension was evaporated to dryness at −20 °C. The residue was purified by column chromatography on silylated silica (15 × 3) at −10 °C. Elution with Et_2O gave a yellow fraction, which was evaporated to dryness. The residue was washed with small portions of Et_2O–*n*-pentane (1:5) to give complex **1a** as a yellow solid (yield, 2.12 g (50%)).

5.2. *trans-Br(CO)$_4$W≡CN^{i}Pr$_2$ (1b)*

A suspension of $Li[(CO)_5WC(O)N^iPr_2]$ in 50 ml of CH_2Cl_2, prepared as described above from 5.06 g (14.38 mmol) of $W(CO)_6$ and 1.61 g (15.03 mmol) of LiN^iPr_2, was treated at −30 °C with a solution of 1.35 ml (14.38 mmol) of $C_2O_2Br_2$ in 20 ml of CH_2Cl_2. The reaction mixture was then warmed to room temperature and stirred for 2 h; the resulting brown suspension was worked up as described for the synthesis of **1a** to afford complex **1b** as a yellow solid (yield, 4.21 g (60%)).

5.3. *Cl(CO)$_2$(pic)$_2$W≡CN^{i}Pr$_2$ (3a)*

380 mg (0.86 mmol) of **1a** were dissolved in 70 ml of cold CH_2Cl_2 (−40 °C) and the yellow solution treated with 0.18 ml (1.85 mmol) of γ-picoline. The mixture was then allowed to warm to room temperature and stirred for 10 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 2105, 2019 and 1981 cm^{-1} by the two ν(CO) absorptions of the product at 1944 and 1842 cm^{-1}). The resulting yellow solution was reduced in volume and a *n*-pentane–Et_2O (5:1) mixture added to precipitate complex **3a**. The supernatant pale-yellow solution was decanted off, the residue washed once with Et_2O and dried in vacuo at −20 °C to give a yellow solid (melting point (m.p.), 108 °C (decomposition); yield, 480 mg (98%)). Anal. Found: C, 43.62; H, 5.02; Cl, 6.22; N, 7.24; W, 32.28. $C_{21}H_{28}ClN_3O_2W$ (573.77) Calc.: C, 43.96; H, 4.92; Cl, 6.18; N, 7.32; W, 32.04%.

5.4. *Br(CO)$_2$(pic)$_2$W≡CN^{i}Pr$_2$ (3b)*

690 mg (1.41 mmol) of **1b** were dissolved in 30 ml of cold CH_2Cl_2 (−40 °C), and the orange solution treated with 0.35 ml (3.60 mmol) of γ-picoline. The mixture was then allowed to warm to room temperature and stirred for 12 h until the reaction was complete (IR monitoring). The resulting orange–yellow solution was worked up as described above for the synthesis of **3a** to give **3b** as a yellow solid (m.p., 98 °C (decomposition); yield: 860 mg (98%)). Anal. Found: C, 40.80; H, 4.57; Br, 13.09; N, 6.60; W, 22.26. $C_{21}H_{28}BrN_3O_2W$ (618.23) Calc.: C, 40.80; H, 4.56; Br, 12.92; N, 6.80; W, 29.74%.

5.5. $Cl(CO)_2(pic)_2W{\equiv}CNCy_2$ (4a)

A solution of 290 mg (0.55 mmol) of *trans*-$Cl(CO)_4W{\equiv}CNCy_2$ (**2a**) in 50 ml of CH_2Cl_2 was treated at −30 °C with 0.16 ml (1.64 mmol) of γ-picoline and the mixture warmed to room temperature and refluxed for 2 h. Completion of the reaction was confirmed by IR spectroscopy. The resulting yellow solution was worked up as described above for the synthesis of **3a** to give **4a** as a yellow solid (m.p., 166 °C (decomposition); yield: 325 mg (90%)). Anal. Found: C, 48.62; H, 5.54; Cl, 5.52; N, 6.27. $C_{27}H_{36}ClN_3O_2W$ (653.90) Calc.: C, 49.59; H, 5.55; Cl, 5.42; N, 6.43%.

5.6. $Cl(CO)_2(bpy)W{\equiv}CN^iPr_2$ (5a)

1.47 g (3.31 mmol) of **1a** were dissolved in 100 ml of cold CH_2Cl_2 (−30 °C), and the yellow solution treated with 560 mg (3.59 mmol) of bpy. The mixture was then allowed to warm to room temperature and stirred for 3 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 2105, 2019 and 1981 cm^{-1} by the two ν(CO) absorptions of the product at 1946 and 1848 cm^{-1}). The resulting purple solution was reduced in volume and Et_2O was added slowly to precipitate complex **5a**. The supernatant solution was decanted off and the residue washed once with Et_2O and dried in vacuo to give a purple microcrystalline solid (yield, 1.69 g (94%)). Anal. Found: C, 41.33; H, 4.07; N, 7.82. $C_{19}H_{22}ClN_3O_2W$ (543.70) Calc.: C, 41.97; H, 4.08; N, 7.73%.

5.7. $Cl(CO)_2(phen)W{\equiv}CN^iPr_2$ (6a)

A solution of 1.60 g (3.61 mmol) of **1a** in 100 ml of CH_2Cl_2 was treated at −30 °C with 650 mg (3.61 mmol) of phen and the mixture warmed to room temperature and stirred for 2h until the reaction was complete (IR monitoring). The resulting purple solution was worked up as described for the synthesis of **5a** to give **6a** as a deep purple solid (yield, 1.95 g (95%)). Anal. Found: C, 44.34; H, 3.85; N, 7.13. $C_{21}H_{22}ClN_3O_2W$ (567.72) Calc.: C, 44.43; H, 3.91; N, 7.40%.

5.8. $Br(CO)_2(bpy)W{\equiv}CNCy_2$ (7b)

Following the procedure used for the synthesis of **5a**, **7b** was obtained as a purple microcrystalline solid after treatment of 1.26 g (2.22 mmol) of *trans*-$Br(CO)_4W{\equiv}CNCy_2$ (**2b**) with 420 mg (2.69 mmol) of bpy in 50 ml of CH_2Cl_2 for 24 h (yield, 1.36 g (92%)). Anal. Found: C, 44.20; H, 4.63; N, 6.12. $C_{25}H_{30}BrN_3O_2W$ (668.29) Calc.: C, 44.93; H, 4.52; N, 6.29%.

5.9. $Br(CO)_2(phen)W{\equiv}CNCy_2$ (8b)

Following the procedure described above for the synthesis of **5a**, complex **8b** was obtained as a purple microcrystalline solid after treatment of 1.29 g (2.27 mmol) of *trans*-$Br(CO)_4W{\equiv}CNCy_2$ (**2b**) with 410 mg (2.28 mmol) of phen in 100 ml of CH_2Cl_2 for 19 h (yield, 1.51 g (96%)). Anal. Found: C, 46.47; H, 4.31; N, 5.73. $C_{27}H_{30}BrN_3O_2W$ (692.31) Calc.: C, 46.84; H, 4.37; N, 6.07%.

5.10. $Cl(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$ (9a)

640 mg (1.44 mmol) of **1a** were dissolved in 30 ml of cold CH_2Cl_2 (−40 °C) and the orange solution treated with 0.36 ml (3.18 mmol) of ^{t}BuNC. The reaction mixture was then allowed to warm to room temperature and stirred for 3 h during which evolution of gas was observed. Completion of the reaction was revealed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 2105, 2019 and 1981 cm^{-1} by the two absorptions of the product at 1978 and 1905 cm^{-1}). The resulting yellow solution was then evaporated to dryness and the residue purified by column chromatography on a silylated silica support at −20 °C. Elution with Et_2O–n-pentane (2 : 1) afforded a yellow fraction, from which **9a** was obtained as an intense-yellow microcrystalline solid after removal of the solvent in vacuo (m.p., 106 °C; yield, 720 mg (90%)). Anal. Found: C, 41.28; H, 5.94; Cl, 6.59; N, 7.60; W, 33.01. $C_{19}H_{32}ClN_3O_2W$ (553.78) Calc.: C, 41.21; H, 5.82; Cl, 6.40; N, 7.59; W, 33.20%. Electron impact (EI) MS (70 eV): m/z 553 (M^+), 525 ([M − CO]$^+$), 497 ([M − 2CO]$^+$), 441 ([M − 2CO − $Me_2C{=}CH_2$]$^+$), 385 ([M − 2CO − $2Me_2C{=}CH_2$]$^+$) (base peak), 342 ([M − 2CO − $2Me_2C{=}CH_2$ − ^{i}Pr]$^+$), 300 ([M − 2CO − $2Me_2C{=}CH_2$ − ^{i}Pr − Me(H)C=CH_2]$^+$).

5.11. $Br(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$ (9b)

370 mg (0.60 mmol) of **3b** were dissolved in 30 ml of CH_2Cl_2 and the orange solution treated at −40 °C with 0.16 ml (1.41 mmol) of ^{t}BuNC. The mixture was then allowed to warm to room temperature and stirred for 3h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1947 and 1845 cm^{-1} by the ν(CO) absorptions of the product at 1978 and 1907 cm^{-1}; presence of the $\nu(C_{carbyne}{\equiv}N)$ absorption of the product at 1539 cm^{-1} and the $\nu(C{\equiv}N)_{ring}$ absorption of uncoordinated γ-picoline at 1604 cm^{-1}). The resulting orange solution was worked up as described for the synthesis of **9a** to afford **9b** as a yellow microcrystalline solid (m.p., 83 °C; yield, 320 mg (89%)). Anal. Found: C, 38.30; H, 5.50; Br, 13.49; N, 7.04; W, 29.88.

$C_{19}H_{32}BrN_3O_2W$ (598.24) Calc.: C, 38.15; H, 5.39; Br, 13.36; N, 7.02; W, 30.73%. EI MS (70 eV): *m/z* 518 ($[M - Br]^+$) (base peak), 462 ($[M - Br - Me_2C{=}CH_2]^+$).

5.12. $Cl(CO)(^tBuNC)_3W{\equiv}CN^iPr_2$ (10a)

A solution of 170 mg (0.31 mmol) of **9a** in 30 ml of toluene was treated with 38 μl (0.34 mmol) of ^{t}BuNC and refluxed for 2 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the two ν(CO) absorptions of the starting material at 1981 and 1916 cm^{-1} by that of the product at 1889 cm^{-1}). The resulting orange solution was evaporated to dryness, the residue dissolved in Et_2O–CH_2Cl_2 (10 : 1) and the solution filtered over a short layer (1 × 1 cm) of neutral alumina. The filtrate was evaporated to dryness and the residue recrystallized from Et_2O–*n*-pentane to afford **10a** as a yellow microcrystalline solid (yield, 150 mg (80%)).

5.13. $Cp(CO)_2W{\equiv}CN^iPr_2$ (11)

A mixture of 380 mg (0.61 mmol) of **3b** and 76 mg (0.86 mmol) of NaCp was suspended in 40 ml of cold THF (−60 °C) and stirred for 3 h at −20 °C. Completion of the reaction was revealed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1947 and 1845 cm^{-1} by those of the product at 1942 and 1861 cm^{-1}; presence of the $\nu(C_{carbyne}\ddot{-}N)$ absorption of the product at 1554 cm^{-1} and the $\nu(C\ddot{-}N)_{ring}$ absorption of uncoordinated γ-picoline at 1604 cm^{-1}). The resulting yellow–brown slurry was then evaporated to dryness and the residue purified by column chromatography on a silica support at −20 °C. Traces of γ-picoline were first removed with *n*-pentane. Further elution with Et_2O–n-pentane (1 : 5) afforded a yellow fraction, from which **11** was obtained as an intense-yellow microcrystalline solid after removal of the solvent in vacuo (m.p., 64 °C; yield, 200 mg (78%)). Anal. Found: C, 40.23; H, 4.61; N, 3.24; W, 43.85. $C_{14}H_{19}NO_2W$ (417.16) Calc.: C, 40.31; H, 4.59; N, 3.36; W, 44.07%. EI MS (70 eV): *m/z* 417 (M^+), 374 ($[M - {}^iPr]^+$), 346 ($[M - {}^iPr - CO]^+$) (base peak), 332 ($[M - {}^iPr - Me(H)C{=}CH_2]^+$), 304 ($[M - {}^iPr - Me(H)C{=}CH_2 - CO]^+$), 276 ($[M - {}^iPr - Me(H)C{=}CH_2 - 2CO]^+$), 249 ($[M - {}^iPr - Me(H)C{=}CH_2 - 2CO - HCN]^+$).

5.14. $Cp(CO)_2W{\equiv}CNCy_2$ (12)

A mixture of 240 mg (0.37 mmol) of **4a** and 37 mg (0.42 mmol) of NaCp was suspended in 50 ml of cold THF (−60 °C), the suspension warmed to −20 °C and stirred for 2h. Completion of the reaction was revealed by IR spectroscopy. The resulting yellow–brown suspension was worked up as described above for the synthesis of **11** to afford **12** as a yellow microcrystalline solid (m.p., 139 °C; yield, 140 mg (77%)). Anal. Found: C, 47.65; H, 5.65; N, 2.81. $C_{20}H_{27}NO_2W$ (497.29) Calc.: C, 48.31; H, 5.47; N, 2.82%. EI MS (70 eV): *m/z* 497 (M^+), 415 ($[M - c\text{-}C_6H_{10}]^+$), 414 ($[M - Cy]^+$), 387 ($[M - c\text{-}C_6H_{10} - CO]^+$), 332 ($[M - c\text{-}C_6H_{10} - Cy]^+$), 304 ($[M - c\text{-}C_6H_{10} - Cy - CO]^+$), 276 ($[M - c\text{-}C_6H_{10} - Cy - 2CO]^+$), 249 ($[M - c\text{-}C_6H_{10} - Cy - 2CO - HCN]^+$).

5.15. $Cp^*(CO)_2W{\equiv}CN^iPr_2$ (13)

A mixture of 380 mg (0.61 mmol) of **3b** and 140 mg (0.80 mmol) of KCp^* was suspended in 50 ml of cold THF (−60 °C) and stirred for 2 h at −20 °C. The resulting yellow–brown suspension was worked up as described above for the synthesis of **11** to afford **13** as an intense-yellow microcrystalline solid (m.p., 113 °C; yield, 225 mg (75%)). Anal. Found: C, 47.02; H, 6.19; N, 2.89. $C_{19}H_{29}NO_2W$ (487.29) Calc.: C, 46.83; H, 6.00; N, 2.87%. EI MS (70 eV): *m/z* 487 (M^+), 444 ($[M - {}^iPr]^+$), 429 ($[M - 2CO]^+$) (base peak), 386 ($[M - 2CO - {}^iPr)]^+$).

5.16. $NEt_4[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNCy_2]$ (14b)

To a purple suspension of 850 mg (1.23 mmol) of **8b** in 50 ml of THF was added dropwise at −70 °C an orange solution of 1.90 mmol of $K_2[cis\text{-}Mo(CO)_4(PPh_2)_2]$ in 50 ml of THF, prepared from *cis*-$(CO)_4Mo(PPh_2H)_2$ (**14a**) and KH. The reaction mixture was then warmed to room temperature and stirred for 1.5 h, during which the colour of the solution changed to brown–yellow and precipitation of KBr was observed. The solvent was stripped off in vacuo, the residue washed once with a CH_2Cl_2–Et_2O mixture (1 : 1) and the yellow insoluble solid, containing $K[(CO)_4Mo(\mu\text{-}PPh_2)_2W(CO)_2CNCy_2]$ dried in vacuo. This was then suspended in 100 ml of CH_2Cl_2 and 1.57 g (7.47 mmol) of $[NEt_4]Br$ were added. The resulting cloudy solution was filtered through a filter canula to remove KBr and the filtrate evaporated to dryness. The residue was taken up in THF and the solution freed from insoluble $[NEt_4]Br$ by filtration through a filter canula. The resulting brown–yellow filtrate was concentrated in vacuo and Et_2O slowly added to precipitate **14b** as a yellow solid (yield, 630 mg (45%)). Found: C, 53.70; H, 5.41; Mo, 8.17; N, 2.49; O, 8.48; P, 5.05; W, 15.60. $C_{51}H_{62}MoN_2O_6P_2W$ (1140.80) Calc.: C, 53.70; H, 5.48; Mo, 8.41; N, 2.46; O, 8.41; P, 5.43; W, 16.12%.

5.17. $mer\text{-}Cl_3(DME)W{\equiv}CN^iPr_2$ (15a)

A solution of 290 mg (0.65 mmol) of **1a** in 30 ml of DME was treated at −78 °C with 180 mg (0.65 mmol)

of $PhICl_2$, warmed to room temperature and stirred for 3 h. Evolution of gas and a colour change from bright orange to red to dark green was observed. The resulting solution was evaporated to dryness, the residue dissolved in a CH_2Cl_2–Et_2O mixture (1:5) and cold *n*-pentane (−40 °C) added to bring about precipitation of **15a** as a green solid (m.p., 95 °C (decomposition, extrapolated onset); yield, 270 mg (84%)). Anal. Found: C, 27.20; H, 4.84; Cl, 20.06; N, 3.00; W, 37.70. $C_{11}H_{24}Cl_3NO_2W$ (492.53) Calc.: C, 26.83; H, 4.91; Cl, 21.59; N, 2.84; W, 37.33%.

5.18. *mer-Br$_3$(DME)W≡CN^{i}Pr$_2$* (**15b**)

A solution of 840 mg (1.72 mmol) of **1b** in 50 ml of DME was treated at −78 °C with 88 μl (1.71 mmol) of Br_2, warmed to room temperature and stirred for 4 h during which evolution of gas and a colour change from bright orange to red to dark green was observed. The resulting solution was worked up as described in the synthesis for **15a** to afford **15b** as a green microcrystalline solid (m.p., 93 °C (decomposition, extrapolated onset); yield, 880 mg (82%)). Anal. Found: C, 20.90; H, 3.81; Br, 37.97; N, 2.36; W, 29.70. $C_{11}H_{24}Br_3NO_2W$ (625.88) Calc.: C, 21.11; H, 3.87; Br, 38.30; N, 2.24; W, 29.37%.

5.19. *Cp(CO)(Cl)$_2$W≡CN^{i}Pr$_2$* (**16**)

A solution of 400 mg (0.96 mmol) of **11** in 30 ml of CH_2Cl_2 was treated at −78 °C with 264 mg (0.96 mmol) of $PhICl_2$, warmed to room temperature and stirred for 0.5 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the two ν(CO) absorptions of the starting material at 1939 and 1851 cm^{-1} by that of the product at 2014 cm^{-1}). The resulting purple solution was concentrated in vacuo and an Et_2O–*n*-pentane (1:1) mixture added to precipitate **16**. The supernatant slightly reddish solution was decanted off and the residue dried in vacuo to give a purple solid (m.p., 133 °C (decomposition); yield, 420 mg (95%)). Anal. Found: C, 33.77; H, 4.60; Cl, 15.78; N, 3.13; W, 39.81. $C_{13}H_{19}Cl_2NOW$ (460.06) calc.: C, 33.94; H, 4.16; Cl, 15.41; N, 3.04; W, 39.96%. EI MS (70 eV): *m/z* 431 ($[M - CO]^+$), 388 ($[M - CO - {}^iPr]^+$), 346 ($[M - CO - {}^iPr - Me(H)C{=}CH_2]^+$), 319 ($[M - CO - {}^iPr - Me(H)C{=}CH_2 - HCN]^+$) (base peak), 293 ($[M - CO - {}^iPr - Me(H)C{=}CH_2 - HCN - C_2H_2]^+$).

5.20. *Cp(CO)(Cl)$_2$W≡CNCy$_2$* (**17**)

A solution of 90 mg (0.18 mmol) of **12** in 15 ml of CH_2Cl_2 was treated at −78 °C with 49 mg (0.18 mmol) of $PhICl_2$, warmed to room temperature and stirred for 1 h. The resulting purple solution was worked up as described above for the synthesis of **16** to give **17** as a purple solid (m.p., 155 °C (decomposition); yield, 90 mg (92%)). Anal. Found: C, 41.97; H, 5.24; N, 2.63. $C_{19}H_{27}Cl_2NOW$ (540.18) Calc.: C, 42.25; H, 5.04; N, 2.59%. EI MS (70 eV): *m/z* 511 ($[M - CO]^+$), 428 ($[M - CO - Cy]^+$), 393 ($[M - CO - Cy - Cl]^+$), 346 ($[M - CO - Cy - c\text{-}C_6H_{10}]^+$), 319 ($[M - CO - Cy - c\text{-}C_6H_{10} - HCN]^+$), 311 ($[M - CO - Cy - c\text{-}C_6H_{10} - Cl]^+$), 284 ($[M - CO - Cy - c\text{-}C_6H_{10} - HCN - Cl]^+$).

5.21. *Cp*(CO)(Cl)$_2$W≡CN^{i}Pr$_2$* (**18**)

A solution of 150 mg (0.31 mmol) of **13** in 20 ml of CH_2Cl_2 was treated at −78 °C with 85 mg (0.31 mmol) of $PhICl_2$, warmed to room temperature and stirred for 2 h until the reaction was complete (IR monitoring). The resulting purple solution was worked up as described for the synthesis of **16** to afford **18** as a purple microcrystalline solid (m.p., 185 °C (decomposition); yield, 160 mg (98%)). Anal. Found: C, 40.73; H, 5.11; N, 3.00. $C_{18}H_{29}Cl_2NOW$ (530.19) Calc.: C, 40.78; H, 5.51; N, 2.64%. CI MS (isobutene gas): *m/z* 501 ($[M - CO]^+$) (base peak), 458 ($[M - CO - {}^iPr]^+$).

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