

Synthesis and reactivity of air-stable isolable anionic Group 6 molybdenum and tungsten carbene complexes with a metal-centred negative charge

Fergus J. Lalor*, S.A. O'Neill

Department of Chemistry, University College, Cork, Ireland

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Abstract

The first air-stable anionic carbene complexes with a metal-centred negative charge $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**3a**, $\text{M} = \text{Mo}$; **3b**, $\text{M} = \text{W}$), $[\text{Tp}^{\text{Me}_2,4\text{Cl}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**4**), $[\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**5**) and $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})\text{R}]^-$ (**11a–d**, $\text{R} =$ substituted alkyl) have been synthesised by addition of cyanide anion to the corresponding chlorocarbyne complexes **1**, **6**, **7** or to the alkylcarbyne complexes **9a–d**. Carbene complexes **3** and **11** are stereochemically rigid with the plane of the carbene ligand coinciding with the molecular mirror plane. The electron-rich carbene carbons in these complexes show some of the most highly shielded values of $\delta\text{C}_{\text{carbene}}$ so far observed. The dicyanocarbene complexes (**3**) did not give stable products with electrophiles but the cyano(alkyl)carbene complexes (**11b–d**) could be doubly alkylated at the CN nitrogen to give the cationic dialkylaminoalkyne complexes $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\{\eta^2(\text{C},\text{C})\text{Me}_2\text{N}-\text{C}\equiv\text{C}-\text{R}\}]^+$ (**12**). Complex **11a** ($\text{R} = \text{C}(\text{CN})_2\text{CH}_3$) eliminates $[\text{CH}_3\text{C}(\text{CN})_2]^-$ in the presence of MeI and yields purple $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{CN}$ (**2a**), the first example of a cyanocarbyne complex and a presumed intermediate in the formation of **3a**.

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1. Introduction

The literature contains relatively few reports of anionic carbene complexes with a metal-centred negative charge, (**A**) (Scheme 1) [1]. Complexes of type **A** are not to be confused with the anionic carbene complexes which are formally generated by removal of a proton from a carbon atom or heteroatom α - to the carbene carbon (**B**) (Scheme 1). In carbene complexes of type **B** the resonance form which localises the negative charge on the metal atom has a metal–carbon single bond whereas in complexes of type **A** a metal–carbon double bond is present. All reported complexes of type **A** are air-sensitive and only four are stable enough to have been isolated [1m–p]. In this communication we present the first description of the synthesis, characterisation

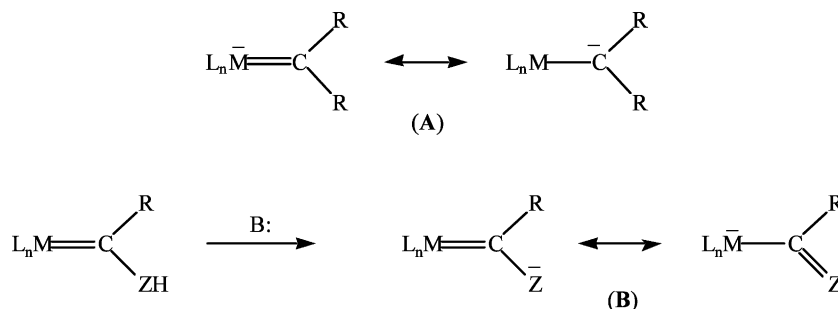
and some reactions of air-stable anionic carbene complexes of type **A**. In the discussion that follows the term ‘anionic carbene complex’ should be understood as referring to type **A** complexes only.

2. Results and discussion

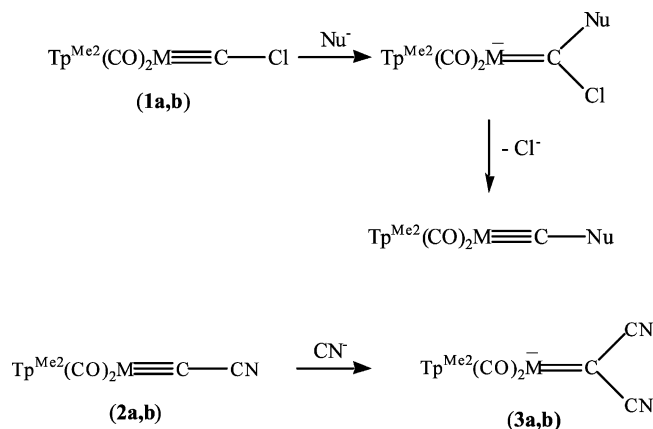
There are few general methods for the synthesis of complexes containing functionalised carbyne ligands. One such route begins with the η^1 -chlorocarbyne complexes $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{Cl}$ (**1a**, $\text{M} = \text{Mo}$; **1b**, $\text{M} = \text{W}$, $\text{Tp}^{\text{Me}_2} =$ hydrotris[3,5-dimethylpyrazol-1-yl]borate) which were first synthesised in these laboratories [2]. We have found that nucleophile-induced addition–elimination at the carbyne carbon of **1** (Scheme 2) offers a versatile synthetic methodology for the preparation of new functionalised carbyne complexes and related species [3]—a discovery that has subsequently been

* Corresponding author. Tel.: +353-21-4902-317; fax: +353-21-4274-097.

E-mail address: f.lalor@ucc.ie (F.J. Lalor).



Scheme 1.



Scheme 2.

confirmed by others, most notably by Templeton and co-workers [4].

In an attempt to synthesise complexes containing the previously unknown cyanocarbene ligand, the chlorocarbene complexes $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{Cl}$ (**1a,b**) were treated with KCN in a $\text{CH}_2\text{Cl}_2-\text{H}_2\text{O}$ phase-transfer system using $[(n-\text{C}_4\text{H}_9)_4\text{N}]\text{Br}$ as the catalyst—conditions which we had previously found to be successful for the reactions of **1a** with sulphur nucleophiles [3a]. No reaction was observed. However treatment of the molybdenum complex **1a** with an equimolar quantity of KCN in dimethylsulphoxide (dmsO) at room temperature resulted in 50% conversion of **1a** to a new green dicarbonyl material, $\nu(\text{CO})$ (CH_2Cl_2) 1894, 1774 cm^{-1} , with the remaining 50% of **1a** being recovered. The optimum yield of the green product—70–80%—was obtained with slightly less than a 2:1 ratio of KCN to **1a**. Under these conditions ca. 20–30% unreacted **1a** was recovered. In the presence of a still greater excess of KCN further reaction led to the formation a paramagnetic anionic species which has been characterised fully and which will be described in a later communication.

Work-up of the **1a**/KCN/dmsO reaction mixture revealed that the product was not the anticipated cyanocarbene complex $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{CN}$ (**2a**) but an anionic species. This suggested that the chlorocarbene complex **1a** was reacting with two equivalents of cyanide anion to form the anionic dicyanocarbene

complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**). The anion **3a** formed green crystalline air-stable salts with a range of organic cations. The $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ and $[(n-\text{C}_4\text{H}_9)_4\text{N}]^+$ salts are described here. The $[(n-\text{C}_4\text{H}_9)_4\text{N}]^+$ salt was particularly useful because its improved solubility properties aided spectroscopic and reactivity studies. Both salts gave microanalytical data in agreement with the proposed formulation. We suggest that the formation of the anionic dicyanocarbene complex **3a** from chlorocarbene **1a** under these conditions proceeds via an initial addition-elimination process to give the cyanocarbene complex **2a** which then reacts with another equivalent of cyanide to yield the observed product (Scheme 2). The proposed intermediate cyanocarbene complex $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{CN}$ (**2a**) is not observed even when the chlorocarbene complex **1a** is present in considerable excess. Evidently complex **2a** is considerably more reactive towards cyanide anion than is the chlorocarbene complex **1a**. Cyanocarbene complex **2a** prepared by an indirect route (see below) gave an excellent yield of the dicyanocarbene complex **3a** when treated with KCN in dmsO.

The reaction of $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}\equiv\text{C}-\text{Cl}$ (**1b**) with cyanide anion in dmsO to give the $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ and $[(n-\text{C}_4\text{H}_9)_4\text{N}]^+$ salts of $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ (**3b**) proceeded more slowly and gave a lower yield of the dicyanocarbene complex **3b** than its Mo analogue, 45–52 versus 70–80%. In addition, as well as formation of the dicyanocarbene complex **3b**, another dicarbonyl material, $\nu(\text{CO})$ (CH_2Cl_2) 1925, 1830 cm^{-1} , was produced in trace quantities. The solubility of this material was very similar to that of the anionic tungsten carbene complex **3b** so it that it was only removed from the latter with difficulty. We were unable to isolate a sufficient quantity of the unknown complex for characterisation.

We also prepared two other anionic molybdenum dicyanocarbene complexes, $[\text{Tp}^{\text{Me}_2,4\text{Cl}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**4**) and $[\text{Tp}^{i-\text{Pr},4\text{Br}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**5**), from the analogous chlorocarbene complexes $\text{Tp}^{\text{Me}_2,4\text{Cl}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**6**) and $\text{Tp}^{i-\text{Pr},4\text{Br}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**7**). ($\text{Tp}^{\text{Me}_2,4\text{Cl}}$ = hydrotris(3,5-dimethyl-4-chloropyrazol-1-yl)borate; $\text{Tp}^{i-\text{Pr},4\text{Br}}$ = hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borate—the symbols employed for the pyrazolylborate ligands in complexes **1–7** and

elsewhere follow the system recommended by Trofimenko [5]). These syntheses were more awkward than those of the Tp^{Me_2} analogues **3a,b**. As mentioned above, reaction of $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**1a**) with more than two equivalents of cyanide anion leads to the formation of an anionic paramagnetic material. Contamination of complexes **3a,b** by the paramagnetic complexes can be avoided by using slightly less than two equivalents of KCN in the preparation. Analogous anionic paramagnetic materials were also encountered in the preparation of the anionic dicyanocarbene complexes **4** and **5** in dmsO—but now they are formed even if an excess of KCN is carefully avoided and the pure dicyanocarbene complexes cannot be isolated satisfactorily from the mixture. The increased reactivity of the dicyanocarbene complexes $[\text{Tp}^{\text{Me}_2,4\text{Cl}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**4**) and $[\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**5**) towards reaction with $[\text{CN}]^-$ vis-à-vis **3a,b** presumably reflects the greater electron-withdrawing character of the halogenated pyrazolylborate ligands $\text{Tp}^{\text{Me}_2,4\text{Cl}}$ and $\text{Tp}^{i\text{-Pr},4\text{Br}}$ compared to Tp^{Me_2} —indicated by the fact that $\nu(\text{CO})_{\text{av}}$ values for complexes **4** and **5** are ca. 8–13 cm^{-1} higher than for $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**). Employing a dmsO– CH_2Cl_2 mixed solvent system in which KCN is less soluble reduced contamination by paramagnetic by-products but at the expense of low yields of the products. Over-reaction of the dicyanocarbene complexes with cyanide does not appear to occur as readily in *N,N*-dimethylformamide (dmf) as it does in dmsO. Reaction of the chlorocarbyne complexes **6** and **7** with 1.6–1.8 equivalents of KCN in dmf—in the presence of a little CH_2Cl_2 to increase the solubility of the chlorocarbyne complexes and repress the solubility of KCN—yielded the dicyanocarbene complexes **4** and **5** free of the anionic paramagnetic contaminants. Complexes **4** and **5** were isolated as their $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salts in 79 and 36% yields, respectively, with the appropriate quantities of unreacted chlorocarbyne complexes **6** and **7** being recovered in both cases.

The reaction of $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**1a**) with $[\text{CN}]^-$ was also investigated using a variety of other reaction conditions. Complex **1a** did not react with KCN under phase transfer conditions using 50 equivalents of KCN in $\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$ at room temperature, in $\text{C}_6\text{H}_6\text{-H}_2\text{O}$ at 70 °C or in toluene– H_2O at 100 °C with $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{Br}$ as the phase transfer catalyst. No reaction took place between complex **1a** and an excess of KCN in refluxing aqueous thf. In refluxing aqueous ethanol an inseparable mixture of the anionic dicyanocarbene complex **3a** and the paramagnetic anionic contaminant was formed. Reaction of the chlorocarbyne complex **1a** and two equivalents of $[(\text{C}_2\text{H}_5)_4\text{N}]\text{CN}$ in dry refluxing tetrahydrofuran (thf) produced the dicyanocarbene complex **3a** in 72% yield at a rate similar to the preparation in dmsO. The $[(\text{C}_2\text{H}_5)_4\text{N}]^+$ salt of **3a** is insoluble in THF and so precipitates out as it is

being formed—thus avoiding over-reaction with cyanide anion.

Prior to the synthesis of compounds **3a,b**, **4** and **5** there had been no reports of complexes containing a terminal dicyanocarbene ligand and only a few reports of complexes containing terminal monocyanocarbene ligands [6]. In the two cases which are closest to the present chemistry [6a,b], neutral monocyanocarbene complexes are formed by nucleophilic attack of cyanide anion on the cationic carbyne complexes $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}\equiv\text{C}-\text{C}_6\text{H}_5]^+$ ($\text{M} = \text{Mn}, \text{Re}$) and $[(\text{CO})_5\text{-Cr}\equiv\text{C}-\text{NMe}_2]^+$. We are not aware of any report of successful monocyanocarbene formation by addition of cyanide anion to neutral carbyne complexes. Equally significant is the fact that complexes **3a,b**, **4** and **5** are among the very few reported anionic transition metal carbene complexes in which the negative charge is metal-centred, i.e. they can be considered as formal derivatives of the $\text{M}(0)$ tricarbonyl anions $[\text{Tp}^{\text{Me}_2}\text{Mo}(\text{CO})_3]^-$ ($\text{M} = \text{Mo}, \text{W}$) in which a $[:\text{C}(\text{CN})_2]$ ligand has replaced a CO ligand. This class of compounds is quite distinct from anionic carbene complexes formed by deprotonation of a carbene substituent, e.g. $[(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Mn}=\text{C}(\text{OEt})\text{CHMe}]^-$ which is formed when $(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Mn}=\text{C}(\text{OEt})\text{CH}_2\text{Me}$ is treated with *n*-BuLi [7].

Coincidentally or otherwise, almost all of the other known carbene complexes with a metal-centred negative charge are derivatives of the Group 6 metals. Up to the time of this communication only four anionic carbene complexes had been isolated—the Cr(–II) complex $[(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Ph}]^{-2}$ by Lee and Cooper [1m], the Mo(VI) complex $[(\text{Mo}(\text{=CHCMe}_2\text{Ph})(\text{NAd})\{\text{OCH}(\text{CF}_3)_2\}_3)]^-$ (Ad = 1-adamantyl) by Schrock and co-workers [1n] and the $\text{M}(0)$ complexes $[(\eta\text{-C}_5\text{Me}_5)\text{Mo}(\text{=CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)]^-$ and $[(\eta\text{-C}_5\text{Me}_5)\text{W}(\text{=CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)]^-$ by Legzdins and Sayers [1o,p]. These complexes are all air-sensitive. A series of anionic Mo(0) carbene complexes of the general type $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{M}=\text{CRR}^1]^-$ ($\text{M} = \text{Mo}, \text{W}$) has been described by Winter and co-workers [1b–k] and, more recently, Templeton and co-workers have reported the preparation of the prototypical anionic W(0) methylene complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{CH}_2]^-$ [1q]. Winter's complexes—and, even more so, Templeton's methylene complex—are closely related to our anionic $\text{M}(0)$ dicyanocarbene complexes **3a,b**, **4** and **5**. Neither Winter's carbene complexes nor Templeton's methylene complex have been isolated and they have been identified on the basis of spectroscopic data and/or derivative formation. Wang and Angelici [11] have reported an anionic carbene complex of rhenium but this too was not observed directly and its presence was inferred by derivative formation. An anionic lutetium carbene complex $[\text{Lu}(\text{=CHSiMe}_3)(\text{CH}_2\text{SiMe}_3)_3]^-$ has been claimed by Schumann and Muller [1a] but only $^1\text{H-NMR}$ data has been reported. The stability of dicyano-

carbene complexes **3a,b**, **4** and **5** presents us with a unique opportunity to investigate the chemistry of this relatively rare class of carbene complex.

The carbonyl and cyanide stretching-frequencies of the new carbene complexes **3a,b**, **4** and **5** are summarised in Table 1. For $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**1a**) $\nu(\text{CO})_{\text{av}}$ is 110 cm^{-1} higher than the 1726 cm^{-1} recorded for the related anionic Mo(0) carbene complex $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}=\text{C}(\text{CH}_2)_3\text{NMe}]^-$ [**1b**] (Fig. 1). Similarly $\nu(\text{CO})_{\text{av}}$ for $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ (**3b**) is 35 cm^{-1} higher than that found for $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{W}=\text{CH}(\text{C}_6\text{H}_5)]^-$ (1781 cm^{-1}) (Fig. 1) [**1d**] and 66 cm^{-1} higher than that observed for $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{CH}_2]^-$ (1750 cm^{-1}) [**1q**]. We conclude that the dicyanocarbene ligands in complexes **3a,b**, **4** and **5** are much stronger π -acceptors than the more conventional carbene ligands in the complexes described by Winter and Templeton. Indeed, since the pyrazolylborate ligands in **3a,b** are stronger electron donors than the cyclopentadienide ligand [8] it is likely that the comparison of $\nu(\text{CO})_{\text{av}}$ with Winter's complexes underestimates the electron withdrawing effect of the dicyanocarbene ligands. We may also conclude from these results that the carbene ligands in our complexes are electron-rich primarily due to the inductive and resonance anion-stabilising effects of the cyano-substituents (Scheme 3) rather than to their anionic character per se. Comparison of the $\nu(\text{CO})_{\text{av}}$ data for complexes **3a,b** with those for $[n\text{-Pr}_4][\text{Tp}^{\text{Me}_2}\text{Mo}(\text{CO})_3]^-$ (1816 cm^{-1}), $[n\text{-Pr}_4][\text{Tp}^{\text{Me}_2}\text{W}(\text{CO})_3]^-$ (1805 cm^{-1}) [9] and $[\text{Et}_4\text{N}][\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}=\text{C}(\text{CN})_2]^-$ (1897 cm^{-1}) [10] shows that the dicyanocarbene ligand is a stronger net π -acceptor than CO but significantly weaker than the homologous dicyanovinylidene, $[\text{C}=\text{C}(\text{CN})_2]$.

A strong absorption at 2142 cm^{-1} in the IR spectrum of dicyanocarbene complex **3a** was assigned to $\nu(\text{C}\equiv\text{N})$ with the aid of the ^{13}C -labelled analogue, $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})_2]^-$ prepared from K^{13}CN . We observed an isotopic shift of 47 cm^{-1} in $\nu(\text{CN})$, the theoretical shift is 45 cm^{-1} . (A very weak band at 2080 cm^{-1} is simultaneously shifted to 2055 cm^{-1} and is thus also associated with the $[\text{C}(\text{CN})_2]$ ligand.) Nitriles typically show weak absorptions in the region of $2260\text{--}2200\text{ cm}^{-1}$ but conjugation both increases the

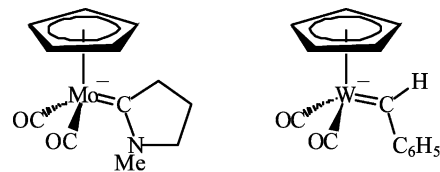


Fig. 1.

strength of the $\nu(\text{CN})$ band and shifts it to lower wavenumber [11]. The strength and position of $\nu(\text{CN})$ in complex **3a** and its analogues is strong evidence for significant delocalisation of electron-density into the carbene cyano-substituents.

The ^1H -NMR spectra of the new dicyanocarbene complexes (Table 2) showed few unexpected features. The resonances of the pyrazolyl H(4) protons are observed as two peaks of relative intensity 1:2 indicating that the anion has effective mirror symmetry in solution. Compared to CO the dicyanocarbene ligand has a deshielding effect on the H(4) protons of the *trans*-pyrazolyl group. In the hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borato chlorocarbene complex $\text{Tp}^{i\text{-Pr,4Br}}(\text{CO})_2\text{M}\equiv\text{C}-\text{Cl}$ (**7**) the isopropyl methyl groups of the pyrazolylborate ligand appear as a pair of doublets at δ 1.39 and 1.33 ppm integrating for 6 and 12 hydrogens, respectively, (Section 4) as anticipated for a molecule with a mirror plane of symmetry. In the dicyanocarbene complex $[\text{Tp}^{i\text{-Pr,4Br}}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**5**) the methyl groups of the isopropyl group lying on the mirror plane (Fig. 2) give rise to a 6H doublet at δ 1.34 ppm. However the methyl groups of the isopropyl substituents flanking the mirror plane are no longer equivalent and are observed as a pair of 6H doublets at 1.31 and 0.81 ppm, respectively. Evidently steric interaction with the more bulky dicyanocarbene ligand in complex **5** prevents free rotation of these isopropyl groups about the $\text{C}_{\text{pyrazole}}-\text{CHMe}_2$ bond axis.

The ^{13}C -NMR spectra of the dicyanocarbene complexes $[\text{L}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**3a**, $\text{L} = \text{Tp}^{\text{Me}_2}$, $\text{M} = \text{Mo}$; **3b**, $\text{L} = \text{Tp}^{\text{Me}_2}$, $\text{M} = \text{W}$; **4**, $\text{L} = \text{Tp}^{\text{Me}_2,4\text{Cl}}$, $\text{M} = \text{Mo}$; **5**, $\text{L} = \text{Tp}^{i\text{-Pr,4Br}}$, $\text{M} = \text{Mo}$) are summarised in Table 3. For carbene complexes $\delta\text{C}_{\text{carbyne}}$ is normally observed in the range 200–400 ppm [12]. For four of the five anionic carbene complexes for which ^{13}C -NMR data is available,



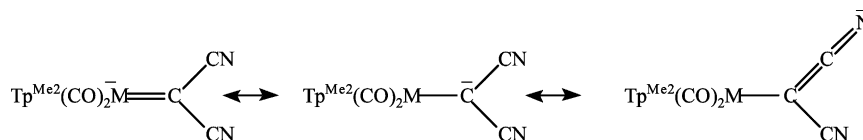
Table 1

IR data ^a for anionic dicyanocarbene complexes of the type $[\text{L}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**3–5**)

No.	L	Metal	$\nu(\text{CN})\text{ cm}^{-1}$	$\nu(\text{CO})\text{ cm}^{-1}$	$\nu(\text{CO})_{\text{av}}\text{ cm}^{-1}$
3a	Tp^{Me_2}	Mo	2142(s), 2080(vw) ^b	1895(vs), 1777(vs)	1836
3b	Tp^{Me_2}	W	2147(s), 2098(vw)	1879(vs), 1753(vs)	1816
4	$\text{Tp}^{\text{Me}_2,4\text{Cl}}$	Mo	2148(s), 2081(vw)	1902(vs), 1786(vs)	1844
5	$\text{Tp}^{i\text{-Pr,4Br}}$	Mo	2149(s), 2083(vw)	1906(vs), 1792(vs)	1849

^a All spectra were recorded using solutions of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salts in CH_2Cl_2

^b These bands appear at 2095(s), 2055(vw) in ^{13}C -labelled **1a** $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})_2]^-$.



Scheme 3.

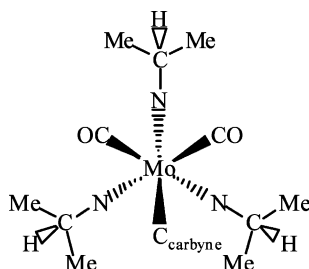


Fig. 2.

(Ad = 1-adamantyl) [1n], $[\text{Mo}(=\text{CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta\text{-C}_5\text{H}_5)]^-$, $[\text{W}(=\text{CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta\text{-C}_5\text{H}_5)]^-$ [1o,p] and $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ [1q] $\delta_{\text{C}_{\text{carbyne}}}$ occurs at 297.9, 257, 223.1 and 265 ppm, respectively. In contrast the carbene carbon resonances of Mo complexes **3a**, **4** and **5** are between 63 and 70 ppm more shielded than that in $[\text{Mo}(=\text{CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta\text{-C}_5\text{H}_5)]^-$, the most shielded of the former molybdenum complexes. The carbene carbon in

the anionic tungsten carbene complex **3b** is 55 ppm more shielded than the corresponding carbon in $[\text{W}(=\text{CHSiMe}_3)(\text{NO})(\text{CH}_2\text{SiMe}_3)(\eta\text{-C}_5\text{H}_5)]^-$ and at 167.8 ppm is probably the most high-field $\delta_{\text{C}_{\text{carbyne}}}$ so far recorded. Only the dianionic Cr(–II) complex $[(\text{CO})_5\text{Cr}=\text{C}(\text{OMe})\text{Ph}]^{2-}$, $\delta_{\text{C}_{\text{carbyne}}} = 171.7$ ppm, [1m] shows a similarly high-field carbyne resonance. The assignment of the carbene carbon resonance in complexes **3a**, **b**, **4** and **5** was confirmed by the preparation of ^{13}C -labelled **3a** $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})_2]^-$ for which the resonance at 187.2 ppm is split into a doublet of doublets ($J = 60.5$ and 70.2 Hz) by coupling to the two inequivalent (see below) cyano substituents. No coupling was observed between the carbene carbon atom in $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ (**3b**) and ^{183}W ($I = 1/2$, natural abundance = 14%). Restricted rotation of the isopropyl groups flanking the dicyanocarbene ligand in complex $[\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**5**) is evidenced by the observation of three resonances for the isopropyl methyl groups instead of the two expected on the basis of the C_{2v} symmetry of the molecule.

Table 2
 $^1\text{H-NMR}^a$ data for the dicyanocarbene complexes $[\text{L}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$

Complex	Metal	L	δ (ppm)	Rel. area	Assignments and comments
3a	Mo	Tp^{Me_2}	5.83	1	s, $\text{Tp}^{\text{Me}_2}\text{C}(4)\text{H}$ <i>trans</i> - to $\text{C}(\text{CN})_2$
			5.73	2	s, $\text{Tp}^{\text{Me}_2}\text{C}(4)\text{H}$ <i>trans</i> - to CO
			2.49	6	s, Tp^{Me_2} 3- or 5-Me group <i>trans</i> - to CO
			2.42	3	s, Tp^{Me_2} 3- or 5-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			2.40	3	s, Tp^{Me_2} 5- or 3-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			1.70	6	s, Tp^{Me_2} 5- or 3-Me group <i>trans</i> - to CO
3b	W	Tp^{Me_2}	5.83	1	s, $\text{Tp}^{\text{Me}_2}\text{C}(4)\text{H}$ <i>trans</i> - to $\text{C}(\text{CN})_2$
			5.79	2	s, $\text{Tp}^{\text{Me}_2}\text{C}(4)\text{H}$ <i>trans</i> - to CO
			2.49	6	s, Tp^{Me_2} 3- or 5-Me group <i>trans</i> - to CO
			2.39	3	s, Tp^{Me_2} 3- or 5-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			2.37	3	s, Tp^{Me_2} 5- or 3-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			1.88	6	s, Tp^{Me_2} 5- or 3-Me group <i>trans</i> - to CO
4	Mo	$\text{Tp}^{\text{Me}_2,4\text{Cl}}$	2.48	6	s, $\text{Tp}^{\text{Me}_2,4\text{Cl}}$ 3- or 5-Me group <i>trans</i> - to CO
			2.44	3	s, $\text{Tp}^{\text{Me}_2,4\text{Cl}}$ 3- or 5-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			2.41	3	s, $\text{Tp}^{\text{Me}_2,4\text{Cl}}$ 5- or 3-Me group <i>trans</i> - to $\text{C}(\text{CN})_2$
			1.72	6	s, $\text{Tp}^{\text{Me}_2,4\text{Cl}}$ 5- or 3-Me group <i>trans</i> - to CO
5	Mo	$\text{Tp}^{i\text{-Pr},4\text{Br}}$	7.72	1	s, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)\text{H}$ <i>trans</i> - to $\text{C}(\text{CN})_2$
			7.50	2	s, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)\text{H}$ <i>trans</i> - to CO
			3.98	1	septet, $J = \text{ca. } 6.7$ Hz $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Me}_2\text{CH}$ <i>trans</i> - to $\text{C}(\text{CN})_2$
			2.75	2 ^b	septet, $J = \text{ca. } 6.7$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Me}_2\text{CH}$ <i>trans</i> - to CO
			1.34	6	d, $J = 6.7$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Me}_2\text{CH}$ <i>trans</i> - to CO
			1.31	6	d, $J = 6.7$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Me}_2\text{CH}$ <i>trans</i> - to CO
			0.81	6	d, $J = 6.7$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Me}_2\text{CH}$ <i>trans</i> - to $\text{C}(\text{CN})_2$

^a All spectra were recorded in CDCl_3 and are reported in ppm downfield from TMS. All spectra are of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salts, the ^1H resonances of the cation were observed as multiplets at ca. 3.3 (8H), 1.7 (8H), 1.5 (8H) and 1.0 (12H) ppm.

^b Accidental equivalence (see text).

Table 3
 ^{13}C -NMR data^a for the anionic dicyanocarbene complexes $[\text{L}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**3–5**)

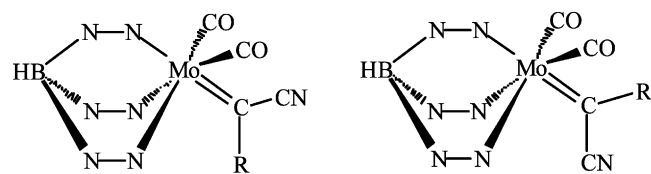
No.	3a	3b	4	5
M	Mo	W	Mo	Mo
L	$\text{Tp}^{\text{Me}2}$	$\text{Tp}^{\text{Me}2}$	$\text{Tp}^{\text{Me}2,4\text{Cl}}$	$\text{Tp}^{i\text{-Pr},4\text{Br}}$
CO	257.8	259.3	255.1	253.0
$\text{C}_{\text{carbene}}$	187.2	167.8	190.4	194.5
Pyrazolyl	155.8	158.2	152.5	160.4
C3'				
Pyrazolyl	149.1	150.5	146.5	156.1
C3				
Pyrazolyl	145.1	145.5	141.9	138.4
C5'				
Pyrazolyl	143.1	143.3	140.0	137.2
C5				
CN	127.8, 125.4	133.8, 133.5	127.1, 124.8	127.3, 125.1
Pyrazolyl	107.1	107.3	109.7	90.9
C4'				
Pyrazolyl	105.7	106.2	108.4	90.3
C4				
Others	15.0 (3- and 3'-Me), 12.0 (5- and 5'-Me)	16.9 (3-Me), 16.6 (3'-Me), 12.8 (5-Me), 12.6 (5'-Me)	13.8 (3-Me), 12.6 (3'-Me), 10.8 (5- and 5'-Me)	29.9 (CHMe_2), 29.3 (CHMe_2), 20.4, 20.3, 20.0 (CHMe_2)

^a All spectra were recorded using solutions of the $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ salts in CDCl_3 and data are reported in δ ppm downfield from TMS. Carbon atoms indicated by a prime are those of the unique substituted pyrazolyl group which lies on the mirror plane of the complexes. The resonances for the $[(n\text{-C}_4\text{H}_9)_4\text{N}]^+$ cation were observed at ca. 58, 24, 19 and 13 ppm. The ^{13}C -NMR spectrum of the labelled complex **3a** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{C}^{13}\text{CN})_2]^-$ was also recorded: $\delta = 187.2$ (dd, $J = 60.5, 70.2$ Hz, $\text{C}(\text{C}^{13}\text{CN})_2$); 127.84, 125.38 (CN) ppm.

The fact that the carbene carbon resonances in the anionic dicyanocarbene complexes **3a,b**, **4** and **5** are considerably more shielded than all but one of the other anionic carbene complexes for which ^{13}C -NMR data is available is doubtless related to the strong π -acceptor nature of the dicyanocarbene ligand already suggested by the relatively high $\nu(\text{CO})_{\text{av}}$ values of these complexes. The contrasting $\delta\text{C}_{\text{carbyne}}$ values of $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ (**3b**), 167.8 ppm and $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{W}=\text{CH}_2]^-$, 265 ppm, [1q] demonstrates that the anomalous shielding of the carbyne carbon in our complexes is more a consequence of the electron-withdrawing effect of the cyano substituents than it is of the fact that the complexes are anionic. The shielding effect of a cyano group as a carbene substituent is also demonstrated by a comparison of the ^{13}C -NMR spectra of $(\text{TPP})\text{Fe}=\text{CCl}_2$ and $(\text{TPP})\text{Fe}=\text{C}(\text{Cl})\text{CN}$ (TPP = tetraphenylporphyrin) where substitution of a CN group for a Cl substituent shifts the carbene carbon resonance from 224.7 to 210.0 ppm, i.e. 14.7 ppm to a higher field [13]. In the anionic molybdenum dicyanocarbene complexes **4** and **5**, containing the $\text{Tp}^{\text{Me}2,4\text{Cl}}$ and $\text{Tp}^{i\text{-Pr},4\text{Br}}$ ligands respectively, the carbene carbon resonances are at 190.4 and 194.5 ppm, i.e. slightly less shielded than in the $\text{Tp}^{\text{Me}2}$ complex **3a** due, presumably, to the more electron-withdrawing character of the halogen-substituted pyrazolylborate ligands in these complexes.

The ^{13}C -NMR spectra of all four dicyanocarbene complexes **3a,b**, **4** and **5** show two separate resonances which are assigned to the carbon atoms of non-equivalent carbene cyano-substituents. The assignment

was confirmed by the preparation of carbon-13 labelled **3a** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{C}^{13}\text{CN})_2]^-$. The fact that there are two distinct CN resonances indicates that in solution the plane of the $\text{C}(\text{CN})_2$ group coincides with the molecular mirror plane with one CN group oriented towards the $\text{Tp}^{\text{Me}2}$ ligand and the other towards the CO ligands as illustrated schematically in Fig. 3. There is no rotation about the $\text{Mo}=\text{C}$ bond at room temperature. This is also the structure found in the solid state for **3a** by an X-ray crystallographic study [14] which shows that steric interaction between the dicyanocarbene and the $\text{Tp}^{\text{Me}2}$ ligand prevents free rotation of the carbene ligand. The orientation of the carbene ligand in **3a** agrees with molecular orbital calculations on the interaction of the $[\text{CH}_2]$ ligand with the $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}]$, $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}]^+$ and $[(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Fe}]^+$ molecular fragments which show that the preferred orientation of the carbene ligand requires that the substituents on the carbene carbon atom lie in the symmetry plane of the $[(\eta\text{-C}_5\text{H}_5)_2\text{M}]$ fragment [15]. A similar orientation of the $[\text{:CH}_2]$ ligand has also been deduced from the



R = CN, alkyl

Fig. 3.

observation of two separate methylene proton resonances in the 400 MHz $^1\text{H-NMR}$ spectrum of $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{W}=\text{CH}_2]^-$ at -80°C [1q]. However, when the sample was warmed up to -13.1°C the methylene proton resonances coalesced and a barrier to $\text{W}=\text{CH}_2$ rotation of ca. $11.6\text{ kcal mol}^{-1}$ was calculated. The significantly higher barrier to carbene rotation in our complexes **3a,b**, **4** and **5** under similar conditions is ascribed to the steric effect of the carbene cyano-substituents.

In a separate study the cyanocarbyne complex $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{W}\equiv\text{C}-\text{CN}$ (**2b**) was prepared via an indirect route [16] and this material was reacted with one equivalent of K^{13}CN to prepare ^{13}C labelled **3b** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{W}=\text{C}(^{13}\text{CN})(\text{CN})]^-$. The $^{13}\text{C-NMR}$ spectrum of this material showed enhancement of the intensity of the two cyano carbon resonances at 133.8 and 133.5 ppm and indicates that attack of cyanide anion on the intermediate cyanocarbyne complexes **2a,b** to form the anionic dicyanocarbene complexes **3a,b** is not stereospecific.

The results described above suggest that addition of cyanide anion to neutral carbyne complexes of the general type $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}\equiv\text{C}-\text{Z}$ —where Z is a poor leaving group—has potential as a general route to anionic carbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}=\text{C}(\text{Z})(\text{CN})]^-$. To test this hypothesis we investigated the reaction of the arylthiocarbyne complex $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}\equiv\text{C}-\text{SC}_6\text{H}_4\text{Cl}-4$ (**8**) [17] and the functionalised alkylcarbyne complexes $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}\equiv\text{C}-\text{R}$ (**9a**, $\text{R} = \text{C}(\text{CN})_2\text{CH}_3$; **9b**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)$; **9c**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{CH}_3-4)$; **9d**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(1-\text{C}_{10}\text{H}_7)$; **9e**, $\text{R} = \text{C}(\text{CN})(\text{C}_6\text{H}_5)_2$) [3c,10b] with KCN in dmsO. With one equivalent of KCN in dmsO complex **8** gave a 50% yield of the anionic dicyanocarbene complex **3a**—evidently 4-chlorobenzenethiolate anion is a sufficiently good leaving group for the presumed intermediate anionic carbyne complex $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}=\text{C}(\text{SC}_6\text{H}_4\text{Cl}-4)(\text{CN})]^-$ (**10**) to collapse to the neutral cyanocarbyne complex **2a** which reacts with further cyanide anion to give **3a**. The alkyl complexes **9a–d** (though not **9e**) reacted with one equivalent of cyanide anion in dmsO to form the green anionic cyano(alkyl)carbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})(\text{R})]^-$ (**11a**, $\text{R} = \text{C}(\text{CN})_2\text{CH}_3$; **11b**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)$; **11c**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{CH}_3-4)$; **11d**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(1-\text{C}_{10}\text{H}_7)$) which were isolated as crystalline salts with quaternary ammonium cations in purified yields of ca. 48–66%. The cyano(diphenyl)methylcarbyne complex $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{C}(\text{CN})(\text{C}_6\text{H}_5)_2$ (**9e**) was completely unreactive to cyanide anion under these conditions. Reaction of a carbyne complex $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}\equiv\text{C}-\text{R}$ with cyanide anion to form a carbene complex $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}=\text{C}(\text{CN})\text{R}]^-$ requires that the linear, sp-hybridised, $[\text{M}\equiv\text{C}-\text{R}]$ fragment change to sp²-hybridised $[\text{M}=\text{C}(\text{CN})\text{R}]$.

In the process the R group must bend in the molecular mirror-plane, either towards the adjacent methyl-substituents of the $\text{Tp}^{\text{Me}2}$ substituents or towards the two CO ligands. Evidently the $\text{C}(\text{CN})(\text{C}_6\text{H}_5)_2$ substituent is too bulky to be accommodated by bending in either direction.

The new anionic carbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})(\text{R})]^-$ (**11a–d**) were characterised by elemental analysis and by IR, ^1H - and ^{13}C -NMR spectroscopy. The compounds were air stable in the solid state but decomposed slowly in acetone and more rapidly in chlorinated solvents—complex **11a** ($\text{R} = \text{C}(\text{CN})_2\text{CH}_3$) being especially unstable in the latter. Hence acetone was employed for all recrystallisations and NMR spectroscopic studies. At no stage in the syntheses of these complexes was formation of the dicyanocarbene complex **3a** observed and in all cases the remaining mass-balance was accounted for by recovered carbyne starting material.

Selected IR data for the anionic carbene complexes **11a–d** are summarised in Table 4. Containing only one substituent capable of conjugative electron-withdrawal, the cyano(alkyl)carbene ligands $[\text{C}(\text{CN})\text{R}]$ in complexes **11a–d** would be anticipated to be poorer π -acceptors than the dicyanocarbene ligand but significantly stronger than carbene ligands lacking strongly electron-withdrawing substituents. This prediction is confirmed by the IR spectroscopic data. The $\nu(\text{CO})_{\text{av}}$ values for the three molybdenum cyano{(1-cyano)(1-aryl)ethyl}carbene complexes **11b–d** are ca. 85 cm^{-1} to higher wavenumber than for Winter's $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}=\text{C}(\text{CH}_2)_3\text{NMe}]^-$ [1b] (see above) whereas $\nu(\text{CO})_{\text{av}}$ for the dicyanocarbene complex $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**) is 110 cm^{-1} higher than in the latter. However the $\nu(\text{CO})_{\text{av}}$ value for the cyano(1,1-dicyanoethyl)carbene complex **11a** is 100 cm^{-1} higher than in Winter's complex indicating that inductive effects are also significant in determining the net electron-withdrawing capacity of these ligands.

All the cyano(alkyl)carbene complexes **11a–d** show two $\nu(\text{CN})$ bands in their IR spectra. One is a very weak absorption occurring at ca. 2225 cm^{-1} and is assigned to the cyano group(s) in the carbene alkyl substituent. A medium intensity $\nu(\text{CN})$ band is found in the range $2121\text{--}2114\text{ cm}^{-1}$ and is assigned to the cyano group attached directly to the carbene carbon with the aid of the spectrum of ^{13}C -labelled **11b** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})\{\text{C}(\text{CN})(\text{Me})(\text{C}_6\text{H}_4\text{Br}-4)\}]^-$ prepared from $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}\equiv\text{C}-\text{C}(\text{CN})(\text{Me})(\text{C}_6\text{H}_4\text{Br}-4)$ (**9b**) and K^{13}CN .

The $^1\text{H-NMR}$ spectra of the cyano(alkyl)carbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})(\text{R})]^-$ (**11a–d**) (Table 5) show no unexpected features. Complex **11a** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})\{\text{C}(\text{CN})_2(\text{CH}_3)\}]^-$ has overall C_{2v} symmetry and the resonances of the pyrazolyl H(4)

Table 4

IR data ^a for the anionic cyano(alkyl)carbene complexes [Tp^{Me2}(CO)₂Mo=C(CN)(R)]⁻ (**11a–d**)

No.	R	$\nu(\text{CN}) \text{ cm}^{-1}$	$\nu(\text{CO}) \text{ cm}^{-1}$	$\nu(\text{CO})_{\text{av}} \text{ cm}^{-1}$
11a	C(CN) ₂ CH ₃	2231(w) 2121(m)	1887(vs) 1766(vs)	1826
11b	C(CN)(CH ₃)(C ₆ H ₄ Br-4)	2223(w) ^b 2114(m)	1873(vs) 1751(vs)	1812
11c	C(CN)(CH ₃)(C ₆ H ₄ Me-4)	2223(w) 2114(m)	1871(vs) 1749(vs)	1810
11d	C(CN)(CH ₃)(1-C ₁₀ H ₇)	2222(vw) 2114(m)	1870(vs) 1750(vs)	1810

^a All spectra were recorded using solutions of the [(C₂H₅)₄N]⁺ salts in CH₂Cl₂.^b These bands appear at 2223(vw) and 2067(m) in ¹³C-labelled complex **11b**, i.e. [Tp^{Me2}(CO)₂M=C(¹³CN){C(CN)(CH₃)(C₆H₄Br-4)}]⁻.

Table 5

¹H-NMR ^a data for the anionic cyano(alkyl)carbene complexes [Tp^{Me2}(CO)₂M=C(CN)(R)]⁻ (**11a–d**)

Complex	M	R	δ (ppm)	Rel. area	Assignments and comments			
11a	Mo	C(CN) ₂ CH ₃	5.94	1	s, Tp ^{Me2} C(4)H <i>trans</i> - to C(CN)(R)			
			5.90	2	s, Tp ^{Me2} C(4)H <i>trans</i> to CO			
			2.63	6	All s, 21H Tp ^{Me2} C(3) and C(5) Me groups			
			2.61	3	and C(CN) ₂ CH ₃			
			2.57	3				
			2.51	3				
			2.04	6				
			11b	Mo	C(CN)(CH ₃)(C ₆ H ₄ Br-4)	7.64	2	d, (<i>J</i> = 7.83 Hz) C ₆ H ₄ Br-4
						7.45	2	d, (<i>J</i> = 7.83 Hz) C ₆ H ₄ Br-4
						5.74	1	All s, 3H, Tp ^{Me2} C(4)H
5.70	1							
5.52	1							
2.49	9	All s, 21H, Tp ^{Me2} C(3) and C(5) Me groups						
2.42	3	and C(CN)(CH ₃)(C ₆ H ₄ Br-4)						
2.37	3							
1.83	3							
1.15	3							
11c	Mo	C(CN)(CH ₃)(C ₆ H ₄ CH ₃ -4)	7.57	2	d, (<i>J</i> = 8.1 Hz) C ₆ H ₄ CH ₃ -4			
			7.05	2	d, (<i>J</i> = 8.1 Hz) C ₆ H ₄ CH ₃ -4			
			5.73	1	All s, 3H, Tp ^{Me2} C(4)H			
			5.69	1				
			5.54	1				
			2.49	6	All s, 24H, Tp ^{Me2} C(3) and C(5) Me groups			
			2.45	3	and C(CN)(CH ₃)(C ₆ H ₄ CH ₃ -4)			
			2.42	3				
			2.37	3				
			2.26	3				
1.86	3							
1.15	3							
11d	Mo	C(CN)(CH ₃)(1-C ₁₀ H ₇)	9.43	1	Overlapping multiplets, 7H, 1-C ₁₀ H ₇			
			7.81	3				
			7.40	3				
			5.70	1	All s, 3H, Tp ^{Me2} C(4)H			
			5.57	1				
			5.55	1				
			2.56	3	All s, 21H, Tp ^{Me2} C(3)- and C(5)-Me groups			
			2.54	3	and C(CN)(CH ₃)(1-C ₁₀ H ₇)			
			2.42	6				
			2.36	3				
1.60	3							
1.57	3							

^a All spectra were recorded in acetone-d₆ using the [(C₂H₅)₄N]⁺ salts for complexes **11a–c** and the [(*n*-C₄H₉)₄N]⁺ salt of **11d**. Data are reported in δ ppm downfield from TMS. The resonances of the [(C₂H₅)₄N]⁺ cations were found at ca. 3.0 (8H, q) and 1.1 (12H, t) ppm and those of the [(C₄H₉)₄N]⁺ cation as multiplets at ca. 3.3 (8H), 1.7 (8H), 1.5 (8H) and 1.0 (12H) ppm.

atoms each appear as two peaks of 2:1 relative intensity. Like $[:C(CN)_2]$, the carbyne ligand $[:C(CN)\{C(CN)_2(CH_3)\}]$ has a deshielding effect on H(4) of the *trans*-pyrazolyl group. For complexes **11b–d** there is a chiral centre β - to the metal atom and the mirror symmetry is lost so that the pyrazolyl H(4) resonances appear as three distinct peaks. The resonance of the methyl groups in the carbene alkyl substituents occur in the same region as those due to the pyrazolyl methyl groups and could not be definitely assigned.

Table 6 summarises the ^{13}C -NMR spectra of the cyano(alkyl)carbene complexes **11a–d**. In the spectrum of complex **11a** both the $[Tp^{Me_2}(CO)_2Mo]$ fragment and the carbene alkyl substituent have C_{2v} symmetry and the resonances of the Tp^{Me_2} pyrazolyl carbons appear as two peaks of approximately 2:1 relative intensity while the two carbonyl ligands are equivalent. In complexes **11b–d** this symmetry is lost due to chirality at the carbon of the alkyl substituent directly bonded to the carbene carbon. In these complexes the two carbonyl ligands are inequivalent and each of the pyrazolyl carbon resonances appears as three distinct peaks of

approximately equal intensity except where accidental equivalence occurs.

The IR spectra of the dicyanocarbene complexes **3a, b, 4** and **5** indicate that the dicyanocarbene ligand is a more powerful net electron acceptor than carbene ligands lacking strongly electron withdrawing substituents on the carbene carbon. It seems reasonable to assume that the electron-withdrawing capacity of the $[:C(CN)_2]$ ligand is also responsible for the very shielded $\delta C_{carbyne}$ observed for these complexes (Table 3). From the IR data for the cyano(alkyl)carbene complexes **11a–d** (Table 4) we deduce that these ligands have ca. 80% of the electron-withdrawing capacity of dicyanocarbene. A less-straightforward picture emerges from consideration of the ^{13}C -NMR spectra of **11a–d** (Table 5). The assignments of the carbene carbon resonances were confirmed by the observation of coupling ($J = ca. 42.3$ Hz) with the ^{13}C -labelled CN group in **11b** $[Tp^{Me_2}(CO)_2Mo=C(^{13}CN)\{C(CN)(CH_3)(C_6H_4Br-4)\}]^-$. Whereas $\delta C_{carbyne}$ in the dicyanocarbene complex **3a** is more shielded by 70 ppm than that in $[Mo(=CHSiMe_3)(NO)(CH_2SiMe_3)(\eta-C_5H_5)]^-$ [10,p]—the

Table 6
 ^{13}C -NMR ^a data for the cyano(alkyl)carbene complexes $[Tp^{Me_2}(CO)_2Mo=C(CN)(R)]^-$ (**11a–d**)

No.	11a	11b	11c	11d
R	C(CN) ₂ CH ₃	C(CN)(CH ₃)(C ₆ H ₄ Br-4)	C(CN)(CH ₃)(C ₆ H ₄ Me-4)	C(CN)(CH ₃)(1-C ₁₀ H ₇)
CO	256.9	258.8, 257.7	258.7, 257.9	258.7, 256.9
C _{carbene}	228.1	247.2 ^b	249.3	248.9
C(3')	155.4	155.1	155.0	155.1
C(3'')	150.4	150.5 ^c	150.6	151.0
C(3''')	150.4	150.5 ^c	150.5	150.3
C(5')	144.8	144.4	144.3	144.2
C(5'')	143.5	143.2	143.1 ^c	143.3
C(5''')	143.5	143.1	143.1 ^c	143.0
=C(CN)	125.8	126.4	126.7	126.2
C(4')	107.1	106.9	106.8	106.8
C(4'')	106.3	106.3	106.2	106.1 ^c
C(4''')	106.3	106.1	106.0	106.1 ^c
3'-Me	16.1	16.1	16.1	16.9
3''-Me	16.1	15.4	15.5	16.3
3'''-Me	15.2	15.2	15.4	15.3
5'-Me	13.0	13.0 ^c	13.0 ^c	13.1 ^c
5''-Me	13.0	13.0 ^c	13.0 ^c	13.1 ^c
5'''-Me	12.7	13.0 ^c	12.8	13.1 ^c
R	117.6 C(CN) ₂ CH ₃ ; 50.4 C(CN) ₂ CH ₃ ; 28.3 C(CN) ₂ CH ₃	141.5, 131.5, 129.6, 120.4 C ₆ H ₄ Br-4; 124.7 C(CN)(CH ₃)Ar; 60.7 C(CN)(CH ₃)Ar; 12.7 C(CH ₃)(CN)Ar	138.4, 136.1, 129.0, 127.4 C ₆ H ₄ CH ₃ -4; 124.8 C(CN)(CH ₃)Ar; 60.7 C(CN)(CH ₃)Ar; 21.0 C ₆ H ₄ CH ₃ -4; 12.7 C(CH ₃)(CN)Ar	139.1, 135.3, 132.0, 123.0, 128.9, 128.6, 125.7c, 125.2 1-C ₁₀ H ₇ ; 61.1 C(CN)(CH ₃)(Ar); 12.8 C(CH ₃)(CN)(Ar)
Cation	52.8, 7.6	52.9, 7.6	52.2, 7.7	59.2, 24.4, 20.3, 14.2

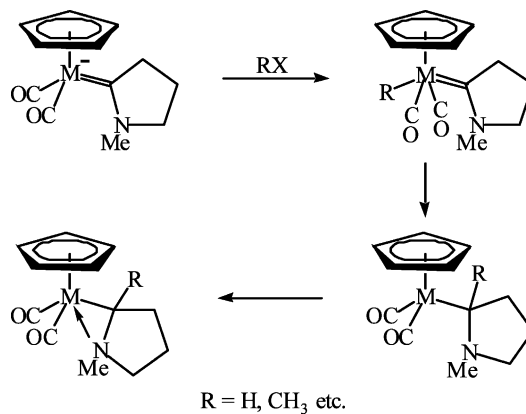
^a All data are reported in δ ppm downfield of TMS and all spectra were recorded in CD₂Cl₂ solution using the $[(C_2H_5)_4N]^+$ salts except for complex **11d** where the $[(n-C_4H_9)_4N]^+$ salt was employed. The symbols ', '' and ''' are used to distinguish the resonances of the 3-, 4- and 5-carbons of the Tp^{Me_2} ligand and of the attached methyl groups when these are rendered inequivalent by the overall symmetry of the complex. Complex **11a** has C_{2v} symmetry so that pairs of these resonances are identical.

^b In carbon-13 labelled **11b** $[Tp^{Me_2}(CO)_2Mo=C(^{13}CN)\{C(CN)(CH_3)(C_6H_4Br-4)\}]^-$ this resonance is split into a doublet, $J = 42.3$ Hz, and the intensity of the resonance at 126.4 ppm is enhanced.

most shielded of the previously known anionic Mo(0) carbene complexes— $\delta_{\text{C}_{\text{carbyne}}}$ in complexes **11a–d** is only ca. 8–29 ppm more shielded than the latter. It is possible that the apparent discrepancy arises from the presence of two substituents in $[:\text{C}(\text{CN})_2]$ —but only one in $[:\text{C}(\text{CN})\text{R}]$ —that are capable of conjugative electron-withdrawal. The relatively small decrease in the net electron acceptor capacity indicated by the IR data may mask a larger decrease in π -back-bonding to the cyano(alkyl)carbyne ligands which—in the IR data, but not the ^{13}C NMR—is partially compensated for by the inductive effects of the cyano-substituted alkyl groups.

In the ^{13}C -NMR spectra of complexes **11a–d** a peak at ca. 126 ppm is identified as arising from the carbene cyano-substituent on the basis of the enhancement of the intensity of the resonance at 125.8 ppm in the spectrum of ^{13}C -labelled **11b** $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})\{\text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)\}]^-$. A second CN resonance in the same region corresponds to the CN group or groups in the alkyl substituent. In complex **11d** the latter resonance is hidden due to overlap with the resonances of the 1-naphthyl group. The bulky alkyl substituents should ensure even greater inhibition of rotation about the $\text{Mo}=\text{C}$ bond in the cyano(alkyl)carbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})\text{R}]^-$ (**11a–d**) than in the dicyanocarbene complexes **3a,b** (see above). As illustrated schematically in Fig. 3 (above) there are two possible non-interconverting isomers for each of these complexes—one with the R group pointing towards the CO ligands and the other with the R group directed towards the $\text{Tp}^{\text{Me}2}$ ligand. For the complexes **11a–d** the enhancement of a single resonance in ^{13}C -labelled **11b** shows that only one isomer is present and we assume that it has the configuration with the bulky R groups directed away from the sterically demanding $\text{Tp}^{\text{Me}2}$ ligand. Hence the cyano-substituents in complexes **11a–d** are all likely to be directed towards the $\text{Tp}^{\text{Me}2}$ ligand. Since the $\delta_{\text{C}_{\text{CN}}}$ resonances in these complexes all occur close to 126 ppm we can use this information to tentatively suggest that the CN resonance at 125.4 ppm in the ^{13}C -NMR spectrum of the dicyanocarbene complex $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**) should be assigned to the CN substituent adjacent to the $\text{Tp}^{\text{Me}2}$ ligand and that at 127.8 ppm to the CN group adjacent to the CO ligands.

The only extensive study of the reactivity of anionic carbene complexes has been carried out by Winter's group. The typical chemical behaviour of these species (Scheme 4) involves attack by electrophiles at the metal atom. This is followed by spontaneous migration of the electrophile to the carbene carbon yielding a transient 16-electron σ -organyl species which is then stabilised by coordination of a lone-pair from the carbene heteroatom substituent (Scheme 4) or, in the absence of a heteroatom, by rearrangement such as an η^1 - to η^3 -



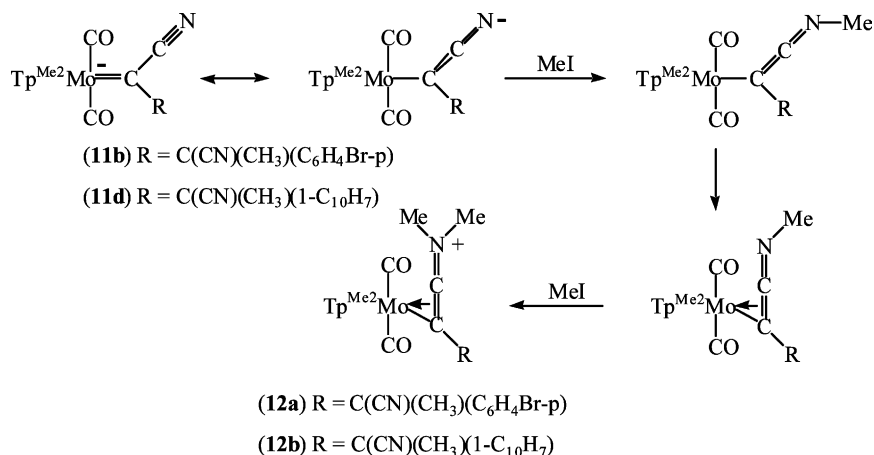
Scheme 4.

transformation of a benzyl ligand [**1b–k**]. In our complexes **3a,b**, **4**, **5** and **11a–d** it would be expected that the electron-withdrawing cyano-substituents on the carbene carbon should effect an umpolung of the normal reactivity of a Fischer-type carbene ligand so that the $\text{C}(\text{CN})_2$ ligand would behave as a nucleophile rather than as an electrophile. Compared to Winter's complexes direct electrophilic attack on the carbene ligand is also rendered more likely by the known preference of complexes containing $\text{Tp}^{\text{Me}2}$ and related ligands for six- rather than seven-coordination [18]. The IR spectrum of the crude product of reaction of the dicyanocarbene complexes $[\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}=\text{C}(\text{CN})_2]^-$ (**3a**, $\text{M} = \text{Mo}$; **3b**, $\text{M} = \text{W}$) with neat MeI or Me_3OBF_4 in dichloromethane at room temperature showed $\nu(\text{CN})$ bands at 2201(w), 2155(w) and 2096(vw) as well as $\nu(\text{CO})$ bands at 1993(m), 1912(m) cm^{-1} consistent with the formation of a neutral product. The relatively low intensity of the $\nu(\text{CO})$ bands vis-à-vis the bands in the fingerprint region suggested that decomposition had already taken place and attempts at isolation of the products led to complete loss of the $\nu(\text{CO})$ bands. Neither was it possible to trap the presumed 16-electron alkylation product by methylation at -40°C in the presence of CO. Complexes **3a,b** were also inert to reaction with chloromethylmethylsulphide, $\text{ClCH}_2\text{SCH}_3$, in boiling thf—it had been hoped that the S donor site in the alkyl halide would act to stabilise a coordinatively unsaturated alkylation product. The complexes did react with Sanger's reagent (2,4-dinitrofluorobenzene) under similar conditions but only carbonyl-free material resulted. These results are not entirely surprising since there is no obvious way that the 16-electron metal centre in a hypothetical 16-electron $\text{Tp}^{\text{Me}2}(\text{CO})_2\text{M}-\text{C}(\text{CN})_2\text{Me}$ intermediate could be stabilised other than by side-on coordination from one of the CN groups to the metal atom and this seems unlikely on steric grounds. It may also be the case that conversion of the sp^2 -hybridised carbene to an sp^3 -hybridised alkyl group is sterically unfavourable in view

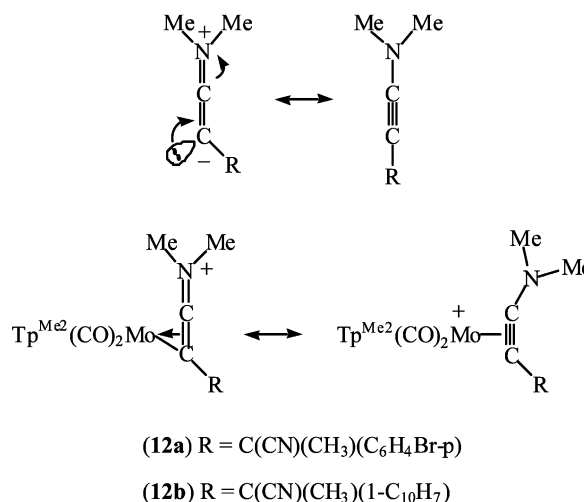
of the bulk of the Tp^{Me_2} ligand and that electrophilic attack is actually occurring at the carbene cyano substituents (see below). Whatever the case, stable products are not formed.

More interesting results were obtained with the anionic cyano(alkyl)carbene complexes $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})(\text{R})]^-$, **11b**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)$ and **11d**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(1-\text{C}_{10}\text{H}_7)$. Treatment of these complexes with a large excess of MeI in acetone for four hours led to the formation of new green air stable cationic dicarbonyl complexes **12a,b**, conveniently isolated in ca. 70% yield as their $[\text{BF}_4]^-$ salts. The IR spectra of the products showed a weak band at ca. 2238 cm^{-1} assignable to $\nu(\text{CN})$ of the alkyl substituent in **11b,d** (compare Table 4) but the medium-intensity $\nu(\text{CN})$ band of the carbene CN-substituent was missing, suggesting that reaction was taking place at the latter site.

The suggested sequence of events leading to the formation of complexes **12a,b** is illustrated in Scheme 5. Delocalisation of negative charge from the metal atom into the carbene cyano-substituent renders it electrophilic and methylation on the cyano nitrogen would form a 16-electron complex containing an $\eta^1(\text{C})N$ -methylketeniminyl ligand. Conversion of the latter to an $\eta^2(\text{C},\text{C})$ bonding mode would restore an 18-electron configuration at the metal atom. A second methylation at nitrogen then generates the products **12a,b**. The latter can be regarded as Mo(II) complexes in which the organic ligand is formally a dipolar four-electron donor derived by deprotonation of the ketenimmonium cation $[\text{RHC}=\text{C}=\text{NMe}_2]^+$ at the carbon- β to nitrogen. As shown in Scheme 6 complexes **12a,b** can be alternatively, and more conveniently, formulated as Mo(II) complexes of N,N -dimethylaminoalkyne ligands $\text{Me}_2\text{N}-\text{C}\equiv\text{C}-\text{R}$ [$\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)$, $\text{C}(\text{CN})(\text{CH}_3)(1-\text{C}_{10}\text{H}_7)$] which are behaving as four-electron [19] donors.



Scheme 5.

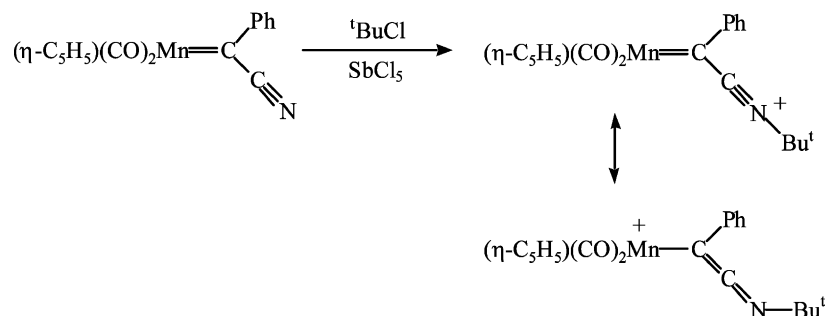


Scheme 6.

Fischer and Schambeck [6e] have described formation of a cationic N -alkyl keteniminyl complex via N -alkylation of a neutral cyanocarbene complex (Scheme 7)—an alternative η^2 -formulation for the product was considered but not favoured. There is no evidence that this keteniminyl complex is susceptible to further N -alkylation—presumably because the overall positive charge reduces the nucleophilicity of the monoalkylated nitrogen atom.

Microanalytical data for complexes **12a,b** were in agreement with the proposed formulation, assuming that—as was confirmed by the $^1\text{H-NMR}$ spectra (see Section 4)—both complexes crystallised with half a molecule of dichloromethane. Representative spectroscopic data for the complexes are presented in Table 7.

The IR spectra of complexes **12a,b** both show a medium intensity absorption at ca. 1712 cm^{-1} which is within the range of $1620\text{--}1782\text{ cm}^{-1}$ typical of $\nu(\text{C}\equiv\text{C})$ for complexes containing a single four-electron donor internal alkyne ligand complexed to Mo(II) or W(II) [19]. This absorption showed an isotopic shift of 35



Scheme 7.

cm^{-1} – 1680 cm^{-1} in ^{13}C -labelled $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}-\{\text{Me}_2\text{N}^{13}\text{C}\equiv\text{C}-\text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)\}]^+$ (**12a**), prepared by reaction of MeI with labelled **11b** $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})\{\text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)\}]^-$. Because the central carbon atom of the alkyne $[\text{C}(\text{CN})(\text{CH}_3)(\text{Ar})]$ substituent is a chiral centre the complexes lack the C_{2v} symmetry typical of many complexes of the general type $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{MoZ}$. This is evident from the appearance of three separate ^1H -NMR resonances for H(4) and the 3-methyl groups of the Tp^{Me_2} ligand and of two resonances for the *N*-methyl protons of the dimethylaminoalkyne. The same asymmetry results in the presence of two ^{13}C -NMR resonances for the carbonyl ligands (Table 7) and three resonances for the C(3) and C(4) carbons and the 3-methyl substituents of the Tp^{Me_2} ligand. A pair of resonances close to 215 and 198 ppm in the spectra of the two complexes were assigned to the alkyne carbons—the typical range for δC_{alkyne} in four-electron donor alkyne carbon resonances is 180–240 ppm [19]. The assignment of the alkyne carbon resonances was confirmed by carbon-13 labelling studies. In the spectrum of the labelled complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}-\{\text{Me}_2\text{N}^{13}\text{C}\equiv\text{C}-\text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)\}]^+$ (**12a**) the intensity of the resonance at 197.6 ppm was enhanced confirming that the more shielded alkyne resonance corresponds to the carbon derived from the CN group in the starting carbene complexes **11a,b**, i.e. that to which the NMe_2 group is now bonded. This resonance lies within the range of 182–203 ppm reported for a range of Mo(II) complexes containing various 1,2-diaminoacetylene ligands [19]. The lower-field resonance at 214.1 ppm was split into a doublet, $J = 59\text{ Hz}$, in the labelled

complex confirming that this resonance is due to the second alkyne carbon.

While the available data on compounds **12a,b** are certainly compatible with their formulation as cationic alkyne complexes it is probable that the $\eta^2(\text{C},\text{C})$ -keteneimmonium form (Scheme 6) also makes a contribution to the ground state of the complexes and we cannot assess the extent of this contribution on the basis of the information presently available. Neither can we tell which of the two possible orientations of the alkyne ligand shown schematically in Fig. 4 is adopted in practice. What we can say is that the simplicity of the ^1H - and ^{13}C -NMR spectra show that only one rotamer is present and that, on steric grounds, this is likely to have the bulky R group remote from the Tp^{Me_2} ligand. Unfortunately we were not able to grow crystals of **12a,b** suitable for an X-ray crystallographic study which would have cast some light on these questions.

Alkylation of the anionic cyano(alkyl)carbene complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})\{\text{C}(\text{CN})_2\text{CH}_3\}]^-$ (**11a**) with a large excess of methyl iodide in acetone deviated from the pattern established by the analogues **11b,d**. The product was neutral rather than cationic and its colour was purple rather than the green characteristic of

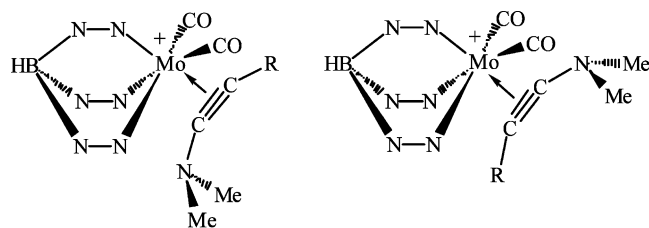


Fig. 4.

Table 7
Representative spectroscopic data^a for the cationic alkyne complexes **12a,b**

No.	$\nu(\text{CO})$	$\nu(\text{CO})_{\text{av}}$	$\nu(\text{C}\equiv\text{C})$	δ_{CO}	$\delta_{\text{C}\equiv\text{C}}$	δ_{NMe}
12a	2060, 1995(vs)	2027	1715	218.2, 216.7	214.1, 197.6 ^b	50.1, 43.8
12b	2060, 1995(vs)	2027	1710	218.6, 218.4	216.6, 198.1	49.1, 44.0

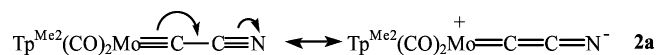
^a IR spectra were recorded in CH_2Cl_2 and all data are reported in cm^{-1} . NMR spectra were recorded in CDCl_3 and are reported in δ ppm downfield of TMS.

^b ^{13}C labelling studies show that this resonance arises from the alkyne carbon which is derived from the carbene CN substituent.

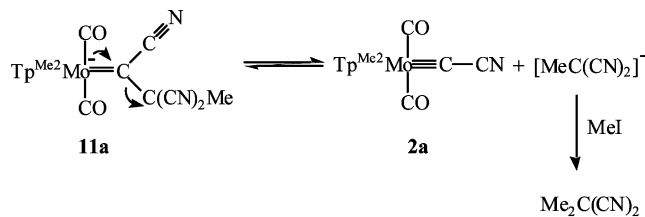
complexes **12a,b**. Its IR spectrum showed a medium intensity $\nu(\text{CN})$ absorption at 2118 cm^{-1} —little changed in position from $\nu(\text{CN})$ of the carbene cyano substituent in **11a** (2122 cm^{-1})—but was lacking the very weak absorption at 2231 cm^{-1} assigned to $\nu(\text{CN})$ of the $[\text{C}(\text{CN})_2\text{CH}_3]$ substituent in **11a**. The proton and ^{13}C -NMR spectra of the product were simpler than expected and ruled out the neutral monoalkylation product of **11a**, the $\eta^2(\text{C},\text{C})$ keteniminyl complex $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}[\text{C}(\text{CH}_3)(\text{CN})_2]\text{C}=\text{NCH}_3$. Microanalytical, spectroscopic and chemical data for the purple complex were compatible with its formulation as the previously unknown cyanocarbyne complex $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{CN}$ (**2a**) suggested already (see above) as an intermediate in the preparation of the anionic dicyanocarbene complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**). The yield of complex **2a** was 74%.

The IR spectrum of complex **2a** shows two $\nu(\text{CO})$ bands at 2026 and 1951 cm^{-1} , consistent with a neutral dicarbonyl complex. The cyanocarbyne ligand is a stronger net electron-acceptor than chlorocarbyne— $\nu(\text{CO})_{\text{av}}$ for **2a** at 1988 cm^{-1} is 25 cm^{-1} higher than for the chlorocarbyne complex $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**1a**). This must reflect, in part, the greater inductive electron withdrawing capacity of a cyano group compared to a chlorine atom (Taft σ_{I} values 0.56 and 0.47, respectively) [20] and the probable importance of contribution from a dipolar resonance form (Scheme 8) in which electron density is delocalised into the cyano group as suggested by the low-wavenumber $\nu(\text{CN})$. Another factor may be less efficient π -donation from the filled π -orbitals of the $\text{C}\equiv\text{N}$ triple bond to the $\text{M}\equiv\text{C}$ π^* -orbitals than from the lone pair orbitals on chlorine in **1a** [21]. The ^1H -NMR spectrum of complex **2a** (Section 4) indicates that the complex has C_{2v} symmetry. The ^{13}C -NMR spectrum shows a single resonance at 226.1 ppm for the two CO ligands and the resonance of the carbyne carbon is found at 229.3 ppm. That the latter is less shielded than the corresponding carbon in the chlorocarbyne complex **1a** ($\delta C_{\text{carbyne}}$ 208.7 ppm [2c]) may also be due to less efficient π -donation from the CN group [21]. The resonance of the CN carbon occurs at 120.8 ppm, somewhat more shielded than those of the cyano groups in the anionic dicyanocarbene complex **3a** (Table 3). The ^1H - and ^{13}C -NMR data (Section 4) show that the cyanocarbyne ligand resembles chlorocarbyne [2c] in having a stronger *trans*-shielding effect than CO on H(4) but a weaker *trans*-shielding effect than CO on C(3–5) of the Tp^{Me_2} ligand.

A rationale for the unexpected formation of the cyanocarbyne complex **2a** as a result of the attempted



Scheme 8.



Scheme 9.

alkylation of the anionic cyano(alkyl)carbyne complex **11a** is presented in Scheme 9. We suggest that in solution the anionic complex **11a** exists in an equilibrium with the cyanocarbyne complex **2a** and the 2,2-dicyanoethyl carbanion, driven by the relief of steric crowding in **11a** and facilitated by the anion-stabilising effect of the two cyano groups in $[\text{CH}_3\text{C}(\text{CN})_2]^-$. In the presence of MeI capture of $[\text{CH}_3\text{C}(\text{CN})_2]^-$ would force this equilibrium to the right. The existence of the suggested equilibrium also explains the observed instability of complex **11a** in chlorinated solvents. The latter can also act as traps for the anion $[\text{CH}_3\text{C}(\text{CN})_2]^-$ and indeed slow formation of cyanocarbyne complex **2a** has been observed when complex **11a** is stirred in dichloromethane. The proposed reactivity of the anionic carbene complex **11a** parallels the behaviour of the cationic bis(phosphonio)carbene complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{PMe}_3)_2]^+$. Templeton and co-workers [22] have shown that in solution this complex exists in equilibrium with the phosphonocarbyne complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}\equiv\text{C}-\text{PMe}_3]^+$ and free PMe_3 . Addition of MeI to a solution of $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{PMe}_3)_2]^+$ irreversibly removes PMe_3 as $[\text{PMe}_4]^+$ and so drives the process quantitatively to the carbyne complex $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}\equiv\text{C}-\text{PMe}_3]^+$. The fact that similar chemistry is not observed for $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**) or $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})(\text{R})]^-$ (**11b**), $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{Br}-4)$; **11d**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(1-\text{C}_{10}\text{H}_7)$] presumably reflects the fact that $[\text{CH}_3\text{C}(\text{CN})_2]^-$ is a better leaving group than CN^- or $[\text{C}(\text{CN})(\text{CH}_3)\text{Ar}]^-$ ($\text{Ar} = \text{C}_6\text{H}_4\text{Br}-4$; $1-\text{C}_{10}\text{H}_7$). Reaction of cyanocarbyne complex **2a** with KCN in dmsO gave, as expected, the dicyanocarbene complex **3a** in 83% yield.

3. Conclusion

The work described here further demonstrates the usefulness of the chlorocarbyne complexes $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{Cl}$ (**1a**, $\text{M} = \text{Mo}$; **1b**, $\text{M} = \text{W}$) as starting materials for the synthesis of new and unusual organometallic compounds—in the present case the first air-stable anionic carbene complexes, doubly unique because they are also the first examples of complexes containing the dicyanocarbene ligand. The new complexes themselves show interesting reactivity towards

electrophiles resulting in the synthesis of cationic dialkylaminoalkyne complexes and of the first complex containing a cyanocarbyne ligand. We have also found that some of the anionic dicyanocarbene complexes show unusual reactivity towards nucleophiles and this chemistry will be the subject of a subsequent communication.

4. Experimental

The starting materials KTp^{Me_2} [23], $\text{KTp}^{\text{Me}_2,4\text{Cl}}$ [2c,24] and $[(\text{C}_6\text{H}_5)_2\text{I}]\text{PF}_6$ [25] were prepared by literature methods. $\text{KTp}^{i\text{-Pr},4\text{Br}}$ was a gift from S. Trofimenko. Tricarbonyl complexes $[\text{R}_4\text{N}][\text{LM}(\text{CO})_3]$ ($\text{M} = \text{Mo}$, $\text{L} = \text{Tp}^{\text{Me}_2}$, $\text{Tp}^{\text{Me}_2,4\text{Cl}}$, $\text{Tp}^{i\text{-Pr},4\text{Br}}$, $\text{M} = \text{W}$, $\text{L} = \text{Tp}^{\text{Me}_2}$) were prepared by the general method of Trofimenko [26]. Synthesis of the chlorocarbyne complexes $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{Cl}$ (**1a**, $\text{M} = \text{Mo}$; **1b**, $\text{M} = \text{W}$) and $\text{Tp}^{\text{Me}_2,4\text{Cl}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**6**) are described in Refs. [2a,c,d]. The alkylcarbyne complexes $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{M}\equiv\text{C}-\text{R}$ (**9a**, $\text{R} = \text{C}(\text{CN})_2\text{CH}_3$; **9b**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)-(\text{C}_6\text{H}_4\text{Br}-4)$; **9c**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(\text{C}_6\text{H}_4\text{CH}_3-4)$; **9d**, $\text{R} = \text{C}(\text{CN})(\text{CH}_3)(1\text{-C}_{10}\text{H}_7)$; **9e**, $\text{R} = \text{C}(\text{CN})(\text{C}_6\text{H}_5)_2$) were prepared as described by Chaona et al. [3c,10b]. All other reagents whose preparation is not described in this section were commercially available and were used without further purification. Solvents were distilled prior to use and dried by standard methods. All reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. In reactions involving air sensitive reagents all glassware was oven dried at 120 °C and cooled to room temperature (r.t.) under a flow of nitrogen. Infrared spectra were measured on a Perkin–Elmer Paragon 1000 FT-IR spectrometer. The NMR spectra were recorded on JEOL FX-60 or JEOL GSX 279 MHz instruments. Elemental analysis were determined by the staff of the Microanalytical Laboratory of University College Cork.

4.1. $\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ (**7**)

Solid $[(\text{C}_6\text{H}_5)_2\text{I}]\text{PF}_6$ (4.26 g, 10 mmol) was added portionwise to a suspension of 7.5 g (7.9 mmol) of $[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_3][\text{Tp}^{i\text{-Pr},4\text{Br}}\text{Mo}(\text{CO})_3]$ in 100 ml of CH_2Cl_2 and the mixture was stirred at r.t. for 60 min. The reaction mixture was then filtered, washed with water, dried ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and concentrated to dryness in vacuo. The crude $\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$ was purified by dry flash chromatography on silica using CH_2Cl_2 –hexane mixtures as eluent. The first yellow fraction yielded pure $\text{Tp}^{i\text{-Pr},4\text{Br}}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{Cl}$, yellow crystals, m.p. 261–263 °C (decomp), 1.41 g (23%), Anal. Calc. for $\text{C}_{21}\text{H}_{25}\text{Br}_3\text{ClMoN}_6\text{O}_2$: C, 32.53; H, 3.25; N, 10.84. Found: C, 32.25; H, 3.37; N, 10.38%. IR (cm^{-1} , CH_2Cl_2) ν 2002(vs), 1922(vs) (CO).

$^1\text{H-NMR}$ (CDCl_3 , Me_4Si , δ ppm): 7.51(s), 2H, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)\text{H}$ *trans*- to CO; 7.46(s), 1H, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)\text{H}$ *trans*- to C–Cl; 3.84, septet, 2 H, $J = \text{ca. } 10$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CHMe}_2$ *trans*- to CO; 3.48, septet, 1 H, $J = \text{ca. } 10$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CHMe}_2$ *trans*- to C–Cl; 1.39(d), 6 H, $J = 10.8$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CH}(\text{CH}_3)_2$ *trans*- to C–Cl; 1.33(d), 12 H, $J = 10.8$ Hz, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CH}(\text{CH}_3)_2$ *trans*- to CO. $^{13}\text{C-NMR}$ (CDCl_3 , Me_4Si , δ ppm): 222.4, (CO); 211.6, C–Cl; 158.3, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(3)$ *trans*- to C–Cl; 157.7, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(3)$ *trans*- to CO; 138.7, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)$ *trans*- to C–Cl; 138.1, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(5)$ *trans*- to CO; 91.1, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(4)$ *trans*- to C–Cl; 91.1, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{C}(4)$ *trans*- to CO; 29.9, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CHMe}_2$ *trans*- to C–Cl; 29.7, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CHMe}_2$ *trans*- to CO; 20.4, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CH}(\text{CH}_3)_2$ *trans*- to CO; 20.0, $\text{Tp}^{i\text{-Pr},4\text{Br}}\text{CH}(\text{CH}_3)_2$ *trans*- to C–Cl.

4.2. Salts of $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(\text{CN})_2]^-$ (**3a**)

Potassium cyanide (0.25 g, 3.8 mmol), was added to 1 g (2 mmol) of **1a** in 30 ml of dmsO. The heterogeneous reaction mixture was stirred at 25 °C for 24 h (by which time a clear green solution was obtained) and was then poured into a concentrated aqueous solution containing an excess (ca. 10 mmol) of the appropriate cation salt. The resulting precipitate was filtered off, washed with water and dried in vacuo. The crude product was purified by precipitation from CH_2Cl_2 with ether. Unreacted **1a** was recovered from the filtrates.

(i) Tetraethylammonium salt: 0.9 g (70%), crystalline green solid, m.p. 217–218 °C (decomp), Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{BMoN}_9\text{O}_2$: C, 52.27; H, 6.58; N, 19.59. Found: C, 52.22; H, 6.80; N, 19.44%. IR: (cm^{-1} , CH_2Cl_2) ν 2542(w) (BH); 2141(s), 2080(vw) (CN); 1894(vs), 1774(vs) (CO).

(ii) Tetra(*n*-butyl)ammonium salt: procedure as for (i) above. Yield 72%, m.p. 186–187 °C. Anal. Calc. for $\text{C}_{36}\text{H}_{58}\text{BMoN}_9\text{O}_2$: C, 57.22; H, 7.74; N, 16.68. Found: C, 57.16; H, 7.75; N, 16.52%. IR data in Table 1, NMR in Tables 2 and 3. The carbon-13 labelled salt $[(n\text{-C}_4\text{H}_9)_4\text{N}][\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}=\text{C}(^{13}\text{CN})_2]$ was prepared in an identical manner using K^{13}CN , see Tables 1 and 3.

4.3. Salts of $[\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{W}=\text{C}(\text{CN})_2]^-$ (**3b**)

Complex **3b** was prepared from 0.3 g (0.51 mmol) of **1b** as described above for **3a**. The crude product was purified by multiple precipitations from CH_2Cl_2 with ether.

(i) Tetraethylammonium salt: yield 0.17 g (45%), m.p. 263–265 °C (decomp). Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{BN}_9\text{O}_2\text{W}$: C, 45.98; H, 5.79; N, 17.24. Found: C, 45.92; H, 5.94; N, 16.84%. IR: (cm^{-1} , CH_2Cl_2) ν 2546(w) (BH); 2147(s), 2098(vw) (CN); 1877(vs), 1756(vs) (CO).

(ii) Tetra(*n*-butyl)ammonium salt: yield 52%. Anal. Calc. for $\text{C}_{36}\text{H}_{58}\text{BN}_9\text{O}_2\text{W}$: C, 51.26; H, 6.93; N, 14.94.

Found: C, 51.00; H, 7.10; N, 15.00%. IR data in Table 1, NMR in Tables 2 and 3.

4.4. Salts of $[Tp^{Me_2,4Cl}(CO)_2Mo=C(CN)_2]^-$ (**4**)

(i) Reaction in $dmsO-CH_2Cl_2$: to a solution of 0.5 g (0.83 m mol) of **6** in 10 ml of CH_2Cl_2 was added 40 ml of $dmsO$ and 0.056 g (0.86 m mol) of KCN which was only partially soluble. The heterogeneous mixture was stirred at r.t. for 3 h and then 0.94 g (4.13 m mol) of $[C_6H_5CH_2N(C_2H_5)_3]Cl$ was added and the reaction mixture was stirred for a further 30 min. The solution was poured into 50 ml of water and the organic layer was separated, washed several times with water, dried ($MgSO_4 \cdot H_2O$) and the solvent removed on a rotary evaporator. Unreacted **6**, 0.33 g, 66% was recovered by extraction of the crude solid with hot hexane. The residue was purified by precipitation from CH_2Cl_2 with ether to give 0.2 g (29%) of $[C_6H_5CH_2N(C_2H_5)_3][4]$. Anal. Calc. for $C_{33}H_{41}BCl_3MoN_9O_2$: C, 49.00; H, 5.11; N, 15.59. Found: C, 48.80; H, 5.38; N, 15.25%. IR (cm^{-1} , thin film from CH_2Cl_2) ν 2144(m) (CN); 1885(vs), 1780(vs) (CO).

(ii) Reaction in $dmf-CH_2Cl_2$: to 0.3 g (0.5 m mol) of **6** dissolved in 2 ml of CH_2Cl_2 was added 20 ml of DMF and 0.059 g (0.9 m mol) of KCN. The reaction mixture was stirred at r.t. for 90 min, 0.31 g (0.96 m mol) of $[(n-C_4H_9)_4N]Br$ was added and the mixture stirred for a further 30 min. Water, 40 ml, was added and following work-up as in the previous example unreacted **6**, 0.05 g, 17% yield, and $[(n-C_4H_9)_4N][4]$, 0.34 g (79%) were isolated. Anal. Calc. for $C_{36}H_{55}BCl_3MoN_9O_2$: C, 50.34; H, 6.45; N, 14.68. Found: C, 50.57; H, 6.49; N, 14.86%. IR data in Table 1, NMR in Tables 2 and 3.

4.5. Tetra(*n*-butyl)ammonium salt of $[Tp^{i-Pr,4Br}(CO)_2Mo=C(CN)_2]^-$ (**5**)

Complex **7**, 0.15 g (0.19 m mol) and KCN, 0.02 g (0.31 m mol) were reacted together in 2 ml of CH_2Cl_2 and 15 ml of dmf as described above. After 24 h at r.t. 0.31 g (0.96 m mol) of $[(n-C_4H_9)_4N]Br$ was added and the reaction mixture was worked-up as before to yield unreacted **7**, 0.09 g (60%) and $[(n-C_4H_9)_4N][5]$ 0.07 g (36%). Anal. Calc. for $C_{39}H_{61}BBr_3MoN_9O_2$: C, 45.28; H, 5.94; N, 12.19. Found: C, 45.33; H, 5.98; N, 11.92%. IR data in Table 1, NMR in Tables 2 and 3.

4.6. Tetraethylammonium salt of $[Tp^{Me_2}(CO)_2Mo=C(CN)(C(CN)_2CH_3)]^-$ (**11a**)

An inhomogeneous mixture of **9a**, 0.5 g (0.93 m mol) and 0.06 g (0.92 m mol) of KCN in 40 ml of $dmsO$ was stirred at r.t. for 4 h during which time the colour of the solution changed from orange to green. The solution was poured into a concentrated aqueous solution of 1.9

g (9.0 m mol) of $[(C_2H_5)_4N]Br$ and the resulting precipitate was filtered off, washed with water and dried in vacuo. The crude precipitate was purified by precipitation from acetone with ether to give 0.311 g (48%) of green crystalline $[(C_2H_5)_4N][11a]$, m.p. 151–153 °C (decomp.). Anal. Calc. for $C_{31}H_{45}BMoN_{10}O_2$: C, 53.46; H, 6.51; N, 20.11. Found: C, 53.90; H, 6.38; N, 19.62%. IR data in Table 4, NMR in Tables 5 and 6. Unreacted **9a**, 0.23 g (46%), was recovered from the acetone–ether filtrate.

4.7. Tetraethylammonium salt of $[Tp^{Me_2}(CO)_2Mo=C(CN)\{C(CN)(CH_3)(C_6H_4Br-4)\}]^-$ (**11b**)

Complex **9b** was reacted with KCN as for **9a** above except that the reaction time was 6 h. The yield of $[(C_2H_5)_4N][11b]$ was 60%, m.p. 145–147 °C (decomp.). Anal. Calc. for $C_{36}H_{49}BBrMoN_9O_2$: C, 52.32; H, 5.98; N, 15.25. Found: C, 52.11; H, 5.78; N, 14.95%. IR data in Table 4, NMR in Tables 5 and 6. Unreacted **9b** was recovered in 35% yield. Carbon-13 labelled **11b** $[(C_2H_5)_4N][Tp^{Me_2}(CO)_2Mo=C(^{13}CN)\{C(CN)(CH_3)(C_6H_4Br-4)\}]$ was prepared similarly from **9b** and $K^{13}CN$, see Tables 4 and 6.

4.8. Tetraethylammonium salt of $[Tp^{Me_2}(CO)_2Mo=C(CN)\{C(CN)(CH_3)(C_6H_4Me-4)\}]^-$ (**11c**)

Complex **9c** was reacted with KCN as for **9a** above except that the reaction time was 3 h. The yield of $[(C_2H_5)_4N][11c]$ was 53%, m.p. 139–141 °C (decomp.). Anal. Calc. for $C_{37}H_{52}BMoN_9O_2$: C, 58.35; H, 6.88; N, 16.55. Found: C, 57.90; H, 6.88; N, 16.22%. IR data in Table 4, NMR in Tables 5 and 6. Unreacted **9c** was recovered in 47% yield.

4.9. Salts of $[Tp^{Me_2}(CO)_2Mo=C(CN)\{C(CN)(CH_3)(1-C_{10}H_7)\}]^-$ (**11d**)

Complex **9d** was reacted with KCN as for **9a** above except that the reaction time was 72 h.

(i) Tetraethylammonium salt: the yield of $[(C_2H_5)_4N][11d]$ was 43%, m.p. 152–153 °C (decomp.). Anal. Calc. for $C_{40}H_{52}BMoN_9O_2$: C, 60.23; H, 6.57; N, 15.80. Found: C, 59.94; H, 6.78; N, 15.40%. IR data in Table 4. Unreacted **9d** was recovered in 52% yield.

(ii) Tetra(*n*-butyl)ammonium salt: the yield of $[(n-C_4H_9)_4N][11d]$ was 66%, m.p. 118–121 °C. Anal. Calc. for $C_{48}H_{68}BMoN_9O_2$: C, 63.36; H, 7.53; N, 13.85. Found: C, 63.00; H, 7.45; N, 13.81%. IR: (cm^{-1} , CH_2Cl_2) ν 2520(w) (BH); 2231(vw), 2116(m) (CN); 1875(vs), 1754(vs) (CO). Unreacted **9d** was recovered in 27% yield. NMR in Tables 5 and 6.

4.10. Preparation of

$[Tp^{Me_2}(CO)_2Mo\{\eta^2(C,C)Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)\}][BF_4]\cdot 0.5CH_2Cl_2$
 ($[12a][BF_4]\cdot 0.5CH_2Cl_2$)

A solution of 0.25 g (0.3 mmol) of the $[(C_2H_5)_4N][11b]$ salt, 6 ml of acetone and 40 ml of CH_3I was left stand at r.t. for 4 h. Volatiles were removed in vacuo and the residue was dissolved in acetone and treated with 0.165 g (1.5 mmol) $NaBF_4$ in aqueous acetone. This solution was diluted further with water and extracted with CH_2Cl_2 . The combined extracts were washed several times with water and dried over $MgSO_4\cdot 1H_2O$. The CH_2Cl_2 solution was concentrated to dryness and the residue was recrystallised from CH_2Cl_2 -ether to yield 0.183 g (71%) of $[12a][BF_4]\cdot 0.5CH_2Cl_2$ as a green crystalline solid, m.p. 162–164 °C. Anal. Calc. for $C_{61}H_{72}B_4Br_2Cl_2F_8Mo_2N_{16}O_4$: C, 42.82; H, 4.24; N, 13.10; Found: C, 42.48; H, 4.60; N, 12.91%. IR: (cm^{-1} , KBr) ν 2559(w) (BH); 2238(vw) (CN); 2054(vs), 1982(vs) (CO); 1719(m) (C≡C); 1069(vs) (BF). IR (cm^{-1} CH_2Cl_2) ν 2562(w) (BH); 2060(vs), 1995(vs) (CO); 1715(m) (C≡C).

1H -NMR ($CDCl_3$, Me_4Si , δ ppm): 7.66(d) 2H, 7.49(d) 2H, $J = 8.1$ Hz, C_6H_4Br-4 ; 6.10(s), 5.96(s), 5.94(s), 1:1:1 H, $Tp^{Me_2}C(4)H$; 5.31(s), 1H, 0.5 CH_2Cl_2 ; 3.07(s), 2.84(s), 3:3 H, $(CH_3)_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 2.51(s), 2.46(s), 2.34(s), 2.26(s), 1.65(s), 1.50(s), 6:3:3:3:3:3 H, $Tp^{Me_2}C(3)Me$ and $C(5)Me$ groups and $(CH_3)_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$.

^{13}C -NMR ($CDCl_3$, Me_4Si , δ ppm): 218.2, 216.7, CO; 214.1, $Me_2NC\equiv C-C(CN)(Me)(C_6H_4Br-4)$; 197.6, $Me_2NC\equiv C-C(CN)(Me)(C_6H_4Br-4)$; 154.0, 150.9, 150.6, $Tp^{Me_2}C(3)$; 148.7, $Tp^{Me_2}C(5)$ *trans*- to $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 146.9, $Tp^{Me_2}C(5)$ *trans*- to CO; 135.1, 133.1, 128.3, 124.6, $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 121.9, $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 109.2, 107.8, 107.7, $Tp^{Me_2}C(4)$; 54.0, $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 50.1, 43.8, $(CH_3)_2N-C\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 24.1, $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 15.9, 14.3, 14.1, $Tp^{Me_2}C(3)Me$ groups; 12.9, $Tp^{Me_2}C(5)Me$ group *trans*- to $Me_2NC\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 12.6, $Tp^{Me_2}C(5)Me$ groups *trans*- to CO.

A sample of $[12a][BF_4]$ labelled with ^{13}C at the amino-substituted carbon of the alkyne ligand, $[Tp^{Me_2}(CO)_2Mo\{\eta^2(C,C)Me_2N^{13}C\equiv C-C(CN)(CH_3)(C_6H_4Br-4)\}][BF_4]$ was similarly prepared from $[(C_2H_5)_4N][11b]$ isotopically labelled at the carbene cyano-substituent. IR: (cm^{-1} , KBr) ν 2556(w) (BH); 2241(vw) (CN); 2053(vs), 1981(vs) (CO); 1686(m) (C≡C); 1069(vs) (BF); (CH_2Cl_2) ν 2563(w) (BH); 2060(vs), 1995(vs) (CO); 1680(m) (C≡C).

^{13}C -NMR ($CDCl_3$, Me_4Si , δ ppm): 197.6 $Me_2N^{13}C\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$; 214.1, d, $J = 59$ Hz, $Me_2N^{13}C\equiv C-C(CN)(CH_3)(C_6H_4Br-4)$.

4.11. Preparation of $[Tp^{Me_2}(CO)_2Mo\{\eta^2(C,C)Me_2C\equiv C-C(CN)(CH_3)(1-C_{10}H_7)\}][BF_4]\cdot 0.5CH_2Cl_2$
 ($[12b][BF_4]\cdot 0.5CH_2Cl_2$)

Reaction of 0.77 g (0.96 mmol) of $[(C_2H_5)_4N][11d]$ with methyl iodide as described above for $[(C_2H_5)_4N][11b]$ yielded 0.58 g (73%) of green crystalline $[12b][BF_4]\cdot 0.5CH_2Cl_2$, m.p. 154–157 °C. Anal. Calc. for $C_{69}H_{78}B_4Cl_2F_8Mo_2N_{16}O_4$: C, 50.12; H, 4.75; N, 13.55; Found: C, 50.00; H, 4.90; N, 13.00%. IR: (cm^{-1} , KBr) ν 2559(w) (BH); 2236(vw) (CN); 2055(vs), 1985(vs) (CO); 1714(m) (C≡C); 1069(vs) (BF). IR: (cm^{-1} , CH_2Cl_2) ν 2564(w) (BH); 2237(vw) (CN); 2060(vs), 1995(vs) (CO); 1710(m) (C≡C).

1H -NMR ($CDCl_3$, Me_4Si , δ ppm) 8.31(m), 7.98(m), 7.78(m), 7.64(m), 7.57(m), 1:2:1:1:2 H, $1-C_{10}H_7$; 6.09(s), 5.97(s), 5.89(s), 1:1:1 H, $Tp^{Me_2}C(4)H$; 5.30(s), 1H, 0.5 CH_2Cl_2 ; 2.86(s), 2.75(s), 3:3 H, $(CH_3)_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 2.59(s), 2.49(s), 2.46(s), 2.26(s), 1.71(s), 1.44(s), 3:6:3:3:3:3 H, $Tp^{Me_2}C(3)Me$ and $C(5)Me$ groups and $C(CN)(CH_3)(1-C_{10}H_7)$.

^{13}C -NMR ($CDCl_3$, Me_4Si , δ ppm): 218.6, 218.4, CO; 216.6, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 198.1, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 154.1, 151.1, 150.9, $Tp^{Me_2}C(3)$; 148.7, $Tp^{Me_2}C(5)$ *trans*- to $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 146.9, $Tp^{Me_2}C(5)$ *trans*- to CO; 134.6, 132.0, 131.5, 130.0, 129.3, 127.1, 126.5, 126.0, 125.7, 123.7, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 121.4, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 109.3, 107.9, 107.6, $Tp^{Me_2}C(4)$; 52.9, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 49.1, 44.0, $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 27.0 $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 16.1, 14.7, 14.7, $Tp^{Me_2}C(3)Me$ groups; 13.1, $Tp^{Me_2}C(5)Me$ group *trans*- to $Me_2NC\equiv C-C(CN)(CH_3)(1-C_{10}H_7)$; 12.7, $Tp^{Me_2}C(5)Me$ group *trans*- to CO.

4.12. Preparation of $Tp^{Me_2}(CO)_2Mo\equiv C-CN$ (**2a**)

A solution of $[(C_2H_5)_4N][11a]$, 0.23 g (0.33 mmol) in 10 ml of acetone and 5 ml of MeI was allowed to stand at r.t. for 9 h. Volatiles were removed in vacuo and the solid residue was taken up in CH_2Cl_2 . The solution was washed with water, dried ($MgSO_4\cdot H_2O$), concentrated to small volume and diluted with hexane to precipitate the crude product. Recrystallisation from CH_2Cl_2 -hexane yielded 0.12 g (74%) of purple $Tp^{Me_2}(CO)_2Mo\equiv C-CN$ (**2a**). Anal. Calc. for $C_{19}H_{22}BMoN_7O_2$: C, 46.84; H, 4.55; N, 20.13; Found: C, 47.17; H, 4.90; N, 19.84%. IR: (cm^{-1} , cyclohexane) ν 2540(w) (BH); 2118(w) (CN); 2026(vs), 1951(vs) (CO).

1H -NMR (acetone- d_6 , Me_4Si , δ ppm): 6.03(s), 2H, $Tp^{Me_2}C(4)H$ *trans*- to CO; 5.89(s), 1H, $Tp^{Me_2}C(4)H$ *trans*- to C-CN; 2.47(s), 2.44(s), 2.38(s), 2.35(s), 6:6:3:3 H, $Tp^{Me_2}C(3)Me$ and $C(5)Me$ groups.

^{13}C -NMR (acetone- d_6 , Me_4Si , δ ppm); 229.3, C–CN, 226.1, CO; 152.4, $\text{Tp}^{\text{Me}_2}\text{C}(3)$ *trans*- to C–CN; 151.6, $\text{Tp}^{\text{Me}_2}\text{C}(3)$ *trans*- to CO; 147.5, $\text{Tp}^{\text{Me}_2}\text{C}(5)$ *trans*- to C–CN; 146.7, $\text{Tp}^{\text{Me}_2}\text{C}(5)$ *trans*- to CO; 120.8, C–CN; 108.0, $\text{Tp}^{\text{Me}_2}\text{C}(4)$ *trans*- to C–CN; 107.6, $\text{Tp}^{\text{Me}_2}\text{C}(4)$ *trans*- to CO; 15.9, $\text{Tp}^{\text{Me}_2}\text{C}(3)\text{Me}$ group *trans*- to C–CN, 14.7, $\text{Tp}^{\text{Me}_2}\text{C}(3)\text{Me}$ group *trans*- to CO; 12.8, $\text{Tp}^{\text{Me}_2}\text{C}(5)\text{Me}$ group *trans*- to C–CN; 12.6, $\text{Tp}^{\text{Me}_2}\text{C}(5)\text{Me}$ group *trans*- to CO ppm.

4.13. Reaction of $\text{Tp}^{\text{Me}_2}(\text{CO})_2\text{Mo}\equiv\text{C}-\text{CN}$ (**2a**) with KCN

KCN, 0.027 g, 0.41 mmol was added to a stirred solution of complex **2a** (0.1 g, 0.205 mmol) in dmsO. The purple colour changed to greenish–yellow and after 24 h at r.t. the reaction was worked up as described above to yield 0.11 g, 0.17 mmol, 83% of $[\text{Et}_4\text{N}][\mathbf{3a}]$ identical to authentic material prepared as described above.

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