On the Control of the Site of Methylation of the Cyanide Complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ by the Substituents of the Thiolate Bridges (R = Me, Pr^i, CF_3)

Marie-Laurence Abasq, François Y. Pétillon and Jean Talarmin*

URA CNRS 322 'Chimie, Electrochimie Moléculaires et Chimie Analytique', Département de Chimie, Université de Bretagne Occidentale, BP 809, 29285 Brest Cédex, France

The substituents of the bridging sulfur atoms exert an electronic control on the site of methylation of the cyanide complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SR)_2]^-$: the methylation can be diverted from a sulfur lone pair to the cyanide ligand on changing the electronic properties of the R groups from electron-releasing to electron-withdrawing, respectively.

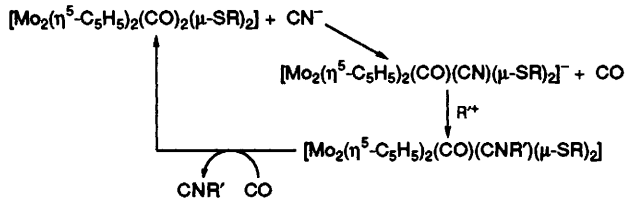
In earlier studies,[1] we have shown that the reaction of the dicarbonyl complex *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2]$ with isocyanides (R = Bu^t, xylyl, CH_2Ph) affords the substituted complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}SMe)_2]$ (R = Bu^t, xylyl CH_2Ph), and that the reaction can be reversed by CO [eqn. (1)].

$$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2] + RNC \rightleftharpoons [Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CNR)(\mu\text{-}SMe)_2] + CO \quad (1)$$

These results suggested that *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SR)_2]$ could be used for the synthesis of isocyanide molecules: provided this complex reacts with cyanide ions, the alkylation of the resulting complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ could provide a way to synthesize isocyanide ligands in the coordination sphere of the metal centres. This type of reaction has been reviewed recently;[2] the special interest of the complexes described herein is that the new isocyanide ligand can be easily released by reaction of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CNR')(\mu\text{-}SR)_2]$ with CO. This regenerates the parent dicarbonyl and therefore establishes the basis of a cyclic process (Scheme 1).

The cyanide complex possesses two potential sites for the alkylating agent, *i.e.* the CN^- ligand and the sulfur lone pairs. In a first step, we have investigated the influence of the steric and electronic characteristics of the R groups on the site of attack of *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SR)_2]^-$ by an electrophile, $[Me_3O]BF_4$. The preliminary results reported here demonstrate that the site of methylation (R' = Me) of the cyanide complex is controlled by the electronic properties of the sulfur substituents R.

Cyclic voltammetry monitoring of the reaction of *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2]$ with NBu_4CN demonstrates that a 1:1 complex, stable to further cyanide addition, is formed (Figs. 1 and 2). The assignment of this complex as $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ is confirmed by ^1H and ^{13}C NMR and by infrared spectroscopy.† Addition of the methylating agent $[Me_3O]BF_4$ to a solution of the above complex leads to changes in the CV characterised by the loss of the reversible oxidation of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ at −0.89 V and by the presence of new reduction and oxidation systems at less negative potentials, in agreement with the neutralisation of the negative charge of the cyanide complex. In contrast to what is observed in the case of authentic isocyanide complexes,[1] the product of the above reaction does not regenerate the parent dicarbonyl upon treatment with CO, and this suggests that the site of methylation was not the cyanide ligand but a sulfur lone pair.



Scheme 1

A comparison of the cyclic voltammetry of the product formed as indicated above with that resulting from the addition of CN^- to an authentic sample of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)(\mu\text{-}SMe_2)]^+$[3] confirmed that the methylation reaction afforded $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$‡ instead of the expected isocyanide complex.

In order to check whether increasing the size of the R substituents would promote methylation of the cyanide ligand, we have investigated the reactivity of complexes with isopropyl and *tert*-butyl thiolate bridges. The electronic properties of the different alkyl groups (R = Me, Pr^i, Bu^t) are similar, as demonstrated by a comparison of the redox potentials of the different complexes.§ The substitution of bulkier substituents for the Me groups on the bridging sulfur atoms did not favour methylation of the cyanide ligand: the CV of the product resulting from the successive reactions of CN^- and Me_3O^+ with *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}S^iPr)_2]$¶ was very similar to that of $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$, and this is also confirmed by NMR. On the other hand, the use of bulky substituents such as Bu^t totally prevented the reaction of the dicarbonyl complex with cyanide. Therefore, the size of the sulfur substituents appears to affect the reactivity of the complexes but not the site of the alkylation reaction.

In order to favour methylation at the cyanide ligand, we have substituted the alkyl groups on the bridging sulphur

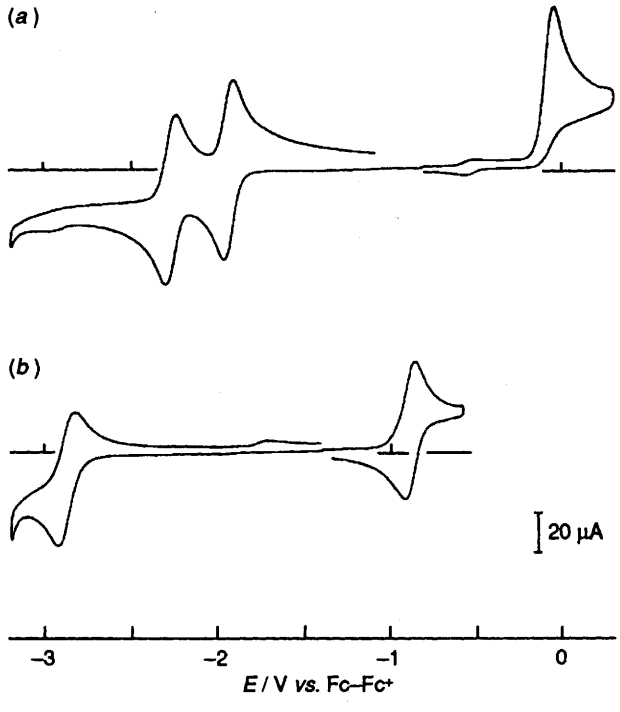


Fig. 1 Cyclic voltammetry of a 2.2 mmol dm^{-3} solution of *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2]$ in MeCN–NBu_4PF_6 (*a*) before and (*b*) after the addition of NBu_4 CN; vitreous carbon electrode, v = 0.2 V s^{-1}

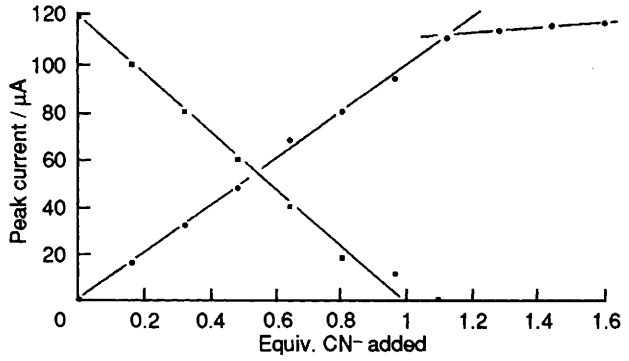


Fig. 2 Variations of the reduction peak currents on addition of NBu_4CN to a 4 mmol dm^{-3} solution of *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2]$ in MeCN–NBu_4PF_6; (■) $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SMe)_2]$, (●) $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$

atoms by CF_3: the presence of electron withdrawing substituents on the S bridges should stabilise the HOMO of the complex as well as the sulfur lone pairs, which could allow the reaction with the electrophile to be switched from orbital- to charge-control. The CV of *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SCF_3)_2]$ confirms that the substitution of CF_3 for CH_3 shifts the redox potentials anodically by 0.3 to 0.5 V, which illustrates the energetic stabilisation of the redox orbitals. The reaction of *trans,syn*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SCF_3)_2]$‖ with 1 equiv. of CN^- affords two isomers of the cyanide complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$** which must differ by the geometry (*cis vs. trans*) of the CO and CN^- ligands since both are different from the product of the reaction of *trans,anti*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SCF_3)_2]$‖‖ with CN^-. These cyanide complexes react with $[Me_3O]BF_4$ to produce methylisocyanide derivatives as evidenced by NMR, infrared and mass spectroscopies.†† The above assignment of the products is supported by the fact that the parent dicarbonyls are regenerated on reaction with CO, a diagnostic criterion of isocyanide derivatives for this type of complexes.[1] This suggests that the energy gap between the sulfur lone pairs and the LUMO of the electrophile is probably small when R = Me, and that the reaction is under orbital control. The substitution of CF_3 for CH_3 allows the reaction to be charge-controlled owing to the stabilisation of the sulfur lone pairs: this substitution redirects the attack of the electrophile towards the cyanide ligand.

Several reports have demonstrated the possibility to switch alkylation or protonation from a metal centre to a sulfur lone pair, or *vice versa*, in thiolate complexes.[4–6] We have now shown that it is possible to discriminate between two potentially reactive ligands within a thiolate complex and to methylate selectively at the selected site by an adjustment of the electronic properties of the sulfur substituents.

The CNRS (Centre National de la Recherche Scientifique) is acknowledged for financial support, and the Ministère de la Recherche et de la Technologie is thanked for providing a studentship to M. L. A.

Received, 3rd May 1994; Com. 4/02566K

Footnotes

† $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$: ^1H NMR (CD_3CN, δ *vs.* $SiMe_4$) 5.19 (s, 5H, C_5H_5), 4.25 (s, 5H, C_5H_5); 2.13 (s, 6H, SMe); ^{13}C NMR (CD_3CN) 243.60 (CO), 89.10, 87.30 (C_5H_5), 32.74 (SCH_3); IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 2060 ν(CN), 1780 ν(CO).

‡ $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$: ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$) 5.48 (s, 5H, C_5H_5), 4.92 (s, 5H, C_5H_5), 3.20 (s, 3H, SMe_2), 3.16 (s, 3H, SMe_2), 2.37 (s, 3H, SMe); ^{13}C NMR ($CDCl_3$) 232.36 (CO), 152.60 (CN); IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 2080 ν(CN), 1850 ν(CO).

§ *trans*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SR)_2]$ $E^{1/2}_{red1} = -1.94$ V, $E^{1/2}_{red2} = -2.27$ V, $Ep_{ox} = -0.03$ V (R = Me); $E^{1/2}_{red1} = -1.93$ V, $E^{1/2}_{red2} = -2.27$ V, $Ep_{ox} = 0$ V (R = Pr^i); $E^{1/2}_{red1} = -1.94$ V, $E^{1/2}_{red2} = -2.40$ V, $Ep_{ox} = -0.01$ V (R = Bu^t) (*E*/*V vs.* Fc^+–Fc in MeCN–NBu_4PF_6).

¶ $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SPr^i)_2]$: IR ($CH_2Cl_2$, $\tilde{\nu}/cm^{-1}$) 1855 ν(CO).

$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SPr^i)_2]^-$: $E^{1/2}_{red} = -2.95$ V, $E^{1/2}_{ox} = -0.87$ V {$E^{1/2}_{red} = -2.86$ V, $E^{1/2}_{ox} = -0.89$ V for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)_2]^-$ in MeCN–$[NBu_4PF_6]$}.

$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)\{\mu\text{-}S(Me)Pr^i\}(\mu\text{-}SPr^i\}$: MS:*m*/*z* 541 $[M]^+$; ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$): 5.49 (s, 5H, C_5H_5), 4.85 (s, 5H, C_5H_5); 2.88 (s, 3H, SCH_3); ^{13}C NMR ($CDCl_3$) 233.29 (CO), 150.63 (CN); $E^{1/2}_{red1} = -2.23$ V; $E_{red2} = -2.84$ V, $E^{1/2}_{red3} = -2.95$ V, $Ep_{ox} = -0.23$ V {$E^{1/2}_{red1} = -2.18$ V, $Ep_{red2} = -2.78$ V, $E^{1/2}_{red3} = -2.87$ V, $Ep_{ox} = -0.28$ V for $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SMe)(\mu\text{-}SMe_2)]$ in MeCN–$[NBu_4PF_6]$}.

‖ *trans,syn*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SCF_3)_2]$: ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$): 5.58 (s, 5H, C_5H_5), 5.35 (s, 5H, C_5H_5), ^{13}C NMR ($CDCl_3$) 241.17, 239.76 (CO), 91.99, 91.12 (C_5H_5), 136.23 (q, *J*(C–F) = 320 Hz, CF_3); IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 1950, 1890 ν(CO).

trans,anti-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}SCF_3)_2]$: ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$) 5.50 (s, 10H, C_5H_5); ^{13}C NMR ($CDCl_3$) 240.97 (CO), 91.53 (C_5H_5), 136.41 (q, *J*(C–F) = 320 Hz, CF_3); IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 1900 ν(CO).

** *syn*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$: Isomer 1; ^1H NMR (CD_3CN, δ *vs.* $SiMe_4$) 5.20 (s, 5H, C_5H_5), 4.81 (s, 5H, C_5H_5); IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 2040 ν(CN), 1885 ν(CO) (Isomer 1 + Isomer 2).

anti-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CN)(\mu\text{-}SCF_3)_2]^-$: ^1H NMR (CD_3CN, δ *vs.* $SiMe_4$) 5.31 (s, 5H, C_5H_5), 4.63 (s, 5H, C_5H_5); ^{13}C NMR (CD_3CN) 237.80 (CO), 151.06 (CN).

†† *syn*-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$: Isomer 1: ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$) 5.31 (s, 5H, C_5H_5), 5.25 (s, 5H, C_5H_5), 3.36 (s, 3H, CH_3NC); ^{19}F NMR ($CDCl_3$) −40.99.

Isomer 2: ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$) 5.47 (s, 5H, C_5H_5), 4.94 (s, 5H, C_5H_5), 3.34 (s, 3H, CH_3NC); ^{13}C NMR ($CDCl_3$) 237.85 (CO), 177.01 (CNMe); ^{19}F NMR ($CDCl_3$) −42.9; IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 2140 ν(CN), 1860 ν(CO) (Isomer 1 + Isomer 2); MS: *m*/*z* 593 $[M]^+$, 524 $[M - CO - CNMe]^+$, 455 $[M - CO - CNMe - CF_3]^+$, 386 $[M - CO - CNMe - 2CF_3]^+$.

anti-$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)(CNMe)(\mu\text{-}SCF_3)_2]$ ^1H NMR ($CDCl_3$, δ *vs.* $SiMe_4$) 5.46 (s, 5H, C_5H_5), 5.09 (s, 5H, C_5H_5), 3.38 (s, 3H, CH_3NC); ^{13}C NMR ($CDCl_3$) 237.84 (CO), 181.78 (CNMe); ^{19}F NMR ($CDCl_3$) −39.71, −43.98; IR (CH_2Cl_2, $\tilde{\nu}/cm^{-1}$) 2120 ν(CN), 1860 ν(CO).

References

1 F. Gloaguen, C. Le Floc'h, F. Y. Pétillon, J. Talarmin, M. El Khalifa and J. Y. Saillard, *Organometallics*, 1991, **10**, 2004.
2 W. P. Fehlhammer and M. Fritz, *Chem. Rev.*, 1993, **93**, 1243.
3 N. Kuhn, E. Zauder, R. Boese and D. Bläser, *J. Chem. Soc., Dalton Trans.*, 1988, 2171.
4 M. Y. Darensbourg, W.-F. Liaw and C. G. Riordan, *J. Am. Chem. Soc.*, 1989, **111**, 8051.
5 L. L. Lopez, P. Bernatis, J. Birnbaum, R. C. Haltiwanger and M. Rakowski DuBois, *Organometallics*, 1992, **11**, 2424.
6 P. Bernatis, R. C. Haltiwanger and M. Rakowski DuBois, *Organometallics*, 1992, **11**, 2435.