

Inorganica Chimica Acta 261 (1997) 117-120

Inorganica Chimica Acta

Note

Substitution reactions in dinuclear molybdenum(III) thiolato-complexes induced by isocyanato ligands

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Received 27 August 1996; revised 25 October 1996; accepted 12 November 1996

Abstract

The reactions of $[Cp'_2Mo_2(CO)_4(\mu-SR)_2](BF_4)_2$ with azido compounds proceeds via a mechanism analogous to the Curtius rearrangement to afford isocyanate species $[Cp'_2Mo_2(NCO)(CO)_3(\mu-SR)_2](BF_4)$ ($Cp'=C_5H_5$, $R=Me \ 1$, Ph 2; $Cp'=C_5Me_5$, $R=Me \ 3$). Thermal substitution of CH₃CN or R'NC (R'=t-Bu, xylyl, benzyl) for CO in 1–3 results in the formation of monosubstituted derivatives $[Cp'_2Mo_2(NCO)(CO)_2(L)(\mu-SR)_2](BF_4)$ ($L=CH_3CN$: $Cp'=C_5H_5$, $R=Me \ 4$, Ph 5; $Cp'=C_5Me_5$, $R=Me \ 6$; L=R'NC: $Cp'=C_5Me_5$, $R=Me \ 6$; L=R'NC: $Cp'=C_5Me_5$, $R=Me \ R=Me, R'=t$ -Bu 7, xylyl 8, benzyl 9).

Keywords: Molybdenum complexes; Thiolate complexes; Isocyanate complexes; Dinuclear complexes; Pentamethyl cyclopentadienyl complexes

1. Introduction

We have investigated for some years the influence of metal centres and of the sulfur substituents R or the Cp' rings (C_5H_5 , C_5Me_5) on the electrochemical behaviour and the reactivity of complexes possessing $\{Cp'_2M_2(\mu-SR)_n\}$ core (n=1-3,M=Mo, W, V) [1,2]. We were particularly interested to generate substrate-binding sites and to control their selectivity. Very recently we have reported that the substitution of C_5H_5 (Cp) rings by the C_5Me_5 (Cp^{*}) ligands in the series of complexes $[Cp'_2Mo_2(CO)_4(\mu-SR)_2](BF_4)_2$ (Cp' = C_5H_5 , C_5Me_5) affects the life time of intermediates produced in the reduction processes [2b] and lowers the reactivity of these complexes [2]. Cp* compounds show greater resistance to decarbonylation than their Cp analogues, no substitution of carbonyl by acetonitrile is observed when $[Cp_{2}^{*}Mo_{2}(CO)_{4}(\mu-SR)_{2}](BF_{4})_{2}$ is stirred in refluxing MeCN [2a]. A way to activate such inert carbonyl complexes is to introduce into the metallic framework a halide or pseudohalide ligand [3]. We have tried to activate toward carbonyl substitution the inhibited pentamethylcyclopentadienyl complex $[Cp_{2}^{*}Mo_{2}(CO)_{4}(\mu-SR)_{2}](BF_{4})_{2}$ by transforming one carbonyl group into an isocyanate ligand. Here we report the reaction of the dicationic compound $[Cp'_2Mo_2(CO)_4(\mu-SR)_2](BF_4)_2$ with natrium azide NaN₃, giving the isocyanate products $[Cp'_2Mo_2(NCO)(CO)_3(\mu-SR)_2](BF_4)$ ($Cp' = C_5H_5$, R = Me **1**, R = Ph **2**; $Cp' = C_5Me_5$, R = Me **3**). The reactivity of nitrile (CH₃CN) and isocyanide (*t*-BuNC, xylyNC) towards these isocyanate complexes has been investigated and compared to that with the dicationic tetracarbonyl precursor $[Cp'_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$. We show that the presence in the complexes of a pseudo-halide ligand labilises these dinuclear compounds to carbonyl substitution.

2. Results

A red solution of $[Cp'_2Mo_2(CO)_4(\mu-SR)_2](BF_4)_2$ in acetonitrile reacted instantaneously with one equivalent of NaN₃ in ethanol to give a brown solution from which were isolated the isocyanate products $[Cp'_2Mo_2(NCO)(CO)_3-(\mu-SR)_2](BF_4)$ ($Cp'=C_5H_5$, R=Me **1**, R=Ph **2**; $Cp'=C_5Me_5$, R=Me **3**) **1–3** in quantitative yields (Reaction 1).

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These new compounds have been characterised by various spectroscopic methods (¹H and ¹³C NMR, IR) (Table 1) and elemental analyses. ¹H and ¹³C NMR spectroscopy of 1-3 shows the presence of inequivalent Cp' rings and SR groups, respectively. The infrared spectra of these complexes display three strong bands, between 2500 and 1900 cm^{-1} , which are attributed to carbonyl and isocyanate ligands. The ¹³C{¹H} patterns of 1–3 show three peaks between 240 and 210 ppm, and a resonance at about 137 ppm, which are assigned to carbonyl and NCO groups, respectively. A cis-syn form was proposed for complexes 1-3 on the basis (i) of the geometry of the dicationic precursor $[Cp'_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$, which is cis-syn, and (ii) of the observation that the substitution of one CO by an acetonitrile ligand does not alter the arrangement of the $\{Cp_2Mo_2(\mu-SR)_2\}$ core [2a,4].

On warming in acetonitrile, complexes 1-3 lost carbon monoxide and converted into compounds 4-6 which contain an acetonitrile group (Reaction 2).

 $\frac{\text{refluxing acetonitrile}}{-CO} [Cp'_2Mo_2(NCO)(CO)_2(CH_3CN)(\mu-SR)_2](BF_4)$ $Cp' = C_5H_5, R = Me = 4$ $Cp' = C_5H_5, R = Me = 4$

$$Cp' = C_5H_5, R = Ph - 5$$

 $Cp' = C_5Me_5, R = Me - 6$

The reaction of **3** with R'NC in refluxing THF afforded the brown solids 7-9 (Reaction 3).

 $[Cp*_2Mo_2(NCO)(CO)_3(\mu-SMe)_2](BF_4) + R'NC$

$$(\stackrel{\text{(THF, 66°C)}}{\xrightarrow{-\text{CO}}} [Cp*_{2}Mo_{2}(NCO)(CO)_{2}(R'NC)(\mu-SMe)_{2}](BF_{4})$$

$$\stackrel{\text{R'} = 'Bu \qquad 7}{\text{R'} = Xylyl \quad 8}$$

$$\stackrel{\text{R'} = Benzyl \quad 9}{\text{R'}}$$

Complexes **4–9** have also been characterised by standard spectroscopic (Table 1) and analytical techniques. ¹H and ¹³C NMR spectra of **4–9** show resonances corresponding to one R'NC ligand for one {Cp'₂Mo₂(μ -SR)₂} frame, with two inequivalent Cp' groups and two inequivalent SR groups. IR spectra display the ν (CN) vibration of the isocyanide ligand as a strong band between 2100 and 2150 cm⁻¹. ¹³C NMR patterns show resonances assigned to CH₃CN and R'NC: for acetonitrile two resonances were noted at about 140 ppm (δ (*C*N)) and 5 ppm (δ (*C*H₃)), and for the isocyanide ligand the resonances of the R' groups (*t*-Bu, xylyl, benzyl) and of the carbon of the *C*N group (between 160 and 190 ppm) were observed. Only two peaks were noted in the carbonyl region, this confirms the loss of one CO in the reaction.

3. Discussion

The reaction of N_3^- with the dinuclear tetracarbonyl complexes $[Cp'_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$ leads to the isocyanate products via a mechanism analogous to the Curtius rearrangement which has been proposed by Beck and coworkers with carbonyl monometallic compounds [LnM-CO] [5]. Some examples of di- or polymetallic isocyanate products have been reported. Gladfelter et al. have described the trinuclear ruthenium complex $[Ru_3(NCO)(CO)_4]^-$ obtained by reaction of $[Ru_3(CO)_{12}]$ with N_3^- [6]. Other polynuclear NCO species have been reported: they have been formed by reaction of reagents such as diazoalkanes $C_6H_{10}N_2$, $(CH_3)_2N_2$, or HNCO and azide $[PPN]N_3$ with $[Ru_3(CO)_{12}]$ [7], $[(C_5Me_5)_2Mo_2(CO)_4]$ [8], $[Os_3(CO)_{10}(CH_3CN)_2]$ [9] and $[Os_3(CO)_{11}(\mu-CH_2)]$ [10], respectively.

Unlike in their dicationic precursor $[Cp'_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$, carbonyl substitution by unsaturated substrates such as acetonitrile or isocyanide was easily made in NCO-cyclopentadienyl complexes **1–2** under mild conditions (RT). Temperature or electrochemical activation were required to achieve a similar CO labilisation process in the tetracarbonyl complex $[Cp_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$ [1a]. With pentamethylcyclopentadienyl ligands we have observed an inhibition of the carbonyl substitution and only electrochemical activation allows us to carry out this reaction with CH₃CN or RNC [2]. The transformation of one carbonyl ligand into an NCO group activates carbonyl substitution on metal. The role of the isocyanate ligand can be explained by its hemi-labile character. NCO can act as a three-electron donor bridging [6], and then it moves to a terminal position

| Table 1 Spectroscopic dat | ta of complexes 1–9 | | |
|------------------------------|--|---|--|
| Complexes | IR a | ¹ H NMR | ¹³ C NMR ° |
| 1 ^{a,c} | 2240 (s) ν _{NCO} 2060 (s), 2020 (s), 1970 (sh) ν _{CO} | 6.10 (s, 5H, C ₅ H ₅), 5.83 (s, 5H, C ₅ H ₅) 2.67 (s, 3H, S–CH ₃), 2.52 (s, 3H, S–CH ₃) | 229.78, 228.47, 219.00 (CO), 137.45 (NCO), 98.20, 95.80 (C_5H_5), 31.43, 19.54 (S–CH ₃) |
| 2 a.c | 2240 (s) $\nu_{\rm NCO}$ 2060 (s), 2020 (s), 1940 (sh) $\nu_{\rm CO}$ | 7.7–7.37 (m, 10H, S– C_6H_5) 6.31 (s, 5H, C_5H_5), 6.13 (s, 5H, C_5H_5) | 228.66, 226.32, 217.49 (CO), 139.53–128.84 (S–C ₆ H ₅ and NCO), 99.69, 97.16 (C ₅ H ₅) |
| 3 a.c | 2240 (s) $\nu_{\rm NCO}$ 2040 (s), 2000 (s), 1950 (sh) $\nu_{\rm CO}$ | 2.36 (s, 3H, S-CH ₃), 2.19 (s, 3H, S-CH ₃) 2.01 (s, 15 H, C ₅ (CH ₃) ₅), 1.90 (s, 15H, C ₅ (CH ₃) ₅) | 236.01, 232.81, 224.41 (CO), 137.83 (NCO) 108.81, 108.16 ($C_5(CH_3)_5$), 28.62, 16.82 (S– CH_3), 11.72, 11.35 ($C_5(CH_3)_5$) |
| 4 b.c | 2230 (s) ν _{NCO} 2020 (s), 1980 (s) ν _{CO} | 5.97 (s, 5H, C ₅ H ₅), 5.43 (s, 5H, C ₅ H ₅), 2.66 (s, 3H), 2.53 (s, 3H), 2.46 (s, 3H): (S-CH ₃ , S-CH ₃ , CH ₃ CN) | 234.00, 227.20 (CO), 141.40 (CH ₃ CN), 137.20 (NCO), 99.80, 95.60 (C ₅ H ₅), 24.28, 21.88 (SCH ₃), 5.05 (CH ₃ CN) |
| 5 b.c | 2240 (s) ν _{NCO} 2030 (s), 1980 (s) ν _{CO} | 7.60–7.4 (m, $C_{o}H_{5}$), 6.20 (s, 5H, $C_{3}H_{5}$) 5.79 (s, 5H, $C_{5}H_{5}$), 2.21 (s, 3H, $CH_{3}CN$) | 233.22, 223.45 (CO), 140.00–128.00 (m, S–C ₆ H ₅ and NCO, CH ₃ CN), 101.00, 96.8 (C ₅ H ₅), 4.63 (CH ₃ CN) |
| 6 ^{b,c} | 2300 (s) ν _{NCO} 2000 (s), 1950 (s) ν _{CO} | 2.28 (s, 3H), 2.22 (s, 3H), 2.04 (s, 3H): (S-CH ₃ , S-CH ₃ , CH ₃ CN), 2.06 (s, 15H, $C_5(CH_3)_5$), 1.81 (s, 15H, $C_5(CH_3)_5$) | 239.36, 232.94 (CO), 141.57 (CH ₃ CN), 137.84 (NCO), 108.51, 107.58 (C ₅ (CH ₃) ₅), 21.12, 19.00 (SCH ₃) 12.11, 11.74 (C ₅ (CH ₃) ₅), 5.21 (CH ₃ CN) |
| 7 b.d | 2220 (s) $\nu_{\rm NCO}$ 2140 (s) $\nu_{\rm CN}$ 2000 (s), 1950 (s) $\nu_{\rm CO}$ | 2.30 (s, 3H, S- CH_3), 2.13 (s, 3H, S- CH_3) 1.96 (s, 15H, $C_5(CH_3)_5$), 1.82 (s, 15H, $C_5(CH_3)_5$), 1.60 (s, 9H, $C(CH_3)_3$) | 230.32, 226.04 (CO), 164.97 (<i>t</i> -BuNC), 137.88 (NCO), 107.16, 106.61 (<i>C</i> ₅ (CH ₃) ₅), 61.05 (<i>C</i> (CH ₃) ₃) 30.52 (<i>C</i> (CH ₃) ₃), 27.61, 16.73 (S–CH ₃), 12.13, 10.93 (<i>C</i> ₅ (CH ₃) ₅) |
| 8 b.d | 2220 (s) $\nu_{\rm NCO}$ 2100 (s) $\nu_{\rm CN}$ 2000 (s), 1950 (s) $\nu_{\rm CO}$ | 7.29, 7.26 (m, 3H, $C_6H_3(CH_3)_2NC$) 2.48 (s, 6H, $C_6H_3(CH_3)_2NC$) 2.44 (s, 3H, $S-CH_3$), 2.13 (s, 3H, $S-CH_3$) 1.97 (s, 15H, $C_5(CH_3)_5$), 1.89 (s, 15H, $C_5(CH_3)_5$) | 237.09, 229.52 (CO), 184.21 (R-NC) 138.22, 136.50 (<i>C</i> ₆ H ₃ (CH ₃) ₂ NC and NCO) 131.20, 129.46 (<i>C</i> ₆ H ₃ (CH ₃) ₂ NC) 107.50, 107.38 (<i>C</i> ₅ (CH ₃) ₅), 27.54, 16.16 (S–CH ₃), 19.55 (<i>C</i> ₆ H ₃ (CH ₃) ₂ NC), 12.30, 10.96 (<i>C</i> ₅ (CH ₃) ₅) |
| 9 b.d | 2220 (s) $\nu_{\rm NCO}$ 2150 (s) $\nu_{\rm CN}$ 2000 (s), 1950 (s) $\nu_{\rm CO}$ | 7.45 (m, C_6H_5 -CH ₂ NC), 5.33 (s, C_6H_5 -CH ₂ NC), 2.23 (s, 3H, S-CH ₃), 2.14 (s, 3H, S-CH ₃) 1.95, 1.76 (s, 15H, $C_5(CH_3)_5$) 1.76 (s, 15H, $C_5(CH_3)_5$) | 237.69, 230.07 (CO), 169.82 ($C_6H_5-CH_2NC$) 137.87 (NCO), 133.59–128.59 ($C_6H_5-CH_2NC$) 107.17, 106.87 ($C_5(CH_3)_5$), 50.98 ($C_6H_5-CH_2NC$), 28.06, 15.08 ($S-CH_3$), 12.09, 10.93 ($C_5(CH_3)_5$) |
| a ID CH CN | duti on | | |

^a IR in CH₃CN solution.
 ^b IR in CH₂Cl₂ solution.
 ^c Chemical shifts (δ) measured in CD₃NO₂,
 ^d Chemical shifts (δ) measured in CD₃CN.
 ^e Hydrogen-1 decoupled.

concomitantly with the coordination of a substrate (CO, CH_3CN or R'NC); this parallels the motion observed for halide bridges in some dinuclear complexes [11].

In conclusion, these results are an illustration of the effect of the pseudo-halide ligand NCO on the reactivity of the dinuclear carbonyl framework $[Cp'_2Mo_2(CO)_4(\mu-SR)_2]^{2+}$. The transformation of a carbonyl group into a NCO ligand labilises the remaining carbonyl groups in this bimetallic system.

4. Experimental

4.1. General procedures

The reactions were performed under either a nitrogen or an argon atmosphere using standard Schlenk techniques, and solvents were deoxygenated and dried by standard methods. Literature methods were used for the preparation of $[Cp'_2-Mo_2(CO)_4(\mu-SR)_2](BF_4)_2$ (Cp' = Cp [4], $Cp' = Cp^*$ [2a]).

Infrared spectra were obtained with a Perkin-Elmer 1430 spectrophotometer. NMR spectra were recorded on a Bruker AC300 spectrophotometer. Peak positions were relative to tetramethylsilane as an internal reference. Chemical analyses were performed by the 'Centre de microanalyses du CNRS, Vernaison'.

4.2. Preparation of $[Cp'_{2}Mo_{2}(NCO)(CO)_{3}(\mu-SR)_{2}](BF_{4})$ $(Cp' = Cp, R = Me 1, Ph 2; Cp' = Cp^{*}, R = Me 3)$

In a typical preparation, a solution of NaN₃ (0.65 mmol, in 50 ml EtOH) was added to a solution of $[Cp'_2Mo_2-(CO)_4(\mu-SR)_2)](BF_4)_2$ (0.65 mmol, in 20 ml CH₃CN). The mixture was stirred for a few minutes, and the solution changed from red to brown. The solvents were removed to dryness and the residue was recrystallised from CH₃CN–ether (1:1) mixture. Na(BF₄) precipitated and evaporation of the filtrate afforded **1–3** in quantitative yields as a brown powder which was washed with ether (5 ml) and pentane (5 ml).

3 (brown solid), *Anal*. Found: C, 39.7; H, 4.6; N, 1.9. C₂₆H₃₆ Mo₂NO₄S₂BF₄ Calc.: C, 40.5; H, 4.7; N, 1.8.

4.3. Preparation of $[Cp'_2Mo_2(NCO)(CO)_2(CH_3CN)-(\mu-SR)_2](BF_4)$ (Cp' = Cp, R = Me **4**, Ph **5**; $Cp' = Cp^*$, R = Me **6**)

A solution of $[Cp'_2Mo_2(NCO)(CO)_3(\mu-SR)_2](BF_4)$ (0.65 mmol, in 30 ml CH₃CN) was stirred at 90°C for 12 h, and then the solvent was removed under vacuum. The residue was washed with ether (5 ml) and pentane (5 ml) and was identified by spectroscopic data as **4–6**, which were obtained in quantitative yields.

6 (brown solid), *Anal.* Found: C, 41.7; H, 5.0; N, 3.5. C₂₇H₃₉ Mo₂N₂O₃S₂BF₄ Calc.: C, 41.4; H, 5.0; N, 3.5. 4.4. Preparation of $[Cp^*_2Mo_2(NCO)(CO)_2(R'NC)-(\mu-SMe)_2](BF_4) (R' = t-Bu 7, xylyl 8, benzyl 9)$

A suspension of $[Cp_2^*Mo_2(NCO)(CO)_3(\mu-SMe)_2]$ -(BF₄) (0.65 mmol) in 30 ml of tetrahydrofuran was stirred at 66°C for 12 h in presence of 0.65 mmol of *t*-BuNC, xylylNC or benzylNC. Filtration of the mixture and removal of the solvent gave in quantitative yields the ionic brown complexes $[Cp_2^*Mo_2(NCO)(CO)_2(R'NC)(\mu-SR)_2](BF_4)$ **7–9** which were washed with pentane (2×5 ml).

7 (brown solid), *Anal*. Found: C, 42.7; H, 5.4; N, 3.2. C₃₀H₄₅ Mo₂N₂O₃S₂BF₄ Calc.: C, 43.7; H, 5.5; N, 3.4.

9 (brown solid), *Anal.* Found: C, 45.8; H, 5.0; N, 3.3. C₃₃H₄₃Mo₂N₂O₃S₂BF₄ Calc.: C, 46.1; H, 5.0; N, 3.3.

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