$CH_3OC_6H_4COCl$, 1711-05-3; p-$CF_3C_6H_4COCl$, 329-15-7; $CpRu(CO)_2^-K^+$, 84332-45-6; $CpRu(P(C_6H_5)_3)(CO)Cl$, 32613-25-5; C_6H_5MgBr, 100-58-3; p-FC_6H_4MgBr, 352-13-6; p-$CH_3C_6H_4MgBr$, 4294-57-9; p-$CH_3OC_6H_4MgBr$, 13139-86-1; trimethylsilyl triflate, 27607-77-8; propene, 115-07-1.

Supplementary Material Available: ^{13}C NMR data for **9a–d**, **14a–d**, **16a–d**, **18a–d**, **20a–d**, **22a–d**, ^{13}C NMR data for PPh_3 ligand in **3a–d**, **4a–d**, **13a–d**, **11a–d**, and **15a–d**, and analytical data for **7a–d**, **8a–d**, **10a,c,d**, **11a,c,d**, **13c,d**, and **15a,c,d** (5 pages). Ordering information is given on any current masthead page.

Electrochemical Activation of Dinuclear Thiolato-Bridged Molybdenum Complexes $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{0/2+}$ (R = Me, Ph) toward Carbonyl Substitution Reactions. Electrochemical and Chemical Syntheses of Substituted Derivatives. The X-ray Crystal Structure of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$[†,‡]

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The dinuclear thiolato-bridged molybdenum complexes $[Mo_2Cp_2(CO)_{4-n}(L)_n(\mu\text{-}SR)_2]^{2+}$ (L = t-BuNC, n = 1 or 2, R = Me or Ph; L = MeCN, n = 1, R = Me or Ph) are obtained from the tetracarbonyl species $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ via a substitution process which is either oxidatively induced (z = 0) or catalyzed according to an electron transfer chain (ETC) mechanism (z = 2+). The results demonstrate that the reactive species involved in the substitution of t-BuNC or MeCN for CO is an unstable radical cation, intermediate in a single-step two-electron transfer. The nature or R is shown to have a pronounced effect on the substitution lability of the complexes, and this suggests that the substitution takes place according to a bridge-opening process. X-ray analysis of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$ reveals that the dimeric structure of the cation is based on a butterfly $Mo_2(\mu\text{-}S)_2$ core. The complex crystallizes in the space group $P2_1/n$ with a = 19.145 (3) Å, b = 11.583 (3) Å, c = 13.894 (4) Å, β = 96.62 (2)°, and Z = 4; R = 0.064 for refinement of 356 parameters with 2356 unique observations.

Introduction

Polynuclear transition-metal compounds have been extensively investigated in the past few years, owing to their interest as models for catalysis at metal surfaces.[2] Dinuclear complexes, the simplest models of clusters, are also very attractive, and among these compounds, species where bridging (or capping) groups are designed to maintain the metal centers close to each other throughout the reaction sequence of catalytic processes are particularly interesting.[3-12] In this respect, thiolate or sulfide ligands have been widely used to bridge, for example, molybdenum, tungsten, iron, copper, vanadium, or manganese centers in homo- or hetero(di)nuclear complexes.[4-13]

In the course of an electrochemical study of thiolato-bridged dinuclear molybdenum compounds, we observed that the simple $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ complexes presented the interesting property to form substituted derivatives via oxidatively induced (z = 0) *and* electron transfer chain (ETC)[14] catalyzed (z = 2+) processes. Many reactions of that type, which may or may not be catalytic,[14b] have now been reported for mono-,[15-17] di-,[18-21] and polynuclear[22-26] complexes. Transition-metal complexes[27a-d] or oxides[27e,f] are also used to catalyze substitution reactions.

Table I. Cyclic Voltammetry Data[a] Concerning the First Reduction of the $[Mo_2Cp_2(CO)_{4-x}(L)_x(\mu\text{-}SR)_2]^{2+}$ Complexes in Nonaqueous Solvents

R	x	L	solv	$E^{1/2}$ red.1,[b] V/Fc
Me	0		THF	−0.54[c]
Me	0		MeCN	−0.52[c]
Me	1	MeCN	MeCN	−0.91 (−0.87)
Me	1	t-BuNC	THF	−0.84
Me	2	t-BuNC	THF	−1.10
Ph	0		THF	−0.44[c]
Ph	0		MeCN	−0.41[c]
Ph	1	MeCN	THF	−0.76 (−0.71)
Ph	1	MeCN	MeCN	−0.76 (−0.72)
Ph	1	t-BuNC	THF	−0.71
Ph	2	t-BuNC	THF	−0.97

[a] $E^{1/2}$, E_p, and $E_{p/2}$ are obtained at 0.2 V s^{-1} unless stated otherwise. [b] For irreversible systems, the potentials given are E_p ($E_{p/2}$). [c] See ref 1.

The work reported here is concerned with the substitution of nitrile (MeCN) and isocyanide (t-BuNC) for CO

[†] Part 4 of "Electrochemistry of Dinuclear, Thiolato-Bridged Transition-Metal Compounds". See ref 1 for part 3.

[‡] Throughout this paper, Cp stands for (η^5-C_5H_5).

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Table II. Spectroscopic Data (Room Temperature) of $[Mo_2Cp_2(CO)_{4-x}L_x(\mu\text{-}SR)_2]^{2+}(A^-)_2$

compd				IR (cm^{-1})			
R	L	*x*	A	ν(CO)[a]	ν(CN)	^{1}H NMR δ[c]	$^{13}C\{^1H\}$ NMR δ[c]
Me	CH_3CN	1	BF_4	2060 (s), 2025 (m)	2312 (w),[b] 2295 (w)	6.33 (s,[d] 5 H), 6.13 (s, 5 H); 2.83 (s, 3 H), 2.68 (s, 6 H)	220.8, 217.2, 214.7 (s, CO), 139.8 (s, $CH_3\mathit{C}N$), 93.4, 91.2 (s, C_5H_5), 25.4, 16.8 (s, CH_3), 0.14 (s, $\mathit{C}H_3CN$)
Me	CH_3CN	1	PF_6	2060 (s), 2030 (m)	2310 (w),[b] 2280 (w)	6.34 (s, 5 H), 6.16 (s, 5 H), 2.83 (s, 3 H), 2.68 (s, 6 H)	
Me	*t*-BuNC	1	PF_6	2060 (s), 2030 (m)	2175 (m)[a]	6.35 (s, 5 H), 6.17 (s, 5 H), 2.89 (s, 3 H), 2.82 (s, 3 H), 1.69 (s, 9 H)	
Me	*t*-BuNC	2	PF_6	2015 (s)	2177 (s)[a]	6.03 (s, 10 H), 2.72 (s, 6 H), 2.18 (s, 18 H)	
Ph	CH_3CN	1	BF_4	2060 (s), 2035 (m)	2320 (w),[b] 2280 (w)	7.56 (m, 10 H), 6.59 (s, 5 H), 6.47 (s, 5 H), 2.08 (s, 3 H)	221.2, 214.6, 213.9 (s, CO), 138.9 (s, $CH_3\mathit{C}N$), 132.2, 128.1, 127.7, 126.2, 125.9, 125.6 (s, C_6H_5), 95.03, 92.7 (s, C_5H_5), 0.8 (s, $\mathit{C}H_3CN$)
Ph	CH_3CN	3	BF_4	1955 (s)	2320 (w),[b] 2285 (w)	7.49 (m, 5 H), 7.46 (m, 5 H), 6.14 (s, 5 H), 5.90 (s, 5 H), 2.57 (s, 3 H), 2.25 (s, 3 H), 1.87 (s, 3 H)	
Ph	*t*-BuNC	1	PF_6	2094 (sh), 2070 (s), 2038 (s)	2184 (m)[a]	7.62 (m, 5 H), 7.52 (m, 5 H), 6.59 (s, 5 H), 6.46 (s, 5 H), 1.44 (s, 9 H)	

[a] CH_3CN. [b] KBr pellets. [c] CD_3NO_2. [d] Singlet.

at Mo(II) and/or Mo(III) centers. The X-ray crystal structure of the monoacetonitrile complex $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2]^{2+}$ is described, and a possible substitution mechanism is discussed.

Table III. Electrosyntheses of the Monosubstituted Derivatives $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ from the $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ (z = 0, 2+) Complexes[a]

entry	R	*z*	L	n_{app}, F/mol	% substituted[b] complex	% oxidized[c] or reduced
1	Me	0	MeCN	1.7 (rt)	6	78
2	Me	0	MeCN	1.7	67	5
3	Me	0	*t*-BuNC	1.9 (rt)	6	65
4	Me	0	*t*-BuNC	1.8	50	3
5	Ph	0	MeCN	1.5 (rt)	30	70
6	Ph	0	MeCN	1.4	78	3
7	Ph	0	*t*-BuNC	1.8 (rt)	25	65
8	Ph	0	*t*-BuNC	1.5	53	<1
9	Me	2	MeCN	0.45[d]	72	17
10	Me	2	MeCN	0.72[e]	53	36
11	Me	2	*t*-BuNC	0.48	54	40
12	Ph	2	MeCN	0.50	68	14
13	Ph	2	*t*-BuNC	0.44	60	20
14	Me	2	MeCN	0.05–0.1	90	10
15	Me	2	*t*-BuNC	0.05–0.1	75	10
16	Ph	2	MeCN	0.05–0.1	82	5
17	Ph	2	*t*-BuNC	0.05–0.1	75	10

[a] The electrolyses are carried out at 40 °C unless otherwise stated (rt = room temperature) on solutions 0.2–1.2 mM in complex. [b] Yield of substituted derivatives calculated by the comparison of the cyclic voltammetry peak currents (see ref 30). [c] Amount of starting material recovered as the oxidized or reduced form depending on whether the substituted complex is obtained by oxidation of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ or reduction of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$, respectively. [d] Reduction performed at a potential (E_{el} = −0.53 V) where the neutral complex formed is oxidizable. [e] Reduction performed at a potential (E_{el} = −0.60 V) where the neutral complex formed cannot be oxidized.

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Table IV. Electrochemical Oxidation/Electrochemical Reduction Cycles Carried Out with the *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ Complex in the Presence of MeCN or *t*-BuNC at Room Temperature

medium	a	n_{app},^{b} F/mol	substituted^c/ unsubstituted
THF + 20 equiv of *t*-BuNC	1st ox.	1.8	0.4
	1st red.	0.4	1.7
	2nd ox.	0.4	3.3
	2nd red.	0.1	5.0
neat MeCN	1st ox.	1.8	0.5
	1st red.	0.6	1.8
	2nd ox.	0.5	3.8
	2nd red.	0.2	10.0

^{a} Electrochemical oxidations are performed at the potential of the trans/cis^{2+} process; reductions are carried out at a potential in between the reduction peaks of the unsubstituted and substituted dications. ^{b} n_{app} is in F/mol of *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$. ^{c} Ratio of the substituted dication to the unsubstituted parent (either neutral or dicationic).

A preliminary account of the work presented here has already appeared.[28]

Results and Discussion

1. Electrosyntheses of the Monosubstituted Complexes. a. From the Neutral Tetracarbonyl Compounds. The electrochemical oxidation of the neutral dimers performed at the potential of the *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ → *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$ process[1] in neat MeCN or in THF containing added MeCN or *t*-BuNC, leads to the formation of a byproduct along with the expected tetracarbonyl dication. The additional reduction peaks, which are observed only in the presence of the ligands (MeCN or *t*-BuNC), are assigned to the reduction of the singly substituted nitrile or isocyanide complexes (Table I). The nature of the substituted products formed in an *oxidatively induced process* is confirmed by the analytical and/or spectroscopic data of the compounds (Table II).

The cell current recorded during the controlled-potential electrolyses (CPE) of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ (R = Me, Ph) decays almost linearly with the charge passed, which is shown by coulometry to be close to 2 F/mol of starting material (Table III, entries 1, 3, 5, 7). Under these conditions, the substituted derivative is obtained as a minor product for R = Me (L = MeCN and *t*-BuNC; Table III entries 1, 3), whereas significant amounts of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SPh)_2]^{2+}$ (L = MeCN or *t*-BuNC; Table III, entries 5, 7) are recovered at the end of the electrolyses.[29a,30]

The figures in Table III show that the increase in the temperature favors the oxidatively induced substitution process since the acetonitrile or isocyanide complexes are recovered in moderate to good yield (Table III, entries 2, 4, 6, 8).

In the case of other dinuclear SR-bridged molybdenum complexes, $[Mo_2(CO)_8(\mu\text{-}SR)_2]^{2-}$, oxidatively induced substitution of MeCN for CO has been reported to yield the disubstituted complexes $[Mo_2(CO)_6(MeCN)_2(\mu\text{-}SR)_2]$.[11,12a] The singly substituted derivative was identified electrochemically but could not be isolated.[11] This behavior is in sharp contrast with that of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ described above.

b. From the Tetracarbonyl Dication. The results of a typical experiment in which two successive electrochemical oxidation/reduction cycles are performed on a solution (initially) made of $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ (0.5–1.0 mM) and MeCN (or *t*-BuNC) are presented in Table IV. It can be seen that the amount of the substituted dication formed during the first electrolysis (oxidation) along with the parent dication increases on reducing the latter at −0.5 V (eq 2) with a small amount of charge consumed. The low charge consumption is consistent with the fact that reactant and product of the reduction do not differ in their electron count but only in the environment about one of the Mo centers. Accordingly, these experiments reveal that $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SPh)_2]^{2+}$ (L = MeCN, *t*-BuNC) which is obtained in an *oxidatively induced* substitution can also form according to an *electron-transfer chain (ETC)*[14] *catalyzed process.* Neither $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ nor $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$ reacts with the ligand at room temperature (not even at 40 °C on the time scale of the electrochemical experiment); therefore the substitutionally labile species leading to the acetonitrile or isocyanide complexes formed from both the neutral and the dicationic parent must be a *radical cation* (eq 1 and 2). The initi-

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(26) Bruce, M. I.; Matisons, J. G.; Nicholson, B. K. *J. Organomet. Chem.* **1983**, *247*, 321.

(27) (a) Aime, S.; Botta, M.; Gobetto, R.; Osella, D. *Organometallics* **1985**, *4*, 1475; (b) *Inorg. Chim. Acta* **1986**, *115*, 129. (c) Albers, M. O.; Coville, N. J. *Coord. Chem. Rev.* **1984**, *53*, 227. (d) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Organomet. Chem.* **1987**, *326*, 229. (e) Harris, G. W.; Coville, N. J. *Organometallics* **1985**, *4*, 908. (f) Albers, M. O.; Coville, N. J.; Singleton, E. *J. Organomet. Chem.* **1987**, *323*, 37.

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(29) (a) The presence of PhSSPh after completion of large-scale electrolyses of $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ in the presence of *t*-BuNC is detected by CV and ^1H NMR. This demonstrates that fragmentation of the dimer occurs. (b) The low value of n_{app} might be related to some decomposition of the SPh dimer, suggested by the detection of PhSSPh after electrolysis.

(30) The averaged yields of small-scale electrolyses (0.2–1.2 mM solutions of starting material) listed in Table III are derived from a comparison of the cyclic voltammetry (cv) peak currents measured before and after electrolysis for the tetracarbonyl parent and the substituted dication, respectively. This procedure leads to approximate values of the yields which would be obtained more accurately if (i) the diffusion coefficients of the complexes $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ were the same for L = CO, MeCN, and *t*-BuNC and (ii) the electrode processes were identical in nature (i.e. kinetic, reversibility, potential separation of the charge-transfer steps of the EE process).[33] While it may reasonably be assumed that the first condition is fulfilled, the second is obviously not for L = MeCN.

ation step of the process is represented in eq 2.

$$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2] \underset{\pm 1e}{\rightleftharpoons} [Mo_2Cp_2(CO)_4(SR)_2]^{\bullet+} \quad (1)$$

$$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{\bullet+} \underset{\pm 1e}{\rightleftharpoons} [Mo_2Cp_2(CO)_4(SR)_2]^{2+} \quad (2)$$

The substitution of the ligand L for CO and the conversion of the substituted radical cation into product contribute to the chain propagation.

In addition to the termination steps encountered generally in ETC processes, i.e. decomposition of the reactive species,[14,20c,22d] a specific one, related to the two-electron nature of the process, needs be considered in the present case: the unsubstituted radical cation either can be reduced (reaction 1) at the potential of the electrolysis or disproportionate, both reactions leading to the formation of the neutral parent.

The electrochemical reductions carried out at 40 °C (Table III, entries 9–13) display nonlinear (convex) $i_{cell} = f(Q)$ behavior (i_{cell} = cell current; Q = charge passed) consistent with an ETC mechanism.[23a] These electrolyses are completed in a few minutes and produce substantial amounts of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$. We have checked that at this temperature, thermal substitution reactions are unimportant and do not contribute significantly to the catalyzed process. As shown by entries 9 and 10 in Table III a minor variation of the potential applied for the electrochemical reduction of $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{2+}$ causes large modifications of both n_{app} and the product yield. The potential shift is very small indeed, and at first sight, it may look insignificant, but it is twice as large as the peak separation of the reversible system associated with the $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{0/2+}$ couple. The explanation we propose for the observed differences in n_{app} and in the product distribution (Table III) is as follows: when the electrochemical reduction is performed at −0.53 V, the neutral complex formed (eq 1) can be oxidized, whereas this is not possible when the CPE is conducted at −0.60 V (see $E_{1/2}$ in Table I). In the former situation, both anodic and cathodic currents may be flowing, and this would account for the lower value of n_{app}. The higher yield of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$ may then be rationalized by the fact that the reoxidation of $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]$ gives the radical cation a further opportunity to undergo CO substitution. The experiments reported above (and the importance of the choice of the electrolysis potential) demonstrate that electrode reactions play an important part in the ETC-catalyzed substitution process.

However, as expected for such mechanisms, homogeneous reactions are important as well, and as shown below, the substitution of L (MeCN or t-BuNC) for CO may be triggered by a small amount of electricity. The cathodic current (eq 2) is interrupted after 0.05–0.1 F/mol of starting material have passed, so that the electrode reactions (eq 1 and 2 and the oxidation of the substituted radical cation) cannot take place. The propagation of the substitution is monitored by cyclic voltammetry as illustrated in Figure 1. The presence of isopotential points on these curves indicates the absence of side reaction,[31] confirmed by the almost quantitative formation of the singly substituted derivative, at least for L = MeCN (Table III, entries 14, 16). Although the substitution is much slower than when a cathodic potential is continuously applied (see above), the thermal process contributes little to the overall substitution. As it can be seen from Table III (entries 14–17), only little $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ is produced in the present case, that demontrates that this species was produced at the electrode when a reduction potential was applied.

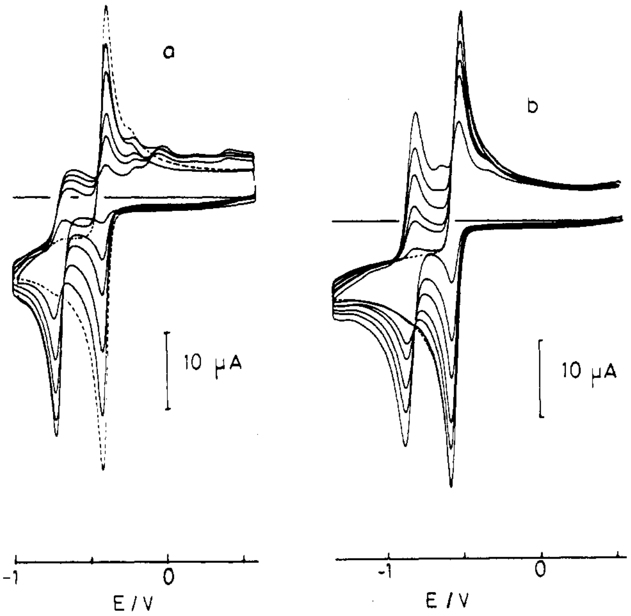

Figure 1. Time dependence of the cyclic voltammetry of a ca. 0.5 mM solution of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$ after initiation of the substitution by a small cathodic current (ca. 5 mn between each recording). **1a**: R = Ph, L = MeCN; charge = 0.1F/mol of starting material; T = 40 °C; MeCN–0.1 M Bu_4NPF_6. **1b**: R = Me, L = t-BuNC; charge = 0.05 F/mol of starting material; T = 40 °C; THF–0.2 M Bu_4NPF_6.

ESR spectra of samples syringed out of the electrochemical cell at different times during the propagation of the electrochemically initiated substitution and immediately frozen have been recorded. The very weak signal observed demonstrates that the amount of paramagnetic species is very low. In a typical experiment on a 1 mM acetonitrile solution of $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{2+}$, the electrolysis was interrupted after 0.1 F/mol of complex has passed so that the concentration of the paramagnetic species should formally[32] be 0.1 mM. The magnitude of the signals observed were not consistent with a 0.1 mM ESR-active species. Since the chain-carrying species of the ETC catalyzed substitution can only be a radical cation, these experiments tell us that the slow step of the process does not involve odd-electron species whose concentration do not build up in the medium.

The disubstituted complexes $[Mo_2Cp_2(CO)_2(t\text{-}BuNC)_2(\mu\text{-}SR)_2]^{2+}$ are prepared from the reduction (T = 40 °C, t-BuNC in excess) of the monosubstituted precursors ac-

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(31) (a) Gaudiello, J. G.; Wright, T. C.; Jones, R. A.; Bard, A. J. *J. Am. Chem. Soc.* **1985**, *107*, 888. (b) Dietrich, M.; Heinze, J.; Fischer, H.; Neugebauer, F. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1021. (c) Hinkelmann, K.; Mahlendorf, F.; Heinze, J.; Schacht, H.-T.; Field, J. S.; Vahrenkamp, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 352.

(32) Because the radical cation is only a thermodynamically unstable intermediate in a two-electron step,[1] the amount of paramagnetic species actually present in the solution cannot be calculated simply from the charge consumed.

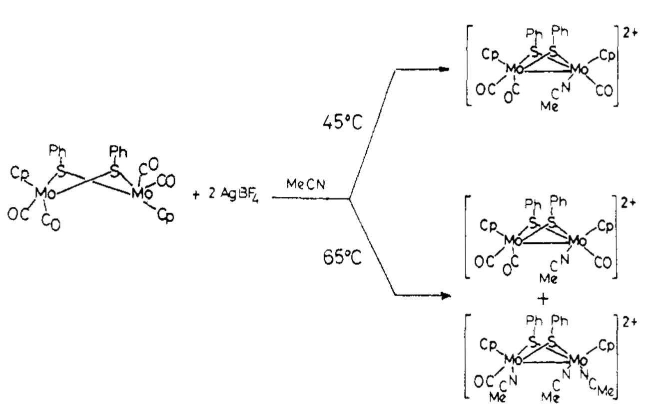
(33) The CV peak current ($i_{p(2e,rev)}$) observed in the case of a single-step, reversible two-electron transfer with a ΔE_p of 29 mV is 2.83 times that of a reversible one-electron transfer, $i_{p(1e,rev)}$.[34a] For a two-electron reversible system with a ΔE_p of 42 mV, $i_p = 2.28 i_{p(1e,rev)}$.[34b]

(34) (a) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods. Fundamentals and Applications*; Wiley: New York, 1980; p 218. (b) This coefficient has been worked out from a comparison of the peak current functions at different values of $\Delta E_{1/2}$ (or ΔE_p) in the paper by Richardson and Taube[35] (compare i_p at $\Delta E_{1/2}$ = 35.61 and $\Delta E_{1/2}$ = 0 in Table II of ref 35). A coefficient of 2.41 has been reported by Heinze.[36]

(35) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

(36) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831.

Scheme I



cording to an ETC catalyzed process.[37] The IR and ^{1}H NMR data (Table II) as well as the redox potentials (Table I) are consistent with the proposed formulation.

2. Chemical Preparation and Structural Analysis of the Substituted Complexes. a. Thermal Syntheses of the MeCN-Substituted Derivatives. As reported previously,[1] the neutral complexes $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ (R = Me, Ph) are readily oxidized by mild oxidizing agents such as silver(I) ions. Thermal treatment of the dimers with $Ag(BF_4)$ in acetonitrile yielded a mono- or trisubstituted derivative depending on the experimental conditions. When R is Ph, only the monosubstituted product was isolated when the experiment was conducted at 45 °C; on heating at 65 °C, both the mono and trisubstituted complexes were formed (Scheme I).

When R = Me, only the monosubstituted complex was obtained at any temperature. The isolated yield of nitrile complexes depends on the nature of R, and it increases in the order Ph < Me.

The monosubstituted derivatives were also obtained on refluxing an acetonitrile solution of the tetracarbonyl dication (eq 3).

$$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+} \xrightarrow[\text{reflux}]{\text{MeCN}} [Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+} \quad (3)$$

$$R = Me, Ph$$

Attempts to substitute *t*-BuNC for CO on reacting the neutral dimers $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ with $Ag(BF_4)$ and 5–10 equiv of *t*-BuNC proved unsuccessful. Furthermore, no reaction occurred after heating the dication $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$ with 7 equiv of *t*-BuNC at 40 °C overnight. In the presence of a reduction current, the substitution reaction is over in a few minutes; the *t*-BuNC-substituted complexes were only obtained under electrochemical activation (section 1).

The MeCN-substituted derivatives behave as 1:2 electrolytes in acetonitrile. They were characterized by IR and NMR spectroscopies (Table II) and elemental analyses (Experimental Section), and a X-ray diffraction study was performed on $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$. The monosubstituted dications are quite insoluble in dichloromethane whereas the trisubstituted compound $[Mo_2Cp_2(CO)(MeCN)_3(\mu\text{-}SPh)_2]^{2+}$ is readily soluble in this solvent.

The ^{1}H NMR spectra of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ (R = Me, Ph) show the expected peaks for the thiophenyl or thiomethyl and cyclopentadienyl protons and a further singlet around 2.5 ppm assignable to the acetonitrile protons. The ^{13}C NMR analysis confirms the presence of three terminal carbonyl groups in these derivatives. Two of the three ν(CO) bands expected for these products are observed with the shift of ca. 40 cm^{-1} to lower frequencies as compared to those in the tetracarbonyl parent,[1] reflecting the weaker π-acceptor power of MeCN relative to CO. As it is usually observed for acetonitrile complexes, two bands are observed around 2300 cm^{-1}; the one at higher frequency (2315 cm^{-1}) is assigned to a combination of $\delta_{sym}(CH_3)$ and ν(C–C), the other one (ca. 2285 cm^{-1}) being ascribed to ν(C–N).[38]

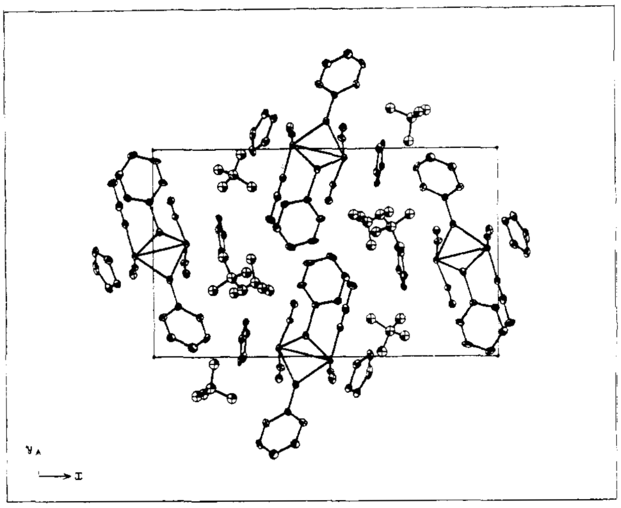


Figure 2. Orthogonal projection of the structure on the (001) plane.

The ^{1}H NMR spectrum of the trisubstituted derivative $[Mo_2Cp_2(CO)(MeCN)_3(\mu\text{-}SPh)_2]^{2+}$ shows as expected three high-field singlets assignable to the MeCN protons as well as two singlets around 6.0 ppm (Cp protons) and the phenyl multiplets at ca. 7.4 ppm. Only one ν(CO) band is observed in the IR spectrum, and this is consistent with the proposed formulation.

The *t*-BuNC derivatives prepared electrochemically were not obtained sufficiently pure to analyze since they were always contaminated by the $[Bu_4N][PF_6]$ supporting electrolyte. Nevertheless, the presence of the *t*-BuNC ligand in the correct ratio is apparent from the ^{1}H NMR spectra. The coordination of the *t*-BuNC at a Mo center is also supported by the presence of a ν(CN) band in the IR spectrum around 2180 cm^{-1} characteristic of a terminal isocyanide ligand. The stretching frequencies are about 30 cm^{-1} higher for these complexes than for the free ligand. This result suggests that the Mo–C(isocyanide) distance in these Mo(III) derivatives is probably very long and excludes the occurrence of significant d → π^* back-donation from the metal to the isocyanide in the dications.

b. Crystal Structure of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$. In order to ascertain the structure indicated by the electrochemical and the spectroscopic results for the nitrile and isocyanide derivatives, an X-ray diffraction study was performed on $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$. Its structure consists of discrete dinuclear dications and BF_4 anions. The packing of these ions is displayed on the orthogonal projection on the (001) plane (Figure 2). The bimetallic group is described with the atom numbering in the ORTEP view (Figure 3). Positional and thermal parameters and selected bond dis-

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[37] R = Me: n_{app} = 0.35 F/mol, average yield 75% based on the monosubstituted complex. R = Ph: n_{app} = ca. 0.4 F/mol, average yield <50% based on the monosubstituted complex.

[38] Storhoff, B. N.; Lewis, H. C. *Coord. Chem. Rev.* **1977**, *23*, 1.

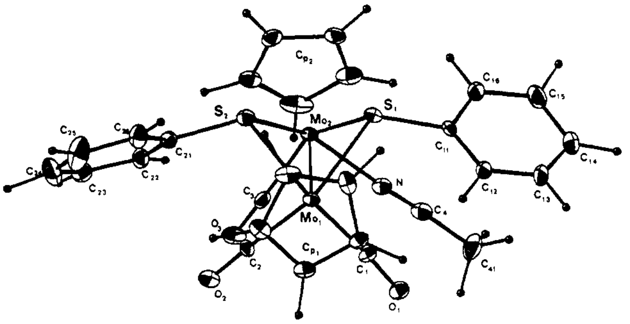

Figure 3. ORTEP view of the bimetallic cation. The atoms are described enclosing 30% probability ellipsoids or spheres. Cp(1) and Cp(2) correspond to the cyclopentadienyl rings (C(61)–C(65)) and (C(51)–C(55), respectively.

tances and angles are listed in Tables IV and V, respectively.

The core of the cationic fragment is defined by the $MoCp(CO)_2$ and MoCp(CO)(MeCN) units connected by a Mo–Mo bond and two sulfur atoms bonded to both Mo centers. A comparison of the bond lengths in the substituted complex and in the related tetracarbonyl compound $[Mo_2Cp_2(CO)_4(\mu\text{-S-}t\text{-Bu})_2](BF_4)_2$ studied previously[1] indicates very similar Mo–Mo distances, but the S···S distance (2.865 (12) Å) tends to be slighly longer (e.g. 2.789 (6) Å in the tetracarbonyl complex). This difference between the two compounds could be due to the different sulfur substituents; the mesomeric effect of the phenyl group would be to induce a positive charge at the sulfur atoms. This could explain the lengthening of the S···S distance in $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SPh})_2](BF_4)_2$. Another possible explanation is the stronger destabilization of the sulfur lone pairs by the *t*-Bu substituents, which in turn allows them to mix more significantly into the vacant molecular orbitals of the complex, the result being a slightly less repulsive (or more attractive) S···S interaction. We hope that MO calculations presently in progress[39] will help to rationalize this trend.

The observed Mo(1)–Mo(2) bond length, 3.006 (3) Å, compares favorably with those found in most of the other complexes of similar geometry (see ref 10f and references cited therein). The Mo–S–Mo angles subtended at the μ-S atoms are acute (75°) and are comparable to those required for a structure in which metal–metal attraction exists.[1,8c,10d]

The coordination geometry about each molybdenum atom can be described as distorted pyramidal. The two pyramids share a common edge defined by two SPh ligands. The metallic atom is capped by a cyclopentadienyl unit. The cyclopentadienyl rings are both planar and form a dihedral angle of 33.9 (1)°. The cyclopentadienyl rings and therefore the two pairs of carbonyl and carbonyl/acetonitrile ligands adopt a mutually cis configuration. The two phenyl rings are syn with respect to the S···S vector. The acetonitrile ligand coordinates to Mo(2) in a linear fashion, and the N–C(4)–C(41) angle deviates only slightly from 180°. The Mo–N bond length of 2.12 (3) Å is very similar to the corresponding distances observed in the complexes $[MoCp_2I(MeCN)](PF_6)$,[40] $[MoI_3(EtCN)_3]$,[41] and $[Mo_2I_4(PhCN)_4]$[41] but is much shorter than for other neutral dinuclear compounds such as $[Mo_2(CO)_6(MeCN)_2(\mu\text{-SCH}_2CO_2Et)_2]$ (2.230 (5) Å).[12b] The Mo–C and C–O distances are in the ranges 2.00–2.02 and 1.14–1.17 Å, respectively, and compare well with those found in the tetracarbonyl parent complex[1] but indicate a somewhat smaller molybdenum electron back-donation to the vacant π^* orbitals of the carbonyls than in similar sulfur-bridged complexes (Mo–C = 1.93–1.94 Å and C–O = 1.17–1.18 Å).[8b,10d,f]

Table V. Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^4$) for $[Mo_2Cp_2(CO)_3(NCMe)(\mu\text{-SPh})_2](BF_4)_2$[a]

atom	*x*	*y*	*z*	U_{eq}
Mo(1)	4244 (1)	432 (1)	7575 (1)	436 (11)
Mo(2)	5740 (1)	−185 (1)	7343 (1)	432 (11)
S(1)	4927 (3)	1005 (5)	6245 (3)	544 (32)
S(2)	4686 (3)	−1318 (5)	6828 (4)	574 (33)
O(1)	4813 (6)	2518 (13)	8882 (10)	684 (40)
C(1)	4646 (10)	1744 (18)	8388 (13)	507 (50)
O(2)	4432 (6)	−1019 (12)	9507 (10)	749 (38)
C(2)	4419 (11)	−504 (17)	8804 (13)	553 (50)
O(3)	5973 (6)	−1032 (13)	9527 (10)	803 (40)
C(3)	5850 (10)	−702 (17)	8729 (16)	608 (54)
N	6062 (9)	1411 (16)	7989 (12)	620 (47)
C(4)	6253 (12)	2285 (23)	8285 (16)	759 (66)
C(41)	6479 (12)	3404 (17)	8706 (18)	1073 (76)
C(11)	5207 (10)	2470 (17)	6203 (12)	529 (50)
C(12)	4842 (13)	3394 (18)	6494 (15)	775 (61)
C(13)	5049 (16)	4459 (19)	6385 (17)	1158 (80)
C(14)	5681 (15)	4750 (25)	6051 (18)	1057 (83)
C(15)	6046 (13)	3806 (22)	5697 (17)	992 (73)
C(16)	5823 (11)	2671 (20)	5815 (15)	726 (61)
C(21)	4507 (11)	−2597 (17)	7503 (13)	617 (52)
C(22)	5007 (12)	−3083 (19)	8238 (16)	729 (63)
C(23)	4818 (13)	−4067 (22)	8680 (17)	838 (74)
C(24)	4176 (18)	−4530 (23)	8474 (22)	1311 (98)
C(25)	3702 (15)	−4078 (27)	7772 (25)	1539 (98)
C(26)	3852 (12)	−3090 (20)	7248 (18)	858 (68)
C(51)	6837 (11)	75 (25)	6815 (20)	911 (73)
C(52)	6397 (13)	−353 (23)	6032 (17)	877 (70)
C(53)	6166 (12)	−1479 (21)	6272 (18)	777 (67)
C(54)	6487 (12)	−1700 (22)	7205 (18)	761 (68)
C(55)	6885 (11)	−746 (29)	7565 (18)	1053 (74)
C(61)	3214 (9)	862 (21)	8169 (15)	641 (53)
C(62)	3148 (8)	−193 (22)	7722 (16)	666 (56)
C(63)	3170 (10)	1 (25)	6695 (17)	765 (65)
C(64)	3242 (10)	1142 (23)	6555 (18)	734 (67)
C(65)	3288 (9)	1687 (20)	7449 (16)	599 (55)
B(1)	2043 (11)	−1458 (18)	4828 (15)	1354 (78)
F(11)	2156 (36)	−332 (12)	4876 (10)	1306 (36)
F(12)	2674 (9)	−1942 (16)	4973 (13)	2135 (60)
F(13)	1696 (54)	−1830 (15)	5525 (12)	1807 (54)
F(14)	1765 (66)	−1725 (17)	3971 (13)	2056 (66)
B(2)	2691 (11)	3769 (96)	5124 (17)	1835 (96)
F(21)	2169 (8)	3182 (13)	5446 (11)	1590 (43)
F(22)	2426 (56)	4766 (15)	4785 (13)	1824 (56)
F(23)	2940 (11)	3191 (18)	4449 (79)	2086 (79)
F(24)	3182 (10)	4021 (18)	5829 (13)	1976 (68)

[a] For Mo, S, C, N, and O atoms the thermal factor was of the form $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)\}$ and $U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$. For other atoms (B, F), $U_{eq} = U_{iso}$.

A feature of the structure is the occupancy by a SR group of a coordination site trans to the acetonitrile ligand which is less strongly bonded to the Mo center than are the carbonyl groups. As a consequence, Mo(2)–S(2), 2.445 (9) Å, is shorter than the average of all the other Mo–S distances in the binuclear unit, 2.472 (9) Å, whereas the four Mo–S distances reported for the parent tetracarbonyl compound were very similar (ca. 2.457 (4) Å). Thus, MeCN appears to be a less efficient competitor than CO for the set of metal p and d orbitals shared with the SR groups.

3. Discussion: Mechanistic Speculations. The essential point that must be recalled before the mechanism of the substitution is discussed further concerns the nature of the reactive species. We have demonstrated in section 1 that the reactive species is in an intermediate redox state

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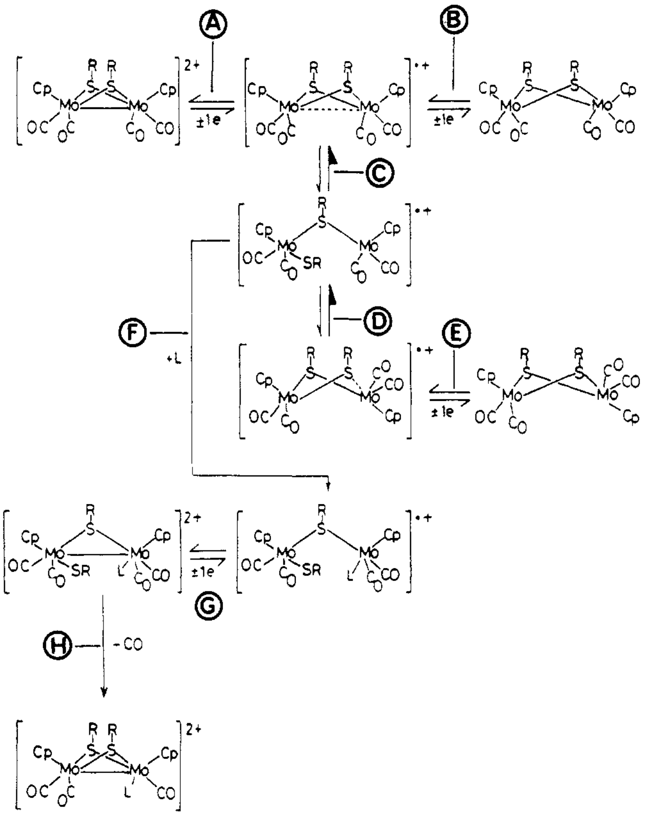
(39) El Khalifa, M.; Pétillon, F. Y.; Saillard, J. Y.; Talarmin, J., to be submitted for publication.

(40) Calhorda, M. J.; de C. T. Carrondo, M. A. F.; Dias, A. R.; Domingos, A. M. T.; Duarte, M. T. L. S.; Garcia, M. H.; Romao, C. C. *J. Organomet. Chem.* **1987**, *320*, 63.

(41) Cotton, F. A.; Poli, R. *J. Am. Chem. Soc.* **1988**, *110*, 830.

Scheme II



between the neutral and the dicationic complexes: it must be a radical cation.

The formation of substituted complexes from an unstable radical cation, involved in a *single-step* two-electron-transfer process,[1] requires the binding of the ligand to be as fast as the electron transfer which it competes with. Nevertheless, the overall substitution reaction is slow as evidenced by the fact that the formation of the product is hardly detected on the CV time scale (see broken line in Figure 1).

The second condition that the proposed mechanism must satisfy is that the rate of the ligand-binding step and that of the electron transfer involving the paramagnetic species are comparable.

The EPR experiments (section 1.b) suggest that the step of the substitution after the ligand binding is the fast oxidation of the radical cation containing a ligand molecule bound to one Mo center into the corresponding dication. The rate-determining step of the process would then be the conversion of this dication into the final product *cis*-$[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$.

Two possible mechanisms may be envisaged. The first one is based on the *bridge-opening* process. An equilibrium allowing the cis and trans radical cations to interconvert via an "open" species with one terminal and one bridging SR group, as shown in Scheme II, steps C and D, would account for the following: (i) rapidity of the substrate-binding step (Scheme II, step F) (the postulated bridge opening would lead to the exposure of a vacant coordination site); (ii) the fast *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ → *cis*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^{2+}$ isomerization, provided the equilibria between the radical cations (Scheme II, steps C and D) lie toward the cis one (this position of the equilibria would also explain why the CV does not allow the substitution or the isomerization of the cis dication to be detected (Figure 1, broken line)); (iii) the substantial effect of the sulfur substituent R on the reactivity of the complex toward substitution and possibly on the distribution of the neutral complex between the cis and trans geometry[1] (the observed effect might result from the easier cleavage of a metal–sulfur bond for thiolate ligands bearing withdrawing substituents, as mentioned previously).[42]

The rate-determining step of the process in the bridge-opening assumption would be the conversion of the "open" dication into product (Scheme II, step H). The isomerization process illustrated in Scheme II (steps A–E) differs from the one we reported previously[1,43] in that it is a radical (steps C and D) rather than a dication[1,43] which undergoes the rapid trans → cis conversion. This is consistent with the "four-component" scheme indicated[44] by the detection of three of the species involved in the isomerization process.

According to our preliminary extended Hückel MO study,[39] the breaking of one Mo–S bond in the radical cation (as well as in the neutral complex) appears easy: we found the open form of the complex to be less stable by only ~0.8 eV and model calculations suggest that steric repulsion can be minimized during the bond-opening reaction by a rotation of the decoordinated $MoCp(CO)_2$ moiety. The question of the localization of the single electron in the open form of the radical complex remains still unsolved, but in any case, its LUMO is preponderantly localized (66%) on the decoordinated Mo atom and can be unambiguously associated with the existence of a vacant coordination site at this metal center.

However, the cleavage of a Mo–S bond is not a priori necessary for the isomerization to occur if one assumes a Mo···Mo bonding interaction in the radical cation. Indeed, since a $MoCp(CO)_2$ fragment bears two π-type frontier orbital close in energy, during the rotation there is always a linear combination of these two orbitals available to stabilize the out-of-phase combination of the sulfur lone pairs (the in-phase combination is stabilized by the σ-type frontier orbital of $MoCp(CO)_2$). Our molecular orbital study[39] is consistent with this hypothesis, but considerable steric problems were encountered in our calculations when one $MoCp(CO)_2$ fragment is rotated.

An alternative mechanism in which the binding of the L ligand to the radical cation and the loss of a CO group from that species would be a concerted process may also be considered. In that case a possible slow step would be the formation of a radical cation from the disproportionation of the neutral and dicationic species. While this process cannot be ruled out in the case where the substitution is triggered by the passage of a small amount of electricity, the substantial effect of the sulfur substituent suggests that the *bridge-opening* process is more likely.

These two possibilities are being further considered from a theoretical point of view and will be reported separately.[39]

Experimental Section

All the experiments (preparations, electrochemistry) were carried out under N_2 or Ar. The purification of the solvents, the electrochemical equipment, and the IR and NMR instruments were described previously.[1]

The neutral dimers $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ were prepared according to published procedures.[10b] Standard Schlenk techniques were used for preparative experiments.

(a) Thermal Syntheses. Preparation of the dicationic complexes $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2](A)_2$ (R = Ph, A = BF_4; R = Me, A = BF_4 or PF_6) and $[Mo_2Cp_2(CO)(MeCN)_3(\mu\text{-}SPh)_2](BF_4)_2$.

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Method 1. The dimeric complex $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ (R = Ph, 5 × 10^{-4} mol; R = Me, 2 × 10^{-3} mol) was added to 2 equiv of $AgBF_4$ in MeCN. The mixture was stirred and heated at 45 °C (R = Ph) or 65 °C (R = Me). The progress of the reaction was monitored by IR spectroscopy; after 30 min, the reaction of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ was nearly complete and the color changed from dark brown to red-brown. The solution was filtered through 10 cm of Celite to remove silver and was then evaporated to dryness. The residue was stirred in dichloromethane. The monosubstituted dications are insoluble in CH_2Cl_2 and were separated by filtration and washed twice with pentane. The products were recrystallized from a $MeCN/CH_2Cl_2$ (1/2) solution (yields: ca. 50%, R = Ph; ca. 75%, R = Me).

When R = Ph, the experiment was also conducted at 65 °C in MeCN. Two substituted products, $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$ (yield: ca. 28%) and $[Mo_2Cp_2(CO)(MeCN)_3(\mu\text{-}SPh)_2](BF_4)_2$ (yield: ca. 26%), were obtained. The two products were separated by filtration, the singly substituted complex being insoluble in dichloromethane, whereas the trisubstituted derivative is fairly soluble in that solvent. The olive-green $[Mo_2Cp_2(CO)(MeCN)_3(\mu\text{-}SPh)_2](BF_4)_2$ was washed twice with pentane.

Anal. Calcd for the monosubstituted molybdenum complex (R = Ph, A = BF_4) $C_{27}H_{23}B_2F_8Mo_2NO_3S_2$: C, 38.6; H, 2.8; N, 1.7. Found: C, 37.9; H, 3.0; N, 1.7. Molar conductivity (in MeCN, *c* 10^{-3}): 406 Ω^{-1} cm^2 mol^{-1}.

Anal. Calcd for the trisubstituted molybdenum complex (R = Ph, A = BF_4) $C_{29}H_{29}B_2F_8Mo_2N_3OS_2$: Mo, 22.2; H, 3.3. Found: Mo, 21.9; H, 3.3. Molar conductivity (in MeCN, *c* 10^{-3}): 350 Ω^{-1} cm^2 mol^{-1}.

Method 2 (A = BF_4 or PF_6). One gram of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2](A)_2$ (R = Ph, A = BF_4; R = Me, A = PF_6; 1.2 × 10^{-3} mol) was heated at reflux in MeCN. The progress of the reaction was monitored by IR; after 1 (R = Ph) and 24 h (R = Me) the dicationic parent compound was not observed anymore. The solution was then evaporated to dryness, and the residue was stirred in dichloromethane. The singly substituted derivatives $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2](A)_2$ are insoluble in dichloromethane and were obtained by filtration, washed with pentane, and dried (yield: ca. 95%).

Anal. Calcd for the monosubstituted molybdenum derivative (R = Me, A = PF_6): C, 24.5; H, 2.3; N, 1.7. Found: C, 24.2; H, 2.4; N, 1.7. Molar conductivity (in MeCN, *c* 10^{-3}): 346 Ω^{-1} cm^2 mol^{-1}.

(b) Electrosyntheses. Due to the low solubility of the tetracarbonyl dications, "large-scale" electrosyntheses (ca. (1–3) × 10^{-4} mol of starting material) were more conveniently carried out by oxidation of the corresponding neutral complex in the presence of the appropriate ligand.

(1) Monosubstituted Complexes. $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2](A)_2$ (L = *t*-BuNC, R = Me, Ph; L = MeCN, R = Me). We describe the experimental procedure for the electrochemical synthesis of $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SR)_2](PF_6)_2$ only. The MeCN analogue was prepared under the same conditions except that *t*-BuNC was replaced by MeCN (the electrolyses were then carried out in neat acetonitrile). The electrolyses were performed in a three-compartment cell. The working electrode was either a carbon rod or a platinum cylinder for oxidations and either of these two electrodes or a Hg pool for reductions. The secondary electrode was a platinum cylinder.

In a typical experiment, a ca. 10^{-2} M solution of $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]$ (0.15 g of complex for R = Me; 0.18 g of complex for R = Ph dissolved in 30 mL of a THF; 0.2 M $[Bu_4N][PF_6]$ electrolyte) was oxidized at 0 V in the presence of 10 equiv of *t*-BuNC at 40 °C; the initial brown solution turned red. After the consumption of ca. 1.7 F/mol of starting material for R = Me (ca. 1.4 F/mol for R = Ph) the electrolysis current decayed to the background level. The resulting solution syringed out of the cell and transferred in a Schlenk flask was taken down to dryness. The solid (substituted complex + degradation products + supporting electrolyte) was stirred twice with 100 mL of toluene in order to remove the unidentified decomposition product. The substituted complex is insoluble in toluene and was obtained (together with some supporting electrolyte) by filtration and washed with hexane.

(2) Disubstituted Complex. $[Mo_2Cp_2(CO)_2(t\text{-}BuNC)_2(\mu\text{-}SMe)_2](PF_6)_2$. The mixture (monosubstituted complex + supporting electrolyte) obtained as described above was dissolved in THF, and the solution was reduced at −0.95 V at 40 °C, in the presence of 5–10 equiv of *t*-BuNC (the concentration of monosubstituted complex was roughly estimated from the peak current in cyclic voltammetry). The cell current decreased very rapidly (ETC process), and the electrolysis was over after about 10–20 min. The same workup as before led to a mixture of disubstituted complex and supporting electrolyte.

(c) Crystal Structure of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$. The specimen was a red-brown plate of dimensions 0.2 × 0.1 × 0.1 mm. All measurements were made with Mo Kα

Table VI. Interatomic Distances (Å), Angles (deg), and Dihedral Angles (deg) with Estimated Standard Deviations

	Bonds Distances		
Mo(1)–Mo(2)	3.006 (3)	Mo(2)–S(1)	2.472 (9)
Mo(1)–S(1)	2.474 (9)	Mo(2)–S(2)	2.445 (9)
Mo(1)–S(2)	2.471 (9)	Mo(2)–C(3)	2.00 (4)
Mo(1)–C(1)	2.00 (3)	Mo(2)–N	2.12 (3)
Mo(1)–C(2)	2.02 (3)	C(3)–O(3)	1.17 (4)
C(1)–O(1)	1.15 (3)	C(4)–N	1.14 (4)
C(2)–O(2)	1.14 (3)	C(4)–C(41)	1.47 (5)
Mo(1)–C(61)	2.28 (3)	Mo(2)–C(51)	2.32 (4)
Mo(1)–C(62)	2.25 (3)	Mo(2)–C(52)	2.34 (3)
Mo(1)–C(63)	2.32 (3)	Mo(2)–C(53)	2.33 (3)
Mo(1)–C(64)	2.39 (4)	Mo(2)–C(54)	2.29 (3)
Mo(1)–C(65)	2.33 (3)	Mo(2)–C(55)	2.27 (4)
mean	2.31	mean	2.31
C(61)–C(62)	1.37 (4)	C(51)–C(52)	1.39 (5)
C(62)–C(63)	1.45 (4)	C(52)–C(53)	1.43 (5)
C(63)–C(64)	1.35 (5)	C(53)–C(54)	1.39 (5)
C(64)–C(65)	1.39 (5)	C(54)–C(55)	1.40 (5)
C(65)–C(61)	1.40 (4)	C(55)–C(51)	1.41 (5)
mean	1.39	mean	1.40
S(1)–C(11)	1.78 (3)	S(2)–C(21)	1.81 (4)
C(11)–C(12)	1.36 (4)	C(21)–C(22)	1.43 (4)
C(12)–C(13)	1.31 (4)	C(22)–C(23)	1.36 (5)
C(13)–C(14)	1.39 (5)	C(23)–C(24)	1.34 (5)
C(14)–C(15)	1.42 (5)	C(24)–C(25)	1.36 (5)
C(15)–C(16)	1.40 (5)	C(25)–C(26)	1.40 (5)
C(16)–C(11)	1.37 (4)	C(26)–C(21)	1.39 (4)
mean	1.38	mean	1.38
B(1)–F(11)	1.32 (3)	B(2)–F(21)	1.33 (3)
B(1)–F(12)	1.32 (3)	B(2)–F(22)	1.33 (3)
B(1)–F(13)	1.31 (3)	B(2)–F(23)	1.29 (3)
B(1)–F(14)	1.29 (3)	B(2)–F(24)	1.31 (3)
	Nonbonding Distances		
S(1)···S(2)	2.865 (12)		
	Bond Angles		
Mo(1)–S(1)–Mo(2)	74.9 (0.3)	Mo(1)–S(2)–Mo(2)	75.4 (0.3)
Mo(1)–S(1)–C(11)	117.8 (1.1)	Mo(1)–S(2)–C(21)	111.1 (1.1)
Mo(2)–S(1)–C(11)	112.3 (1.1)	Mo(2)–S(2)–C(21)	119.2 (1.2)
S(1)–Mo(1)–S(2)	70.8 (0.3)	S(1)–Mo(2)–S(2)	71.3 (0.3)
C(1)–Mo(1)–C(2)	85.1 (1.4)	C(3)–Mo(2)–N	82.0 (1.2)
C(1)–Mo(1)–S(1)	90.9 (1.0)	C(3)–Mo(2)–S(1)	138.4 (1.0)
C(1)–Mo(1)–S(2)	137.2 (1.2)	C(3)–Mo(2)–S(2)	96.4 (1.1)
C(2)–Mo(1)–S(1)	136.5 (1.0)	N–Mo(2)–S(1)	84.6 (0.8)
C(2)–Mo(1)–S(2)	83.3 (1.0)	N–Mo(2)–S(2)	141.6 (0.8)
C(1)–Mo(1)–Mo(2)	86.1 (1.0)	S(1)–Mo(2)–Mo(1)	52.6 (0.2)
C(2)–Mo(1)–Mo(2)	84.0 (1.0)	S(2)–Mo(2)–Mo(1)	52.7 (0.2)
S(1)–Mo(1)–Mo(2)	52.5 (0.2)	C(3)–Mo(2)–Mo(1)	87.9 (1.0)
S(2)–Mo(1)–Mo(2)	51.9 (0.2)	N–Mo(2)–Mo(1)	89.0 (0.8)
Mo(1)–C(1)–O(1)	173.3 (3.1)	Mo(2)–C(3)–O(3)	174.1 (3.1)
Mo(1)–C(2)–O(2)	171.6 (3.2)	Mo(2)–N–C(4)	175.8 (3.3)
		N–C(4)–C(41)	177.3 (4.5)

Least-Squares Best Planes

plane 1	ring [C(11)→C(16)]	plane within 0.04 Å
plane 2	ring [C(21)→C(26)]	plane within 0.02 Å
plane 3	ring [C(51)→C(55)]	plane within 0.02 Å
plane 4	ring [C(61)→C(65)]	plane within 0.02 Å
plane 5	Mo(1)–Mo(2)–C(1)–O(1)	plane within 0.01 Å
plane 6	Mo(1)–Mo(2)–C(2)–O(2)	plane within 0.01 Å
plane 7	Mo(1)–Mo(2)–C(3)–O(3)	plane within 0.01 Å
plane 8	Mo(1)–Mo(2)–N–C(4)–C(11)	plane within 0.02 Å

Dihedral Angles: 1–2, 65.6 (1); 3–4, 33.9 (1); 6–7, 13.8 (1); 5–8, 11.9 (1)

X-rays, $\lambda = 0.71069$ Å, on an Enraf-Nonius CAD4F diffractometer equipped with a graphite monochromator (Centre de Diffraction Automatique de Lyon I).

Crystal data: $C_{27}H_{23}B_2F_8Mo_2NO_3S_2$, $M = 838.6$, monoclinic, space group $P2_{1/n}$, $a = 19.145$ (3) Å, $b = 11.583$ (3) Å, $c = 13.894$ (4) Å, $\beta = 96.62$ (2)°, $V = 3061$ Å^3, $Z = 4$, $D_{\text{calcd}} = 1.82$ g·cm^{-3}, μ(Mo Kα) = 0.9 mm^{-1}, and $T = 293$ K.

Unit-cell dimensions and crystal orientation were determined by a least-squares fit to the setting angles of 25 reflections with $15 < \theta < 20°$. The space group was determined from the systematic absences.

The intensities of 5387 independent reflections with $2 \leqslant \theta$(Mo Kα) $\leqslant 50°$ and $0 \leqslant h \leqslant 22$, $0 \leqslant k \leqslant 13$, and $-16 \leqslant l \leqslant 16$ were measured by using the ω–2θ scan method. One standard reflection ($\bar{5}\bar{1}6$), scanned every 100 reflections, was used to place the intensity data on a common scale; systematic variations in this standard were not observed. Correction was made for Lorentz–polarization effects but not for absorption. A total of 2356 reflections with $F > 5\sigma(F)$ were considered as observed and used in the structure refinement.

Application of automated direct methods followed by a tangent expansion used in the new SHELX-86[45] program gave rise to the location of all the atoms of the asymmetric bimetallic unit (Mo···Mo ≈ 3.00 Å). Subsequent refinement of the molybdenum, sulfur, nitrogen, oxygen, and carbon coordinates and further using of difference Fourier map allowed to the location of the two BF_4 anions. All hydrogen atoms were observed in difference syntheses, but their positions were deduced from geometrical consideration (C–H = 1.08 Å) and they were allowed to ride on the carbon atoms to which they are bonded, with U(H) = 0.075 Å^2. Anisotropic displacement parameters were used for non-hydrogen atoms except for B and F which were refined with isotropic parameters. Final refinement (SHELX-76)[46] of 356 parameters converged with $R = 0.064$ and $R_w = 0.063$ (weighting scheme $w = 3.75/|\sum \sigma^2|F_o| + 0.0001F_o^2)$. The electronic residual densities ranged from −0.60 to +1.00 e Å^{-3}. Final atomic coordinates are listed in Table VI.

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Registry No. $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$, 66212-49-5; $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]^{2+}$, 109031-75-6; $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]$, 109064-10-0; $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{2+}$, 109031-73-4; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2](BF_4)_2$, 117064-06-9; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2]^{2+}$, 113587-89-6; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$, 113587-86-3; $[Mo_2Cp_2(CO)_3(t\text{-}BuCN)(\mu\text{-}SPh)_2]^{2+}$, 116970-08-2; $[Mo_2Cp_2(CO)_3(t\text{-}BuCN(\mu\text{-}SMe)_2]^{2+}$, 116970-09-3; $[Mo_2Cp_2(CO)_2(t\text{-}BuCN)_2(\mu\text{-}SPh)_2]^{2+}$, 116970-10-6; $[Mo_2Cp_2(CO)_2(t\text{-}BuCN)_2(\mu\text{-}SMe)_2]^{2+}$, 116970-18-4.

Supplementary Material Available: Tables of anisotropic displacement parameters and calculated hydrogen atom positions for $[Mo_2Cp_2(CO)_3(NCMe)(\mu\text{-}SPh)_2](BF_4)_2$ and a complete bond length and angle listing (20 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Electrochemistry of Dinuclear, Thiolato-Bridged Transition-Metal Compounds. 5.[†] The Electrochemical Behavior of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ (L = MeCN, *t*-BuNC; R = Me, Ph)[‡]

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The reductive electrochemistry of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ (R = Me, Ph) has been investigated by cyclic voltammetry (CV), controlled-potential electrolyses (CPE), and coulometry. The complexes undergo a two-electron reduction whose characteristics depend on the nature of L. For L = MeCN, the reduction leads to the rapid decoordination of the L ligand, whereas for L = *t*-BuNC the chemical step detected by CV is the geometrical isomerization of the compounds. The ligand dependence of the nature of the two-electron transfer of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ (L = CO or *t*-BuNC) is tentatively assigned to the effect of the ligand on the magnitude of the metal–metal antibonding character of the HOMO of the neutral complex.

Introduction

The chemistry of sulfide[2,3] and thiolate[4-9] complexes of transition metals has received considerable attention for several years, mainly because of their possible implication in biological[10,11] and catalytic[12] processes. The electrochemistry of this type of compounds has also come increasingly under study.[13-21]

This paper is devoted to the reductive electrochemistry of the $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ complexes (L = MeCN,

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[†] See ref 1 for part 4.

[‡] Throughout this paper, Cp stands for (η^5-C_5H_5).

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