X-rays, λ = 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, $Z = 4$, $D_{calcd} = 1.82$ 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.

Acknowledgment. The CNRS (Centre National de la Recherche Scientifique) and the University of Brest are acknowledged for financial support. We are indebted to Prof. J. E. Guerchais (University of Brest) and Dr. A. Darchen (University of Rennes I) for helpful comments. R.M. is grateful to Prof. G. M. Sheldrick for his contribution to the X-ray analyses during the workshop at Göttingen, June 1987) and to Dr. N. Walker (B.A.S.F. Co.) for interesting discussions.

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)[‡]

Monique Guéguen, Francois Y. Pêtillon, and Jean Talarmin*

UA CNRS 322 "Chimie, Electrochimie et Photochimie Moléculaires" Faculté des Sciences et Techniques,
Université de Bretagne Occidentale, 29287 Brest Cedex, France

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

R	x	L	solv	$E^{1/2}_{red.1}$, V/Fc	ΔE_p, mV	$E_{p(red.2)}$, V/Fc	peak width, mV
Me	0		THF	−0.54[b]	40[b]	−2.13	140
Me	0		MeCN	−0.52[b]	35[b]	−1.91	90
Me	1	MeCN	MeCN	−0.91[c]	40[c,d]	*g*	
Me	1	*t*-BuNC	THF	−0.84	50[e]	−2.45	130
Me	2	*t*-BuNC	THF	−1.10	50–65	−2.71	180
Ph	0		THF	−0.44[b]	40[b]	−1.87	90
Ph	0		MeCN	−0.41[b]	35[b]	−1.66	60
Ph	1	MeCN	THF	−0.76[c]	50[c]	*h*	
Ph	1	MeCN	MeCN	−0.76[c]	40[c,d]	*h*	
Ph	1	*t*-BuNC	THF	−0.71	55[e]	−2.22	150
Ph	2	*t*-BuNC	THF	−0.97	60[f]	−2.69	160

[a] $E^{1/2}$, E_p, ΔE_p, and the peak width are cyclic voltammetry data obtained at a scan rate of 0.2 Vs^{-1} unless otherwise stated. [b] See ref 20b. [c] Peak potential E_p and peak width ($E_p - E_{p/2}$). [d] The peak width measured at 22 °C (scan rate = 0.02 V s^{-1}) is 35 mV; under these conditions, ΔE_p = 60 mV for ferrocene. [e] Peak separation measured at 22 °C, scan rate = 0.02 V s^{-1}; under these conditions, ΔE_p = 65 mV for ferrocene. [f] Peak separation measured at 40 °C, 0.2 V s^{-1}; ΔE_p = 70–80 mV for ferrocene. [g] Secondary redox processes due to $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$(*Mo*═*Mo*) are observed (see Table II). [h] Secondary redox processes due to the postulated $[Mo_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SPh)_2]$ intermediate are observed (see text).

t-BuNC; R = Me, Ph) which are obtained from the tetracarbonyl parent $[Mo_2Cp_2(CO)_4(\mu\text{-}SR)_2]^z$ according to an oxidatively induced (z = 0) or to an electron transfer chain (ETC) catalyzed substitution process (z = 2).[1] The reduction mechanism, the nature of the two-electron transfer step, and the stability of the reduced species are shown to depend on the nature of L and/or R.

Results

Electrochemical Behavior of the Monosubstituted Dications $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$. a. L = MeCN⁺. The cyclic voltammograms of the monosubstituted acetonitrile complexes in neat MeCN are displayed in Figure 1. They comprise primary irreversible reduction and oxidation peaks[22] ($E_{p_{red}}$ are in Table I) and secondary redox processes due to the products generated at the primary reduction step. The redox potentials that are only marginally affected by the nature of the solvent[22a] (MeCN, THF) are more sensitive to the nature of R (Table I).

Table II. Redox Potentials of the $[Mo_2Cp_2(CO)_2(\mu\text{-}SR)_2]$(*Mo*═*Mo*) Complexes in Nonaqueous Solvents

R	solv	$E^{1/2}_{red.1}$, V/Fc	$E^{1/2}_{red.2}$, V/Fc	$E_{p(ox.)}$, V/Fc
Me	THF	−2.06	−2.45	0.09
	MeCN	−1.95	−2.31	−0.03
Ph	THF	−1.97	−2.32	0.18
	MeCN	−1.84	−2.15	−0.01

For the primary reduction of both complexes (R = Me and Ph), the current function, $i_p/v^{1/2}$ varies almost linearly as the scan rate, v, increases from 0.02 to 1 V s^{-1}; a comparison of the peak currents for this reduction and for the uncomplicated one-electron oxidation[13-15] of $[Fe_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$[23] demonstrates that two electrons are involved in the reduction step. The primary reduction peak shifts to more negative potentials by 15 (R = Me) and 19 mV (R = Ph) per 10-fold increase in v, which is consistent with the theoretical value of $30/n$ mV expected in the case of a reversible electron transfer preceding a chemical reaction (EC process).[24] The width of the CV reduction peak ($E_p - E_{p/2}$, see Table I) and the scan rate dependence of its potential indicate that the heterogeneous step is reversible.[25]

The chemical step coupled after the electron transfer consists in the irreversible loss of the coordinated acetonitrile molecule. The CV's in Figure 1 demonstrate that the primary products formed on reducing the $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ complexes *under N_2* depend on the nature of R.

When R = Me, the complex loses rapidly the coordinated MeCN molecule on reduction[26] and one CO ligand is ejected as well: the product observed by CV and re-

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(26) The fact that the MeCN molecule is lost *on* reduction is demonstrated by the absence of reaction when CO is bubbled through a solution of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$. This is illustrated by the fact that the primary reduction step and the oxidative part of the CV recorded under N_2 exactly match those obtained under CO (Figure 1a).

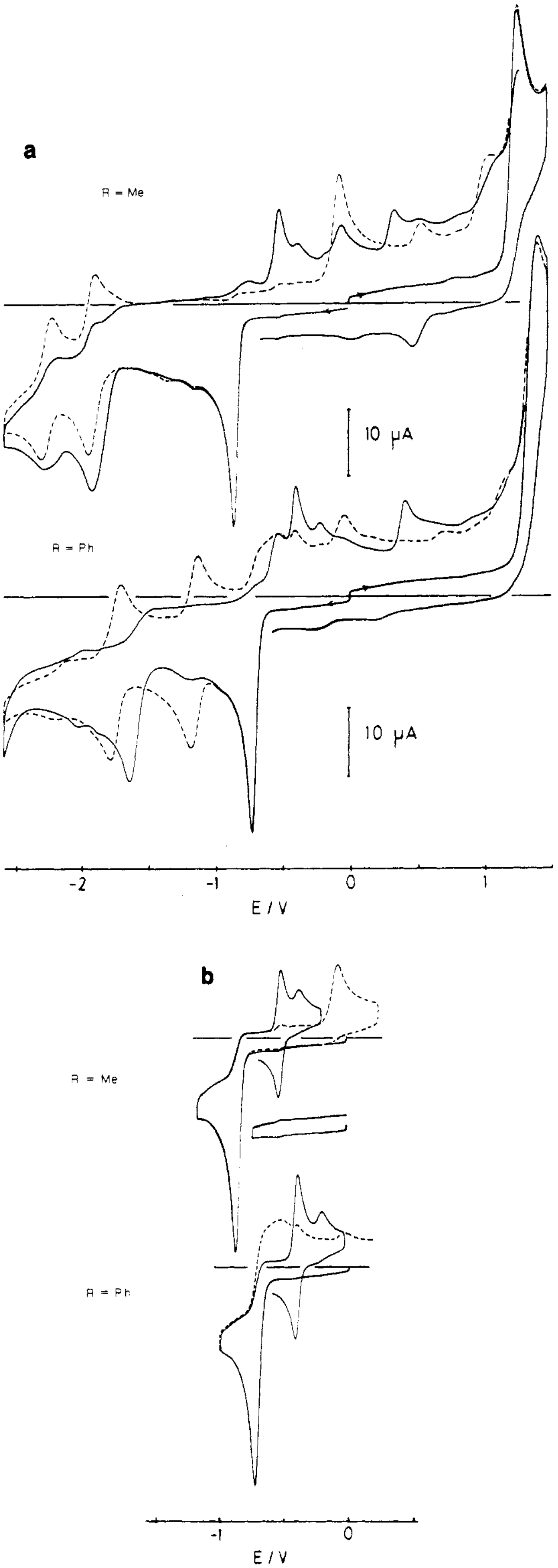

Figure 1. Cyclic voltammetry of a solution of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ (0.45 mM) in MeCN–0.1 M Bu_4NPF_6 under N_2 (dotted line) and under CO (solid line) for R = Me and R = Ph.

covered after controlled-potential electrolyses (n_{app} = 1.9 F/mol of starting material) is $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$ (Mo═Mo, eq 1).

$$[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+} \xrightarrow{+2e} [Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2] + CO + MeCN \quad (1)$$

The latter is identified from the comparison of its redox potentials (Table II) with those of an authentic sample and from its IR spectrum.[27]

In the case where R = Ph, the oxidation current detected on the reverse scan after the reduction has been traversed (Figure 1b, bottom, dotted curve) indicates that some $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2]$ is produced. However, the major reduction product characterized by the reversible reduction systems at $E_{1/2(1)} = -1.16$ V and $E_{1/2(2)} = -1.76$ V in MeCN [$E_{1/2(1)} = -1.26$ V and $E_{1/2(2)} = -1.96$ V in THF] (Figure 1a, bottom, dotted curve) is not the $[Mo_2Cp_2(CO)_2(\mu\text{-}SPh)_2]$ complex. A little reversible reduction couple observed at −2.15 V in MeCN suggests that a small amount of this species is formed on the CV time scale (Table II). The primary (kinetic) product of the reduction, characterized by the two reversible systems, is not stable on the time scale of CPE and therefore it cannot be isolated nor identified with certainty. Nevertheless, this intermediate can be given a reasonable structure from the following observations: (i) controlled-potential electrolyses (n_{app} = 1.5 F/mol) of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2]^{2+}$ under N_2 in a THF electrolyte lead to a mixture of $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ and $[Mo_2Cp_2(CO)_2(\mu\text{-}SPh)_2]$-(*Mo═Mo*); (ii) when the CV of the complex is run *under CO*, the reversible reduction systems (and the irreversible oxidation) associated with the unstable intermediate are replaced by the irreversible reduction (Figure 1a) and the reversible oxidation (Figure 1b) of $[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$ (the cis isomer[20b] is formed on the CV time scale). The oxidation peak assigned to $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SPh)_2]$ is also wiped out (Figure 1b, bottom, solid line). Controlled-potential electrolyses carried out under a CO atmosphere result in the formation of *trans*-$[Mo_2Cp_2(CO)_4(\mu\text{-}SPh)_2]$[20b] only.

These experiments suggest that the kinetic product formed under N_2 can easily bind CO or that its formation is prevented under these conditions. The formulation that we propose for the intermediate $[Mo_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SPh)_2]$ would fit quite nicely the results of the experiments conducted under N_2 or CO as shown in Scheme I.

Although no such species has been detected for R = Me, we believe it is an intermediate between $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$ and $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$. Our reasons are as follows: when either $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$ or the Mo═Mo complex $[Mo_2Cp_2(CO)_2(\mu\text{-}SR)_2]$ are subjected to a CO atmosphere, no reaction takes place.[26,28] Nevertheless, the redox features of $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$ are replaced by those of $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]$ (compare the dotted and solid curves in Figure 1, top) when the CV of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SMe)_2]^{2+}$ is run under CO. These observations therefore indicate that it is an intermediate species between the substituted dication and the Mo═Mo complex which reacts with CO. We propose that this reactive intermediate is the SMe analogue of $[Mo_2Cp_2(CO)_2(\mu\text{-}CO)(\mu\text{-}SPh)_2]$. If this assumption is correct, the difference between the SMe and SPh complexes would lie with the stability of the kinetic product, that is with the lability of

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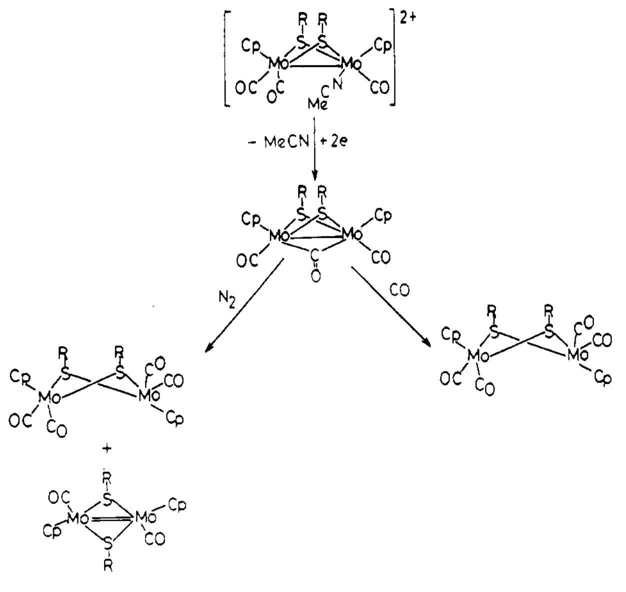
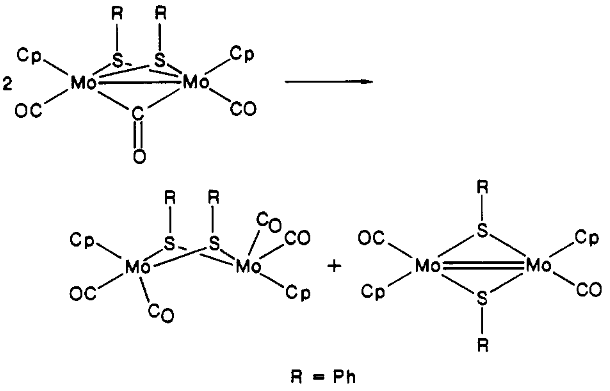
Scheme I[a]



[a] R = Ph. When R = Me, only the $[Mo_2Cp_2(CO)_2(\mu\text{-}SMe)_2]$-($Mo{=}Mo$) species is recovered after electrolyses under N_2.

the bridging carbonyl. The reason why this particular CO would be more tightly held in the phenylthio derivative, which eventually leads to the stable di- and tetracarbonyl complexes (eq 2) via a ligand exchange mechanism, is yet unclear. This exemplifies the effect of R on the half-life of a postulated intermediate of the reduction process.



(2)

Examples of stable complexes with such $M_2(\mu\text{-}SR)_n(\mu\text{-}CO)$ cores are known for M = Fe, R = Et,[29,30] *t*-Bu, or Ph,[30] n = 1, M = Mn, R = H, Me, or $SnMe_3$, n = 2,[31] and M = Mn, R = Me, Ph, or *t*-Bu, n = 2,[19] but as far as we are aware, no examples are known for M = Mo. The occurrence of a *semibridging* CO associated with a thiolate bridge has been reported by us in the case of heterodinuclear Mo–W complexes (R = Me, n = 1).[20a,32] A recent report[19] showed that the $[Mn_2(L)_2(CO)_4(\mu\text{-}SR)_2(\mu\text{-}CO)]$ complexes are involved in an oxidatively induced coordination of MeCN; the resulting cation $[Mn_2(L)_2(CO)_5(MeCN)(\mu\text{-}SR)_2]^+$ rapidly loses the coordinated MeCN molecule upon reduction. In this respect, the behavior of the Mn compounds is quite analogous to that we report for the Mo complexes. However, the order of stability of the complexes appears to be inverted between the Mn and the Mo series: Evans and Treichel[19] reported the crystal structure of the μ-CO complex $[Mn_2(PMe_3)_2(CO)_4(\mu\text{-}SMe)_2(\mu\text{-}CO)]$ while they could only provide electrochemical evidence for the formation of the MeCN species $[Mn_2(L)_2(CO)_5(MeCN)(\mu\text{-}SR)_2]^{0/+/2+}$. In the case of our molybdenum compounds, the μ-CO species that we propose on an electrochemical basis as an intermediate in the reduction of the well-characterized[1] $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ dication is too unstable to isolate. These differences could arise from the electronic properties of the Cp ligand as compared to phosphines.

b. L = *t*-BuNC. Contrasting with the CV of the acetonitrile compounds, that of the *t*-BuNC monosubstituted derivatives (R = Me, Ph) displays a partially reversible primary reduction and an irreversible one at more negative potentials (Table I). When the second reduction is traversed, the anodic current (i_{pa}) for the partially reversible system is severely depressed: the second process is therefore assigned to the reduction of the species generated at the first step, followed by decomposition (eq 3). The reduction process around −2 V was not investigated further.

$$[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SR)_2]^{2+} \underset{\pm 2e}{\rightleftharpoons} [Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SR)_2] \xrightarrow{+ne} \text{product} \rightarrow \text{decomposition} \quad (3)$$

As shown by the $E_{1/2}$ collected in Table I, the substitution of *t*-BuNC for CO results in a complex which is harder to reduce than the parent dication, in agreement with the stronger electron-releasing property of the former ligand. This shift, which is paralleled by the drift of the ν(CO) to lower frequencies,[1] is comparable to those observed for other compounds[33] and illustrates the electronic effect of the ligand on the redox orbital. The peak current ratio i_{pa}/i_{pc} for the first reduction is less than unity, with this value approached only at the fastest scan rate used in this study (1 V s^{-1}), while the current function $i_{pc}/v^{1/2}$ decreases slightly when v increases from 0.02 to 1 V s^{-1}. The scan rate dependence of the reduction peak potential $E_{p(red.1)}$ ($E_{p(red.1)}$ shifts cathodically by 20 mV (R = Me) and by 12–15 mV (R = Ph) per 10-fold increase in v) and of the peak current ratio is consistent with the occurrence of a chemical reaction coupled after the electron-transfer step[24] (EC process). The magnitude of the cathodic current (i_{pc}) as well as the slope of $E_{p(red.1)} = f(\log v)$ are indicative of a two-electron reduction, whose nature is different from that of the parent complex however. This is confirmed by the anodic to cathodic peak separation (ΔE_p) of the corresponding systems in cyclic voltammetry (Table I) and by the slope of the logarithmic plot $E = f[\log (i_d - i)/i]$ for rotating disk electrode (RDE) voltammetry. From the voltammogramms (CV and RDE) of a solution containing the unsubstituted dication, its *t*-BuNC monosubstituted derivative, and ferrocene, the following results are obtained: the CV peak separation is 40, 50, and 70 mV and the slope of the logarithmic plot is 37, 56, and 73 mV for the $[Mo_2Cp_2(CO)_4(\mu\text{-}SMe)_2]^{0/2+}$, $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SMe)_2]^{0/2+}$, and Fc/Fc$^+$ couples respectively. A possible explanation for this difference will be discussed further below.

The chemical step coupled after the electron transfer for L = *t*-BuNC is assigned to the electron-induced cis/trans isomerization of the $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}$

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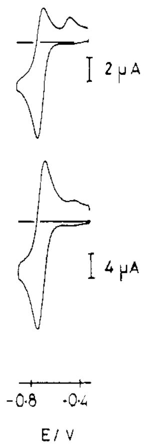

Figure 2. Cyclic voltammetry of $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SPh)_2]^{2+}$ in THF–0.2 M Bu_4NPF_6 at 0.04 (top) and 0.20 V/s (bottom).

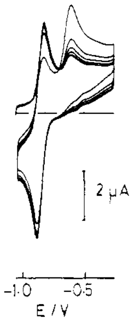

Figure 3. Cyclic voltammetry of an electrogenerated solution of $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SMe)_2]$ in THF–0.2 M Bu_4NPF_6.

$SR)_2]^{0/2+}$ couple, illustrated in Figures 2 and 3. Owing to the similarity of their IR and ^1H NMR spectra with those of *cis*-$[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ (L = CO, MeCN),[1] the *t*-BuNC-substituted dications should also be in the cis geometry. The reversible system is therefore assigned to the redox process of the cis isomer whereas the irreversible peak observed at less negative potentials is assigned to the oxidation of the trans geometry.

The rate constant of the chemical step involving $[Mo_2Cp_2(CO)_2(t\text{-}BuNC)_2(\mu\text{-}SR)_2]^{2+}$ has been evaluated from the scan rate dependence of the peak current ratio[34] i_{pa}/i_{pc}. At room temperature, the subsequent reaction is faster for R = Ph ($k = 0.10\ s^{-1}$) than for R = Me ($k = 0.01\ s^{-1}$). At 40 °C, $k = 0.10\ s^{-1}$ for the SMe derivative.

However, in addition to the isomerization reaction, *t*-BuNC loss also occurs after the reduction of $[Mo_2Cp_2(CO)_3(t\text{-}BuNC)(\mu\text{-}SR)_2]^{2+}$ to the neutral species since $[Mo_2Cp_2(CO)_2(\mu\text{-}SR)_2]$ is the major product of preparative scale electrolyses. Further attempts to produce the neutral substitued complex are in progress.

Discussion

The questions that are addressed in this section are of two different types.

The first question is: why do the substituted complexes with L = *t*-BuNC and L = MeCN behave so differently? And why does the tetracarbonyl neutral (dicationic) complex bind a MeCN molecule on oxidation (reduction)[1] when the resulting product $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-}SR)_2]^{2+}$ loses the coordinated MeCN upon reduction?

Table III. Redox Potentials of the Reversible and Irreversible Oxidation Processes of $[Mo_2Cp_2(CO)_{4-x}(t\text{-}BuNC)_x(\mu\text{-}SR)_2]$

R	x	couple 1[a] $E^{1/2}_{red.1}$, V/Fc	ox. 2[b] $E_{p/2}$, V/Fc
Me	1	−0.84	−0.67
Me	2	−1.10	−0.92
Ph	1	−0.71	−0.51
Ph	2	−0.97	−0.72

[a] The reversible couple 1 is assigned to the cis isomer. [b] The irreversible oxidation is assigned to the trans isomer (see ref 20b).

The second point concerns the nature of the two-electron reduction of the $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ species (L = CO or *t*-BuNC) and the questions are the following: What is the effect of the *t*-BuNC ligand on the characteristics of the EE process? Why do the $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ complexes reduce in a single two-electron step when for similar dinuclear doubly bridged species, discrete redox steps are observed?

a. Influence of R and of L on the Reduction Mechanism of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$. The electrochemical study of the singly substituted complexes has revealed that their behavior is dramatically affected by the nature of L and R. This is ascribed to *electronic effects*.

The reduction of the complexes increases the electron density at the Mo_2S_2 core. The electronic strain may be relieved by a geometrical change which places the added electrons in an orbital of lowest possible energy. This is a classical response of molecules to electron-transfer reactions;[35,36] actually, the occurrence of a geometrical isomerization has been demonstrated for L = CO[20b] and is strongly suggested for L = *t*-BuNC (see Results, part b, and Figure 3). Indeed, the reduction of *cis*-$[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ involves the occupation of its LUMO which is an antibonding Mo–Mo σ-type orbital. Both the lengthening of the metal–metal separation and the cis → trans isomerization provide stabilization to this orbital.[37] The difference in stability of the neutral compounds depending on L suggests that the isomerization may not be sufficient on its own to accomodate the extra electrons and that the L ligand, via its vacant π^* orbitals, may also contribute to dissipate the excess of charge. The effect of L on the redox potentials (Table I) indicates that the LUMO of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-}SR)_2]^{2+}$ contains some ligand character. The reduction of the complex could thus lead to a flux of electrons from the metal d toward the π^* orbitals of the ligand. For L = *t*-BuNC, this could possibly result in the bending of the isocyanide moiety[38-40] as it has been observed for NO[41,42] and aryldiazonium cations[43] on

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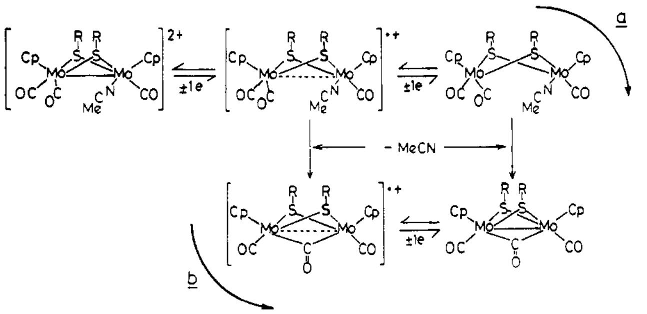
Scheme II[a]



[a] For the reaction of the bridging CO complex, see Scheme I.

electrochemical reduction or on addition of electron-donor ligands. Unfortunately, our attempts to isolate $[Mo_2Cp_2(CO)_3(t\text{-BuNC})(\mu\text{-SR})_2]$ in order to assess the effect of the two-electron reduction on the geometry of the Mo_2S_2 core[44] and on the linearity of the isocyanide ligand have proved unsuccessful so far.

In contrast to CO and *t*-BuNC, MeCN is a mediocre π-acceptor,[38] probably not able to accomodate the increased electron density resulting from the reduction. In this case, a cis/trans isomerization only does not allow the excess of charge to be accommodated and the molecule rearranges to the more stable form $[Mo_2Cp_2(CO)_2(\mu\text{-SR})_2]$ via the loss of MeCN and of one CO group.

A similar effect, although probably less pronounced, might be responsible for the different behavior of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SR})_2]^{2+}$ depending on whether R is an acceptor phenyl group or a donor methyl substituent. From the results reported before, it is quite obvious that R exerts a marked influence not only on the redox potentials of the complexes (Table I) and on the substitution lability of the parents[1] but also on the reduction mechanism of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SR})_2]^{2+}$ and on the stability of their primary reduction products (see Results, part a). Two different routes, illustrated in Scheme II, may be envisaged for the reduction of the MeCN-substituted dication. Owing to the detection of a current that we ascribed to the oxidation of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SPh})_2]$ (see Results, part a), the reduction of the corresponding dication along path a of Scheme II looks very likely. In the case of $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SMe})_2]^{2+}$, the reduction may take place according to either path. The only condition is that the chemical step (MeCN loss) must be fast since neither $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SMe})_2]$ (path a) nor the intervening chemical reaction of the ECE process depicted in path b (Scheme II) have been detected.

Therefore, it appears from this study that the stability of the $[Mo_2Cp_2(CO)_3(L)(\mu\text{-SR})_2]$ molecule is critically dependent on the balance between the electron-acceptor and electron-donor properties of L and R.

b. The Two-Electron Reduction of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-SR})_2]^{2+}$ (L = CO, *t*-BuNC). The results reported above and in a previous paper[20b] demonstrate that two electrons are involved in the reduction of $[Mo_2Cp_2(CO)_3(L)(\mu\text{-SR})_2]^{2+}$. However, the nature (i.e. reversibility and potential) of the electrochemical steps of the EE process (or ECE process if allowance is made that the intervening chemical step C can be a modification of bond angles and/or bond lengths of the Mo_2S_2 core) is dependent on the nature of L.

The nature of the (quasi-) reversible two-electron reduction of the complexes differs depending on L: this is shown by the difference in the peak separation of the cathodic and anodic processes (ΔE_p) and by the slope of the logarithmic plot $E = f[\log (i_d - i)/i]$ (RDE voltammetry).

The larger peak separation observed in the case of $[Mo_2Cp_2(CO)_3(t\text{-BuNC})(\mu\text{-SR})_2]^{2+}$ (Table I) might be the sign of a retardation of the heterogeneous electron transfer,[34] due to the substitution of *t*-BuNC for CO. For the monosubstituted (*t*-BuNC) derivative, the increase in the CV peak separation from 50 mV at 0.02 V s^{-1} to 80 mV at 1 V s^{-1} indicates that the electron transfer is only quasi-reversible. However, there is an alternative that we consider is more likely.

For the tetracarbonyl dication, the values of ΔE_p and of the slope of the logarithmic plot (40 and 37 mV, respectively) are consistent with the 29 mV[47] expected for an EE process, when the second electron transfer (occurring at $E°_2$) is thermodynamically more favorable than the first (occurring at $E°_1$), e.g. for a reduction $E°_2 > E°_1$.

For L = *t*-BuNC, the peak to peak separation and the slope are larger (50 and 56 mV, respectively). Undoubtedly, this is due to the presence of an isocyanide ligand at one Mo center; in the case of $[Mo_2Cp_2(CO)_2(t\text{-BuNC})_2(\mu\text{-SR})_2]^{2+}$ the peak separation is even larger (Table I). The increase in ΔE_p from 40 mV (L = CO) to 50–55 mV (L = *t*-BuNC) is assigned to a modification of the potential separation ($\Delta E°$) of the electron-transfer steps of the EE process: when the two electrons are transferred at the same potential, e.g. $E°_1 = E°_2$, a CV peak separation of 42 mV results.[48] This is consistent with the experimental values (ΔE_p = 50–55 mV) owing to the slight distortion of the CV curves due to uncompensated solution resistance. The modification of $\Delta E°$ is likely to be related to the rather different electronic net effect of *t*-BuNC and CO. The situation of the $E°$'s for the two cases is illustrated schematically in the diagram of Figure 4. The presence of an isocyanide (a comparatively good donor ligand) at a Mo center in the complex can only shift the reduction steps toward more negative potentials. The passage from the situation of the tetracarbonyl complex (Figure 4, top) to that of the *t*-BuNC singly substituted analogue (Figure 4, middle) requires that $E°_2$ be more affected than $E°_1$ by the substitution of *t*-BuNC for CO. The second electron transfer is favored to a much lesser extent, i.e. the stabilization of the redox orbital resulting from the first electron transfer is much less when L = *t*-BuNC than when L = CO. This suggests that the LUMO of the substituted dication $[Mo_2Cp_2(CO)_3(t\text{-BuNC})(\mu\text{-SR})_2]^{2+}$ has a weaker metal–metal antibonding character than the LUMO of the tetracarbonyl dication. This is consistent with the conclusion we arrived at that the LUMO of the former must have some ligand (*t*-BuNC) character.

The substitution of a second CO should have a similar effect on the electrochemical behavior. We observe that in the case of $[Mo_2Cp_2(CO)_2(t\text{-BuNC})_2(\mu\text{-SMe})_2]^{2+}$, the peak separation is about 60 mV at slow scan rate. A close

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(44) From the X-ray crystallographic data reported previously,[28] it appears that the Mo_2S_2 core in $[Mo_2Cp_2(CO)_4(\mu\text{-SPh})_2]$ is highly distorted and that the molecule has only a very low symmetry.[45] The $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]$ complexes are cleaved on reduction.[46]

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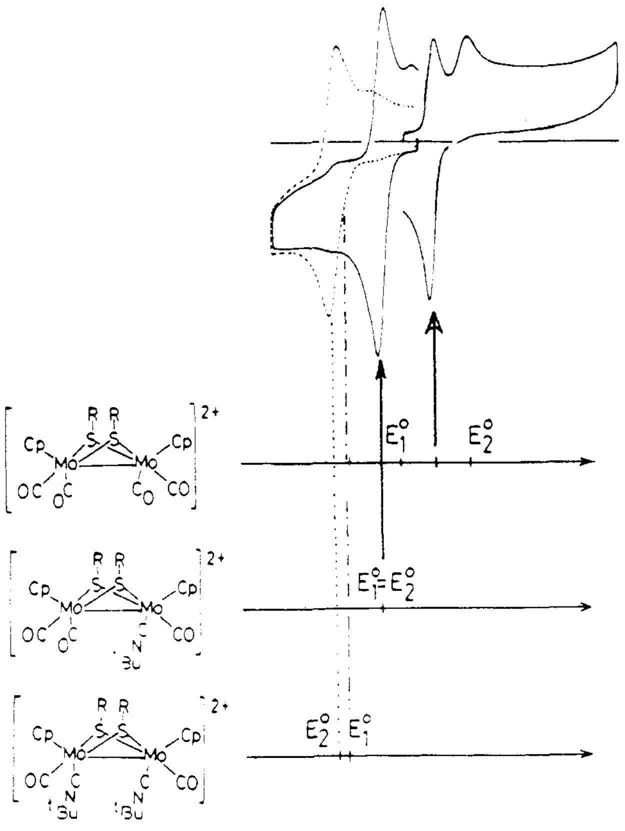

Figure 4. Schematic illustration of the modification of the potential separation $\Delta E° = E_2° - E_1°$ of the two electron-transfer steps of $[Mo_2Cp_2(CO)_{4-x}(t\text{-BuNC})_x(\mu\text{-SR})_2]^{2+}$ for $x = 0$ (top), $x = 1$ (middle), and $x = 2$ (bottom). The value of the potential separation $\Delta E° = E°_1 - E°_2$ chosen for $x = 0$ (top axis) is arbitrary.

inspection of the CV for this complex reveals that both the reduction and the corresponding oxidation peaks of the reversible system present a shoulder. This might be the sign that, under these conditions, the two reduction steps are resolved, the second electron transfer falling just cathodic of the first one; i.e. $E°_1 > E°_2$ (Figure 4, bottom).

The occurrence of such *single step*, two-electron processes has been ascribed to the singly oxidized (reduced) intermediate giving up (accepting) a second electron more easily than the first because of a reorganization of the redox orbitals caused by the transfer of the first electron.[36,49–51] In the case of dinuclear doubly bridged compound, the electron-transfer may result in the formation (or the cleavage) of a metal–metal bond.[18cd,20b,49,52] In this case, parameters such as the M–M separation, the M–E–M and E–M–E angles of the M_2E_2 cores (E = S or P) are strongly affected by the change in the electron count. The variation of the M–M distance on electron transfer demonstrates that the frontier orbitals have a strong dimetal character,[49,53] as predicted by molecular orbital calculations.[54] However, the occurrence of such processes in which two electrons are transferred in a single step is not as general as suggested by Rosenheim et al., even when "metal–metal bonding is present in one form of the couple".[18c] For example, compounds such as $[Fe_2Cp_2(CO)_2(\mu\text{-E})_2]$ (E = $SMe^{13-15,55}$ or PR_2^{55}) undergo two separate one-electron oxidation steps. The decrease of the M–M distance on oxidation[56–58] is an indication of the topological nature of the HOMO in the neutral species.[53] However, at variance with what happens for $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]$[20b] and other complexes,[18d,49] the modification of the energy of the HOMO of $[Fe_2Cp_2(CO)_2(\mu\text{-E})_2]$ (E = SR or PR_2) due to the loss of the first electron is not sufficient to trigger the loss of the second one. This difference in the behavior of otherwise comparable compounds is tentatively assigned to the fact that the HOMO of $[Fe_2Cp_2(CO)_2(\mu\text{-E})_2]$ might not be as strongly M–M antibonding as that of $[Mo_2Cp_2(CO)_4(\mu\text{-SR})_2]$.[45]

Experimental Section

All the experiments (preparations, electrochemistry) were carried out under N_2 or Ar.

Reagents. The synthesis of the molybdenum tetracarbonyl has been reported previously.[20b] The complexes $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SR})_2]^{2+}$ (R = Me, Ph) were prepared either chemically or electrochemically.[1] The *t*-BuNC analogue could not be prepared chemically.[1] The samples used in the electrochemical study were generated in situ from the tetracarbonyl parent (neutral or dication).

Instrumental Data. The electrochemical equipment (cells, sets of electrodes, apparatus) was described previously.[20b] The potentials are quoted against the ferrocene (Fc)/ferrocinium ion couple; Fc was added as an internal standard at the end of the experiments.

Attempted Electrosynthesis of $[Mo_2Cp_2(CO)_3(t\text{-BuNC})(\mu\text{-SMe})_2]$. A mixture of the singly substituted dication $[Mo_2Cp_2(CO)_3(t\text{-BuNC})(\mu\text{-Me})_2]^{2+}$ and supporting electrolyte obtained as described previously[1] was dissolved in THF. The resulting solution was reduced at −0.95 V at room temperature on a Hg pool electrode. The amount of neutral singly substituted complex recovered was always very small, and this species was not separated from the other products of the electrolysis, among which was the disubstituted dication (although the electrolysis was performed in the absence of free *t*-BuNC) and the Mo=Mo dimer $[Mo_2Cp_2(CO)_2(\mu\text{-SR})_2]$. Small-scale electrolyses allowed small amounts of the singly substituted neutral complex to be obtained (see Figure 3).

Acknowledgment. The CNRS (Centre National de la Recherche Scientifique) is acknowledged for financial support. We are grateful to Dr. J. Y. Saillard and to Dr. A. Darchen (University of Rennes I) for helpful discussions and comments.

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; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SPh})_2]$, 116970-11-7; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SPh})_2]^{2+}$, 113587-89-6; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SMe})_2]$, 116970-12-8; $[Mo_2Cp_2(CO)_3(MeCN)(\mu\text{-SMe})_2]^{2+}$, 113587-86-3; $[Mo_2Cp_2(CO)_3(t\text{-BuCN})(\mu\text{-SPh})_2]$, 116970-13-9; $[Mo_2Cp_2(CO)_3(t\text{-BuCN})(\mu\text{-SPh})_2]^{2+}$, 116970-08-2; $[Mo_2Cp_2(CO)_3(t\text{-BuCN})(\mu\text{-SMe})_2]$, 116970-14-0; $[Mo_2Cp_2(CO)_3(t\text{-BuCN})(\mu\text{-SMe})_2]^{2+}$, 116970-09-3; $[Mo_2Cp_2(CO)_2(t\text{-BuCN})_2(\mu\text{-SPh})_2]$, 116970-15-1; $[Mo_2Cp_2(CO)_2(t\text{-BuCN})_2(\mu\text{-SPh})_2]^{2+}$, 116970-10-6; $[Mo_2Cp_2(CO)_2(t\text{-BuCN})_2(\mu\text{-SMe})_2]$, 116970-16-2; $[Mo_2Cp_2(CO)_2(t\text{-BuCN})_2(\mu\text{-SMe})_2]^{2+}$, 116970-18-4; $[Mo_2Cp_2(CO)_2(\mu\text{-SMe})_2]$, 117064-04-7; $[Mo_2Cp_2(CO)_2(\mu\text{-SPh})_2]$, 116970-17-3.

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