Electrochemical Oxidation and Reduction of Rh[Ph₂PC(S)NR]₃ (R = Ph, Me), Rh[Me₂NC(S)NPh]₃ and Rh[Bu₂NC(S)S]₃. Generation of Rhodium(I) Species and Their Reaction with Carbon Monoxide

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Received April 6, 1981

Cyclic voltammetry and pulse polarography show that under nitrogen, the complexes Rh[Ph₂PC(S)-NR]₃ (R = Ph, Me), Rh[Me₂NC(S)NPh]₃ and Rh[Bu₂NC(S)S]₃ are chemically irreversibly oxidised in a one-electron process. Upon oxidation of Rh-[Bu₂NC(S)S]₃, the dimeric species Rh₂[Bu₂NC(S)S]₆²⁺ is most probably formed. Introduction of CO has no influence on the cyclic voltammograms.

Under nitrogen the complexes Rh[Ph₂PC(S)NR]₃ and Rh[Bu₂NC(S)S]₃ are chemically irreversibly reduced in a two-electron process, yielding Rh(I)-species. The reduced product is oxidised in a one-electron step, probably resulting in an unstable Rh(II)-complex. For Rh[Ph₂PC(S)NR]₃ no splitting off of a ligand is observed, whereas under CO one phosphino ligand is displaced by CO after the electrochemical reduction. Even under nitrogen Rh[Bu₂NC-(S)S]₃ displays liberation of dithiocarbamate upon reduction. Under CO the two-electron reduction at the same low potential, is immediately followed by substitution of the ligand with CO and further reduction to presumably [Rh(CO)₄]⁻. This is supported by the considerable increase of the oxidation-wave of the free [Bu₂NC(S)S]⁻ ligand and the observation that the complex Rh(CO)₂[Et₂NC(S)S] is reduced at a lower potential.

Introduction

Rh(III)-tris hetero allyl complexes, Rh[X–C(Z)–Y]₃, are chemically rather inert in ligand substitution reactions [1]. At ambient temperature no reaction with carbon monoxide occurs. It is generally known, that the reactivity of Rh(III)-tris chelate complexes is chiefly restricted to redox reactions with suitable reducing agents. Thus Rh(I)-species can be prepared, which, on the contrary, show reactivity in substitution reactions, *e.g.* towards CO.

In this paper the electrochemical oxidation and reduction of Rh[Ph₂PC(S)NR]₃ (R = Ph, Me), Rh[Me₂NC(S)NPh]₃ and Rh[Bu₂NC(S)S]₃ are described as well as the chemical follow-up reactions of the generated Rh(I) products with carbon monoxide.

Experimental

The complexes Rh[Bu₂NC(S)S]₃ [2], Rh(CO)₂-[Et₂NC(S)S] [3], Rh[Me₂NC(S)NPh]₃ [1], Rh-[Ph₂PC(S)NR]₃ (R = Ph, Me) [1] and Rh(CO)-[Ph₂PC(S)NPh] [Ph₂PC(S)NHPh] [4] were prepared by published procedures.

Electrochemical measurements were made with a three electrode Bruker E 310 instrument with Pt working and auxiliary electrodes. Measurements were made with complex solutions in the range (0.5–1.0) × 10⁻³ mol dm⁻³ in acetone (0.1 mol dm⁻³ Bu₄NClO₄) with potentials referred to a Ag/AgCl (0.1 mol dm⁻³ LiCl-acetone) reference electrode [5]. Normal pulse voltammograms were obtained at a scan rate of 5 mV s⁻¹ with a pulse frequency of 2.0 pulses s⁻¹. Cyclic voltammograms were taken with a scan rate of 150–300 mV s⁻¹. All values reported in this paper are measured on the first and second scan voltammograms.

Results and Discussion

Oxidations

Pulse polarographic and cyclic voltammetric techniques show that the rhodium(III)-tris hetero allyl complexes Rh[X–C(Z)–Y]₃, can be oxidised at a Pt electrode in the potential range +1.10–+1.50 V versus a Ag/AgCl reference electrode in acetone solu-

TABLE I. Electrochemical Data for Rhodium Hetero Allyl Complexes and Their Reaction with CO[a].

Compound	Medium	Pulse polarography[b]		Cyclic voltammetry[c]					
		$E_{1/2}$	$i_{d/c}$	E_p	$i_{p/cv^{1/2}}$	$E_p^{anodic\,e}$	$i_{p/cv^{1/2}}$	$E_p^{anodic\,f}$	$i_{p/cv^{1/2}}$
Oxidations									
$Rh[Ph_2PC(S)NPh]_3$	N_2	1.44	15	1.49	40				
	CO	1.45	12	1.49	30				
$Rh[Ph_2PC(S)NMe]_3$	N_2	1.36	13	1.45	35				
	CO	1.35	12	–	–				
$Rh[Me_2NC(S)NPh]_3$[d]	N_2	–	–	1.09	33				
$Rh[Bu_2NC(S)S]_3$	N_2	1.22	20	1.24	59				
	CO	1.22	20	1.27	62				
Reductions									
$Rh[Ph_2PC(S)NPh]_3$	N_2	−1.21	30	−1.27	72	+0.14	36		
	CO	−1.20	29	−1.26	70	+0.02	28		
$Rh[Ph_2PC(S)NMe]_3$	N_2	−1.26	27	−1.30	65	+0.08	38		
	CO	−1.27	24	−1.29	57	−0.06	23		
$Rh[Bu_2NC(S)S]_3$	N_2	−1.77	40	−1.92	80	−0.70	14	+0.16	7
	CO	−1.79	80	−1.94	169	–	–	+0.16	53
$Rh(CO)_2[Et_2NC(S)S]$	N_2	−1.58	23	−1.65	47	–	–	+0.16	1
	CO	−1.65	39	−1.73	96	+0.39	10	+0.15	17

[a]In acetone vs Ag/AgCl electrode.   [b]Scan rate 5 mV s^{-1}; $E_{1/2}$ in V; $i_{d/c}$ in mA dm^3 mol^{-1}.   [c]Scan rate v = 0.2 V s^{-1}; E_p in V; $i_{p/cv^{1/2}}$ in mA s$^{1/2}$ dm^3 mol^{-1} V$^{-1/2}$.   [d]Measured in CH$_2$Cl$_2$.   [e]Oxidation waves of the electrochemically generated Rh(I) complexes.   [f]Oxidation of the free dithiocarbamate ligand.

tion under nitrogen atmosphere. Due to the insufficient solubility of $Rh[Me_2NC(S)NPh]_3$ in acetone, this complex was measured in CH$_2$Cl$_2$. Table I summarises the data from these electrochemical measurements.

In all cases only one oxidation wave is observed being a one-electron oxidation as can be seen from the measured current functions, i_d/c and $i_p/cv^{1/2}$, respectively. Cyclic voltammetry shows that these oxidations are chemically irreversible.

The species generated by oxidation of $Rh[Ph_2PC(S)NR]_3$ and $Rh[Me_2NC(S)NPh]_3$ are electrochemically inactive, for even on extending the potential to more negative values no cathodic waves are shown. Probably the oxidation products immediately decompose or undergo a rapid chemical follow-up reaction upon their electrochemical generation.
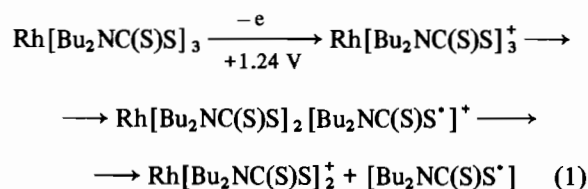
It is remarkable that the electrochemical oxidation of the free protonated ligand Ph$_2$PC(S)NHR (R = Ph, Me) occurs at about the same high potential (*ca.* 1.4 V). However, as $Rh[Ph_2PC(S)NR]_3$ does not display ligand dissociation [3], this is considered to be a coincidence.

The observed oxidation of $Rh[Bu_2NC(S)S]_3$ at +1.22 V agrees well with the value, reported for the methyl analogue [6]. With this oxidation of $Rh[Bu_2NC(S)S]_3$ we further observe small cathodic peaks at −0.79 and −0.29 V (see Fig. 1). We assign the wave at −0.79 V to the formation—though in low concentration—of a dimeric species $Rh_2[Bu_2NC(S)S]_5^+$ (eqns. 2 and 3), for unpurified samples of $Rh_2[Bu_2NC(S)S]_5^+$, prepared *in situ* according to the procedure described in ref. [6], show in the cyclic voltammogram a large reduction wave at −0.81 V.

The binuclear character of $Rh_2[Me_2NC(S)S]_5^+$ complex was reported to be obtained by chemical oxidation of $Rh[Me_2NC(S)S]_3$ with BF$_3$ under aerobic conditions [6] also yielding oxidised ligand products [7], has been well established by an X-ray structure determination [6]. So far we have no explanation for the small reduction wave at −0.29 V.

With these data and the results of the work of Martin *et al.* [6] we suggest the following reaction scheme.
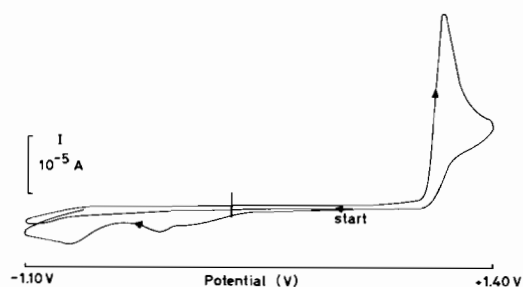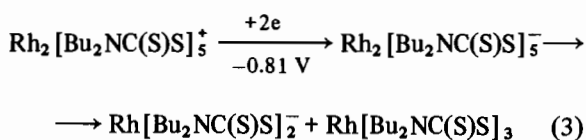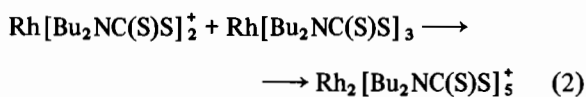
$$Rh[Bu_2NC(S)S]_3 \xrightarrow[+1.24\,V]{-e} Rh[Bu_2NC(S)S]_3^+ \longrightarrow$$

$$\longrightarrow Rh[Bu_2NC(S)S]_2[Bu_2NC(S)S^{\cdot}]^+ \longrightarrow$$

$$\longrightarrow Rh[Bu_2NC(S)S]_2^+ + [Bu_2NC(S)S^{\cdot}] \quad (1)$$

Fig. 1. Cyclic voltammogram, showing the oxidation of Rh[Bu$_2$NC(S)S]$_3$.

$$Rh[Bu_2NC(S)S]_2^+ + Rh[Bu_2NC(S)S]_3 \longrightarrow$$
$$\longrightarrow Rh_2[Bu_2NC(S)S]_5^+ \quad (2)$$

$$Rh_2[Bu_2NC(S)S]_5^+ \xrightarrow[-0.81\ V]{+2e} Rh_2[Bu_2NC(S)S]_5^- \longrightarrow$$
$$\longrightarrow Rh[Bu_2NC(S)S]_2^- + Rh[Bu_2NC(S)S]_3 \quad (3)$$

$$[Bu_2NC(S)S^\cdot] \longrightarrow \tfrac{1}{2}[Bu_2NC(S)S]_2 \quad (4)$$

As there is no indication for the existence of a Rh(IV)-dithiocarbamate species so far, it seems obvious, that on oxidation of Rh[Bu$_2$NC(S)S]$_3$ predominantly the ligand is attacked (eqn. 1). The resulting Rh[Bu$_2$NC(S)S]$_2^+$ species will immediately react with the unconverted starting material, which accounts for the formation of the binuclear product (eqn. 2). The oxidised ligand is known to dimerise rapidly [8]. It is furthermore known that [R$_2$NC-(S)S]$_2$ can be oxidised at about +1.22 V in acetone [9] or at +0.80 V *versus* SCE in acetonitrile [13] solution leading to R$_4$-bitt^{2+} products, shown in eqn. 5.

$$[Bu_2NC(S)S]_2 \xrightarrow[+1.22\ V]{-2e} [Bu_2NC(S)S]_2^{2+} \longrightarrow$$
$$\longrightarrow Bu_4\text{-bitt}^{2+} \quad (5)$$
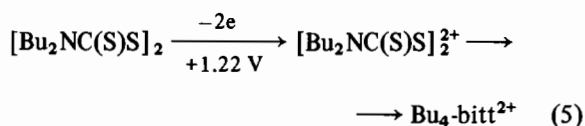
This reaction together with the somewhat faster diffusion of the [Bu$_2$NC(S)S]-complex in comparison with the [Ph$_2$PC(S)NR]-analogue (due to the smaller size of the former one) may contribute to the larger current functions found for the oxidation of Rh[Bu$_2$NC(S)S]$_3$.

Bubbling carbon monoxide through the solution does not affect the values of the oxidation potentials and the currents. This is in accordance with the expectation that the high-valent metal centre has only poor affinity for a π-acid like CO.

Reductions

Rh[Ph$_2$PC(S)NR]$_3$ (R = Ph, Me) and Rh[Bu$_2$NC-(S)S]$_3$ are chemically irreversibly reduced at low potentials, at *ca.* −1.25 V and −1.77 V, respectively. Inspection of the measured i/c values leads to the conclusion that under nitrogen a two-electron transfer process occurs most probably generating Rh(I) species. As the generated compounds exhibit different oxidation behaviour and different chemical follow-up reactions, the systems will be treated separately.

a Rh[Ph$_2$PC(S)NR]$_3$ (R = Ph, Me)

The cyclic voltammograms of these compounds (Fig. 2) show the reduction and the subsequent one-electron oxidation of the generated Rh(I) species. No ligand molecule is split off upon reduction of Rh[Ph$_2$PC(S)NR]$_3$, for in the cyclic voltammogram no reduction peaks of the free ligand are observed (for R = Ph to be expected at −1.79 V). So we conclude that according to eqn. 6 the octahedral Rh[Ph$_2$C(S)NR]$_3$ is reduced in a two-electron step to a square planar rhodium(I) compound. As no ligand is split off, we suppose two of the three ligands to become monodentate coordinated. Based on our chemical experience with complexes of this ligand, the formation of a negatively charged complex containing monodentate [Ph$_2$PC(S)NR]$^-$ seems most improbable. Therefore, we think that the present reduction is attended with immediate protonation. Even in dried solvents sufficient water is available. Moreover, addition of a small drop of water or perchloric acid in a separate experiment has no detectable influence on the voltammograms. The proposed reduction product may be analogous to the rhodium(I) complexes Rh[Ph$_2$PC(S)NR](PPh$_3$)$_2$ [14, 15] and Rh(CO)[Ph$_2$PC(S)NR][Ph$_2$PC(S)NHR] [4], recently reported by us.
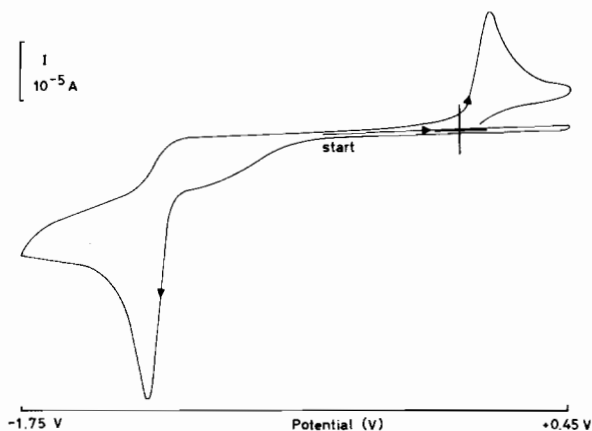
Fig. 2. Cyclic voltammogram, showing the reduction of Rh[Ph$_2$PC(S)NPh]$_3$, measured under nitrogen atmosphere.

The generated Rh(I) complex, then undergoes a one-electron oxidation at about +0.1 V, probably yielding a Rh(II) compound which is not stable and decomposes, because the oxidation wave is not accompanied by a subsequent reduction (eqn. 7).

Reaction with CO

When $Rh[Ph_2PC(S)NR]_3$ is reduced in acetone solution, continuously kept saturated with carbon monoxide, this complex is reduced at the same potential (*ca.* −1.25 V) with the same i/c value (Fig. 3), as when measured under nitrogen. The
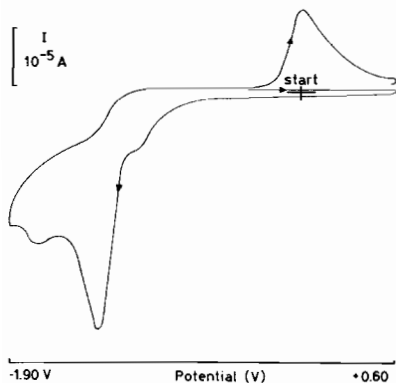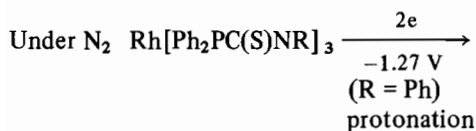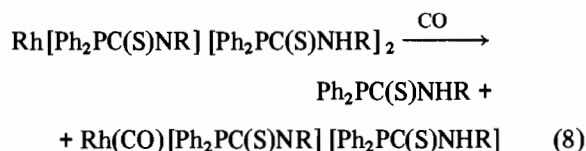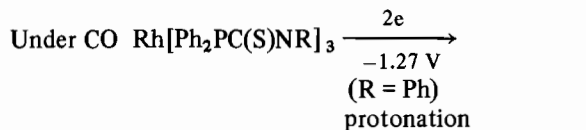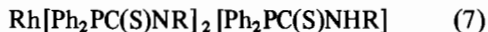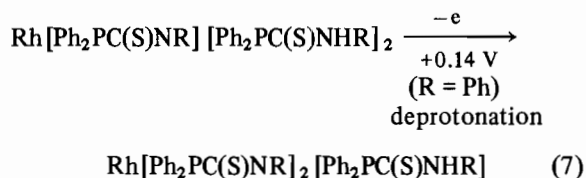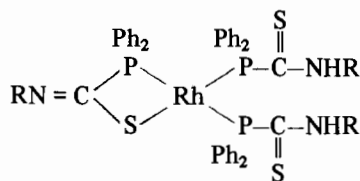
Fig. 3. Cyclic voltammogram, showing the reduction of $Rh[Ph_2PC(S)NPh]_3$, measured under carbon monoxide atmosphere.

resulting Rh(I) species exhibits a rapid reaction with CO (eqn. 8), as indicated by the disappearance of the oxidation at about +0.1 V and the occurrence of an oxidation wave of the thus formed Rh(I) carbonyl species at about −0.02 V and of a new cathodic reduction wave at −1.79 V, in the case of R = Ph, which can be attributed to the reduction of the liberated ligand. In a separate experiment we noted the ligand reduction at −1.79 V (R = Ph) and at −1.47 V (R = Me).
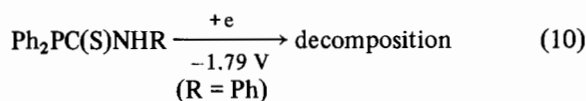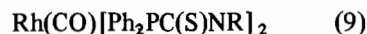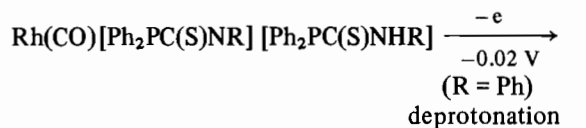
These results lead us to suggest the following scheme for the reduction of $Rh[Ph_2C(S)NR]_3$ and the subsequent oxidation of the generated Rh(I) complex.

$$Under\ N_2\ \ Rh[Ph_2PC(S)NR]_3 \xrightarrow[\substack{-1.27\ V \\ (R = Ph) \\ protonation}]{2e}$$

(6)

$$Rh[Ph_2PC(S)NR][Ph_2PC(S)NHR]_2 \xrightarrow[\substack{+0.14\ V \\ (R = Ph) \\ deprotonation}]{-e}$$

$$Rh[Ph_2PC(S)NR]_2[Ph_2PC(S)NHR] \quad (7)$$

$$Under\ CO\ \ Rh[Ph_2PC(S)NR]_3 \xrightarrow[\substack{-1.27\ V \\ (R = Ph) \\ protonation}]{2e}$$

$$Rh[Ph_2PC(S)NR][Ph_2PC(S)NHR]_2 \quad (6)$$

$$Rh[Ph_2PC(S)NR][Ph_2PC(S)NHR]_2 \xrightarrow{CO}$$

$$Ph_2PC(S)NHR +$$

$$+ Rh(CO)[Ph_2PC(S)NR][Ph_2PC(S)NHR] \quad (8)$$

$$Rh(CO)[Ph_2PC(S)NR][Ph_2PC(S)NHR] \xrightarrow[\substack{-0.02\ V \\ (R = Ph) \\ deprotonation}]{-e}$$

$$Rh(CO)[Ph_2PC(S)NR]_2 \quad (9)$$

$$Ph_2PC(S)NHR \xrightarrow[\substack{-1.79\ V \\ (R = Ph)}]{+e} decomposition \quad (10)$$

b Rh[Bu₂NC(S)S]₃

Figure 4 shows a cyclic voltammogram of the reduction of $Rh[Bu_2NC(S)S]_3$ under nitrogen at a very low potential (−1.77 V) and the subsequent oxidation of the generated species in the second scan

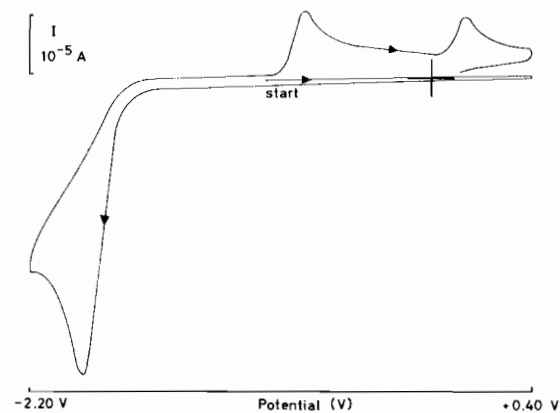Fig. 4. Cyclic voltammogram, showing the reduction of $Rh[Bu_2NC(S)S]_3$, measured under nitrogen atmosphere.

at -0.70 V and $+0.16$ V. As it is well established, that free dithiocarbamate is irreversibly oxidised in a one-electron process at $+0.16$ V to the radical $[Bu_2NC(S)S^\cdot]$, which rapidly dimerises to thiuram disulfide $[Bu_2NC(S)S]_2$ [8], this reaction of Rh-$[Bu_2NC(S)S]_3$ is accompanied with liberation of $[Bu_2NC(S)S]^-$.

So we think that the process at -0.70 V is the one-electron oxidation of the formed $Rh[Bu_2NC(S)-S]_2^-$. The resulting $Rh[Bu_2NC(S)S]_2$ decomposes immediately, for even at scan rates up to 25 Vs^{-1} no subsequent reduction wave could be detected. An analogous two-electron reduction with concomitant splitting off of $[R_2NC(S)S]^-$ has been recently reported for $Pt[R_2NC(S)S]_3$, another d^6 tris-dithiocarbamate system [11] (eqn. 11).

$$Pt[R_2NC(S)S]_3^+ \xrightarrow{2e} Pt[R_2NC(S)S]_2 + $$
$$+ [R_2NC(S)S]^- \quad (11)$$
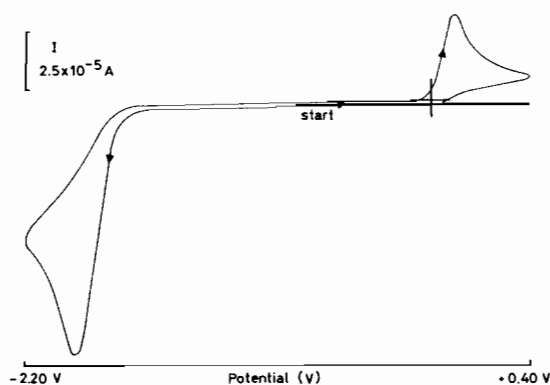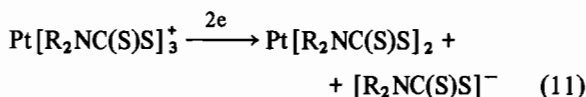

Fig. 5. Cyclic voltammogram, showing the reduction of $Rh[Bu_2NC(S)S]_3$, measured under carbon monoxide atmosphere.

Reaction with CO

The reduction of $Rh[Bu_2NC(S)S]_3$ was also studied under carbon monoxide. The reduction occurs at the same potential (-1.79 V), however, with a twofold increase of the current functions (see Table I; Fig. 5), *i.e.* a four electron transfer process is operating. There is also a remarkable increase of the peak current for the oxidation of free dithiocarbamate. Furthermore, the oxidation wave at -0.70 V, observed when measured under nitrogen, has completely disappeared.
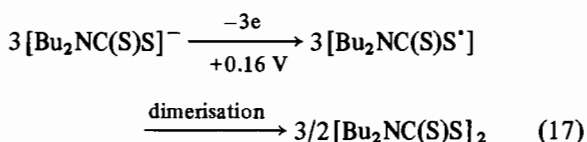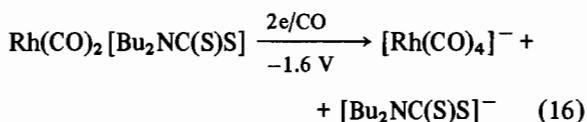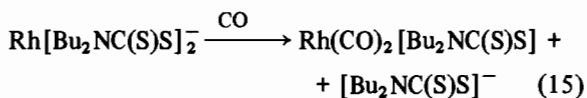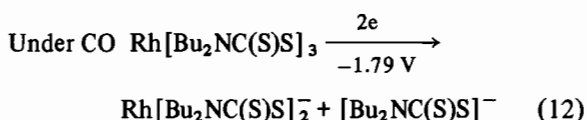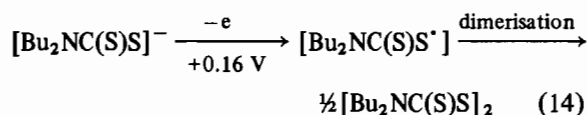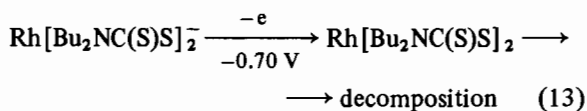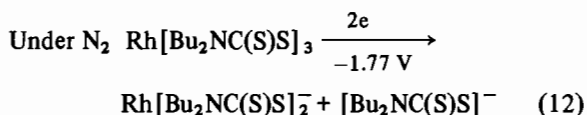
So we conclude, that a rhodium($-$I) species is formed. With the abundant carbon monoxide present and in view of the enormous increase of the dithiocarbamate oxidation peak, the formation of the fully characterised [12] $[Rh(CO)_4]^-$ species seems most probable.

On reducing electrochemically the complex $Rh(CO)_2[Et_2NC(S)S]$, which was prepared in situ according to a literature procedure [2], we noted

that a one-electron reduction under nitrogen and a two-electron reduction under CO takes place at about -1.60 V. From this observation we conclude that $Rh[Bu_2NC(S)S]_3$ is first reduced in a two-electron process at -1.79 V, followed by reaction with CO, to $Rh(CO)_2[Bu_2NC(S)S]$. At this very low potential this complex is immediately reduced to $[Rh(CO)_4]^-$ (which process is found to take place already at about -1.60 V). This also explains that in the overall reduction four electrons are taken up by $Rh[Bu_2NC(S)S]_3$.

Comparing the values of the current functions $i_p/cv^{1/2}$ for the oxidation of the split off dithiocarbamate ligand, a ratio 1:3 for $Rh(CO)_2[Et_2NC(S)S]$ and $Rh[Bu_2NC(S)S]_3$ is observed, as is to be expected from their stoichiometries. So far we have no explanation for the oxidation at $+0.39$ V, observed after reduction of $Rh(CO)_2[Et_2NC(S)S]$. There are no indications, that the formed $[Rh(CO)_4]^-$ is oxidised, because this process probably takes place at low potentials, which is not observed.

The reduction of $Rh[Bu_2NC(S)S]_3$ is shown in the following scheme:

$$\text{Under N}_2 \quad Rh[Bu_2NC(S)S]_3 \xrightarrow[-1.77\,V]{2e}$$
$$Rh[Bu_2NC(S)S]_2^- + [Bu_2NC(S)S]^- \quad (12)$$

$$Rh[Bu_2NC(S)S]_2^- \xrightarrow[-0.70\,V]{-e} Rh[Bu_2NC(S)S]_2 \longrightarrow$$
$$\longrightarrow \text{decomposition} \quad (13)$$

$$[Bu_2NC(S)S]^- \xrightarrow[+0.16\,V]{-e} [Bu_2NC(S)S^\cdot] \xrightarrow{\text{dimerisation}}$$
$$\tfrac{1}{2}[Bu_2NC(S)S]_2 \quad (14)$$

$$\text{Under CO} \quad Rh[Bu_2NC(S)S]_3 \xrightarrow[-1.79\,V]{2e}$$
$$Rh[Bu_2NC(S)S]_2^- + [Bu_2NC(S)S]^- \quad (12)$$

$$Rh[Bu_2NC(S)S]_2^- \xrightarrow{CO} Rh(CO)_2[Bu_2NC(S)S] +$$
$$+ [Bu_2NC(S)S]^- \quad (15)$$

$$Rh(CO)_2[Bu_2NC(S)S] \xrightarrow[-1.6\,V]{2e/CO} [Rh(CO)_4]^- +$$
$$+ [Bu_2NC(S)S]^- \quad (16)$$

$$3[Bu_2NC(S)S]^- \xrightarrow[+0.16\,V]{-3e} 3[Bu_2NC(S)S^\cdot]$$
$$\xrightarrow{\text{dimerisation}} 3/2[Bu_2NC(S)S]_2 \quad (17)$$

c Rh[Me₂NC(S)NPh]₃

Rh[Me$_2$NC(S)NPh]$_3$ could not be reduced under N$_2$ within the measuring limits of the solvent, *viz.* CH$_2$Cl$_2$. This supports our earlier conclusion, that the thio-ureide ligand stabilises high oxidation states. Recently, it has been shown, that for a tris-dithio-carbamato complex with a d^6 metal center the redox stability $E_{\frac{1}{2}ox} - E_{\frac{1}{4}red}$ is large (about 3 V) [10]. For Rh[Ph$_2$PC(S)NR]$_3$ this redox stability amounts to 2.6 V. Ergo, in view of the low value of $E_{\frac{1}{2}ox}$ of Rh[Me$_2$NC(S)NPh]$_3$ (+1.10 V), it is to be expected that the reduction of this complex occurs at the limit of the potential range of the solvent, *i.e.* CH$_2$Cl$_2$ (−1.50 V).

Electrochemical reductions of rhodium sulfur-chelate compounds are scarcely reported. Rh-(SacSac)$_3$ [16] is reduced in a two-electron process to Rh(I) like we have found in our compounds, whereas Rh(mnt)$_2^{2-}$ [17] is reduced in a one-electron process to Rh(I).

The observation that upon reduction Rh[Ph$_2$PC-(S)NR]$_3$ does not split off a ligand, underlines, that phosphines have good coordinating properties towards low valent metal complexes. In order to maintain all three phosphino groups coordinated, two ligands become necessarily bonded in a mono-dentate way. For Rh[Bu$_2$NC(S)S]$_3$, on the other hand, lower potentials are demanded for reduction, implying that [Bu$_2$NC(S)S]$^-$ (and also [Me$_2$NC(S)-NPh]$^-$) stabilises metals in high oxidation states. Upon reduction always liberation of coordinated dithiocarbamate is observed, which indicates, that [R$_2$NC(S)S]$^-$ has a weaker interaction with Rh(I) than [Ph$_2$C(S)NR]$^-$. CO gives facile substitution of one phosphino ligand in Rh[Ph$_2$PC(S)NR] [Ph$_2$PC-(S)NHR]$_2$, whereas CO reacts with Rh(I) [Bu$_2$NC-(S)S]-complexes, yielding [Rh(CO)$_4$]$^-$, thus eliminating all coordinated [Bu$_2$NC(S)S]$^-$. This again demonstrates, that [R$_2$NC(S)S]$^-$ has only strong affinity to Rh(III) compounds, whereas CO is preferred as ligand by metals in low oxidation states.

These results, obtained from electrochemical oxidations and reductions are well in accordance with our chemical findings and the general expectations, dictated by the HSAB principle.

Acknowledgement

References

1 D. H. M. W. Thewissen, J. G. Noltes, J. Willemse and J. W. Diesveld, submitted.
2 J. Willemse, J. A. Cras, J. J. Steggerda and C. P. Keijzers, *Structure and Bonding, 28*, 83 (1976), and references therein.
3 F. A. Cotton and J. A. McCleverty, *Inorg. Chem., 10*, 1398 (1964).
4 D. H. M. W. Thewissen, J. G. Noltes and J. J. Steggerda, *Inorg. Chim. Acta, 51*, 135 (1981).
5 A. M. Bond, A. R. Hendrickson and R. L. Martin, *J. Electrochem. Soc., 119*, 1325 (1972).
6 A. R. Hendrickson, R. L. Martin and D. Taylor, *Austr. J. Chem., 29*, 269 (1976).
7 S. H. Wheeler, B. M. Mattson, G. L. Miessler and L. H. Pignolet, *Inorg. Chem., 17*, 340 (1978).
8 G. Cauquis and D. Lachenal, *J. Electroanal. Chem., 43*, 205 (1975).
9 A. Nieuwpoort, A. H. Dix, P. A. T. W. Porskamp and J. G. M. van der Linden, *Inorg. Chim. Acta, 35*, 221 (1979).
10 H. L. M. van Gaal and J. G. M. van der Linden, *Proceedings of the XXIth ICCC*, Toulouse, 274 (1980).
11 J. G. M. van der Linden and A. H. Dix, *Inorg. Chim. Acta, 35*, 65 (1979).
12 P. Chini and S. Martinengo, *Inorg. Chim. Acta, 3*, 21 (1969).
13 C. Scrimager and L. J. Dehayes, *Inorg Nucl. Chem. Lett., 14*, 125 (1978).
14 D. H. M. W. Thewissen, H. P. M. M. Ambrosius, H. L. M. van Gaal and J. J. Steggerda, *J. Organomet. Chem., 192*, 101 (1980).
15 A. W. Gal, J. W. Gosselink and F. A. Vollenbroek, *J. Organomet. Chem., 142*, 357 (1977).
16 A. M. Bond, G. A. Heath and R. L. Martin, *Inorg. Chem., 10*, 2026 (1971).
17 A. Vlček Jr. and A. A. Vlček, *Inorg. Chim. Acta, 41*, 123 (1980).