Journal of Organometallic Chemistry, 341 (1988) C39–C44
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Synthesis and electrochemistry of di-η^5-cyclopentadienyl-tungsten(IV) and -molybdenum(IV) crown ether complexes

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(Received July 21st, 1987)

Abstract

Reaction of $Na_2[SCH_2(CH_2OCH_2)_3CH_2S]$ (**1**) with $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**2**) yielded the metalla-crown ether complex $[W\{SCH_2(CH_2OCH_2)_3CH_2S\}(\eta\text{-}C_5H_5)_2]$ (**3**). Compound **3** undergoes a reversible one-electron redox reaction, the $E_{1/2}$ of which was insensitive to the presence of alkali metal cations. The new compounds, $[M(\eta^5\text{-}C_5H_5)_2(\text{4-thiobenzo-15-crown-5})_2]$ (M = Mo, **5**; M = W, **6**) were prepared by the reaction of the sodium salt of 4-thiobenzo-15-crown-5 with $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**4**) or **2**, respectively. These complexes also exhibited reversible electrochemistry, the $E_{1/2}$ of which was quite sensitive to the presence of alkali metal cations.

There is currently considerable interest in the synthesis of electroactive ionophores. Several groups have reported organic [1], inorganic [2] and organometallic [3] compounds which display shifts in electrochemical potentials upon ion binding, or changes in ion binding constants upon oxidation and reduction [4]. These studies have relevance to the fields of ion transport and biosensors.

We have initiated a synthetic programme to synthesize electroactive transition metal complexes containing ionophoric ligands. Here, we report preliminary results on our attempts to synthesize compounds which incorporate the bent di-η^5-cyclopentadienyl-molybdenum(IV) or -tungsten(IV) fragment. We chose to study this system due to the well-established reversible electrochemistry associated with these d^2 systems. Also, it has been noted that there are small structural changes upon oxidation which would, in principle, affect the relative ion affinities of oxidized or reduced states of the compound [5,6].

Our initial synthetic work was directed towards the synthesis of an crown ether in which the tungsten atom was a member of the macrocyclic ring. The bis-alkoxide

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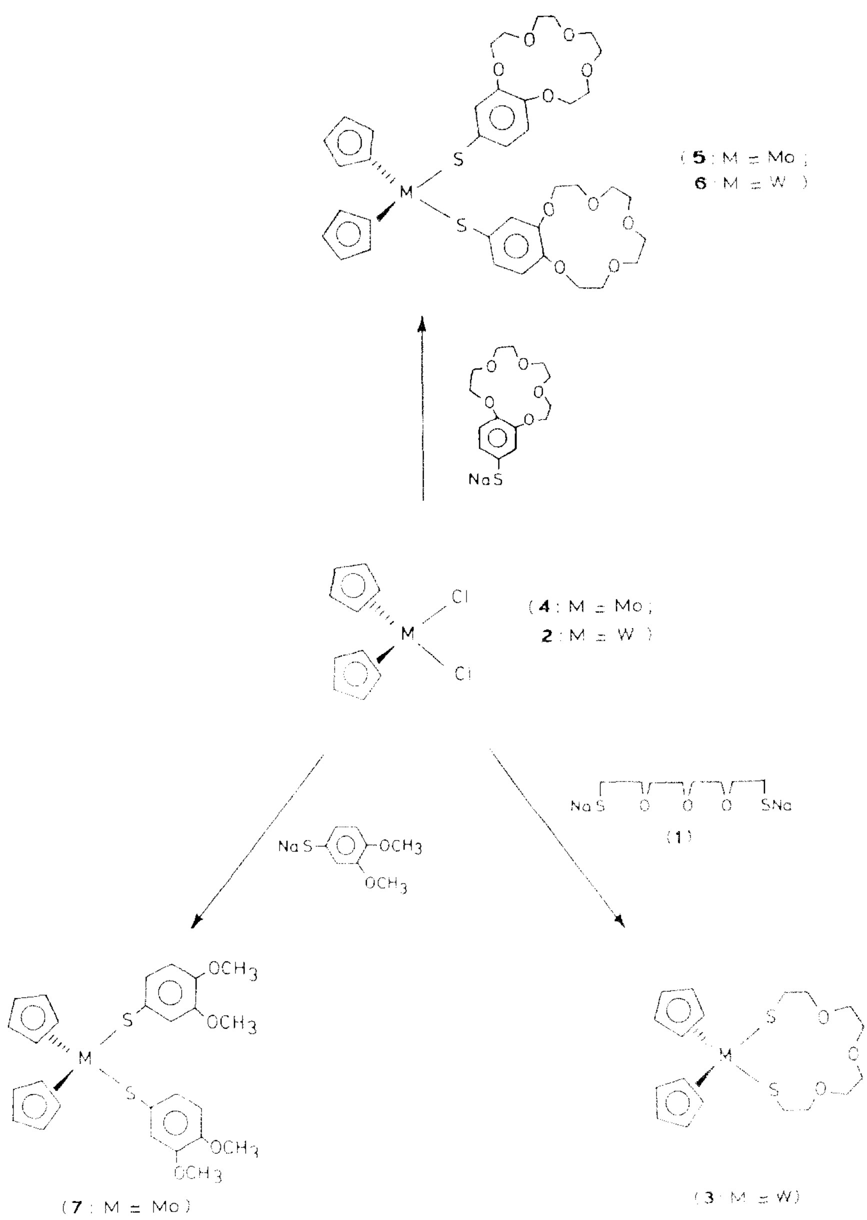
* I wish to express my appreciation to Professor Colin Eaborn for a long and fruitful collaboration, and in particular in connection with his rôle as editor of the Journal of Organometallic Chemistry.

0022-328X/88/$03.50

derivatives of di-η^5-cyclopentadienyl-tungsten(IV) or -molybdenum(IV) are known to be unstable with respect to β-hydrogen elimination, whilst compounds of the type $[M(\eta^5\text{-}C_5H_5)_2(SR)_2]$ are well known [7]. We, therefore, selected the ligand $[SCH_2(CH_2OCH_2)_3CH_2S]^{2-}$ so that sulphur atoms could be bonded onto the metal centre.



Scheme 1. Synthesis of di-η^5-cyclopentadienyltungsten(IV) derivatives and di-η^5-cyclopentadienylmolybdenum(IV) derivatives.

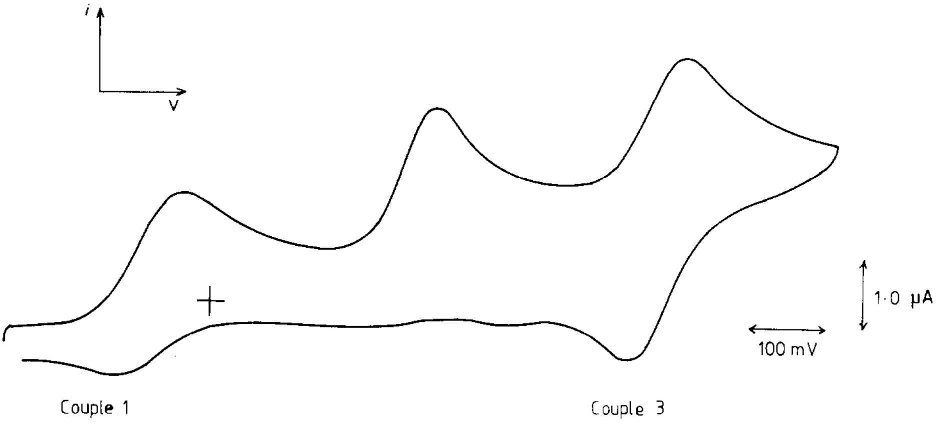


Fig. 1. Cyclic voltammogram of **6** in 0.1 *M* $[NEt_4][PF_6]/CH_3CN$. Scan range −0.1 to +1.0 V, ambient temperature.

Slow addition of an ethanolic solution (50 cm^3) of $Na_2[SCH_2(CH_2OCH_2)_3CH_2S]$ (**1**) (0.70 g) [8 *] to a stirred slurry of $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**2**) (1.0 g) [10] in ethanol (150 cm^3) at 65 °C yielded, after column chromatography (alumina III, and 5% ethanol in dichloromethane as eluant), 0.132 g (7%) of the metalla-crown ether complex **3** [11 *]. Compound **3** can be crystallized from 'wet' methanol yielding analytically pure transparent orange crystals.

The structure of **3**, shown in Scheme 1, was deduced from spectroscopic and analytical data. Cyclic voltammetry studies in 0.1*M* $[NEt_4][ClO_4]$//*N*,*N*′-dimethylmethanamide showed a one-electron oxidation with $E_{1/2}$ − 30 mV (vs. SCE). At 20 mV s^{-1} scan rate, the peak separation was 60 mV and a plot of $(I_p)_a$ against $\nu^{1/2}$ (ν = scan rate) was linear, showing the system to be reversible [12]. Unfortunately, upon changing the electrolyte to 0.1 *M* $Li[4\text{-}CH_3C_6H_4SO_3]$, $Na[4\text{-}CH_3C_6H_4SO_3]$ or $K[4\text{-}CH_3C_6H_4SO_3]$, no changes (> 10 mV) were observed in the $E_{1/2}$ of this couple. This observation is not completely surprising in view of the presence of "soft" sulphur atoms incorporated into the macrocycle, which are not optimal for binding of the "hard" alkali metal cations [13 *].

We anticipated that use of a crown ether in which all donor atoms were oxygens would greatly enhance ion binding. We therefore treated the sodium salt of 4-thiobenzo-15-crown-5 [14] with $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**4**) [10] and $[W(\eta^5\text{-}C_5H_5)_2Cl_2]$ (**2**), which formed $[Mo(\eta^5\text{-}C_5H_5)_2$(4-thiobenzo-15-crown-5)$_2]$ (**5**) (14% yield) [15 *] and $[W(\eta^5\text{-}C_5H_5)_2$(4-thiobenzo-15-crown-5)$_2]$ (**6**) (14% yield) [16 *]. Both the compounds were obtained in a pure form. We examine the electrochemistry of **6** in 0.1*M* $[NEt_4][PF_6]/CH_3CN$. As shown in Fig. 1, there are 3 oxidation peaks in the range −0.1 to +0.1 V (vs. SCE). The first and third peaks are due to quasi-reversible electron transfer with $E_{1/2}$ of +0.10 and +0.77 V, respectively. The second oxidation appears to be irreversible and has an $(E_p)_c$ of +0.455 V (ν 20 mV s^{-1}). Upon changing the electrolyte to 0.1 *M* $Na[PF_6]$, $K[PF_6]$ or $Li[ClO_4]$ in CH_3CN, marked reproducible changes in both the $E_{1/2}$ values and the peak separations were

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* This and other references marked with asterisks indicate notes occurring in the list of references.

Table 1

Electrochemical data for compounds **5** and **6**

Compound	Electrolyte [a]	Couple 1 [b]		Couple 3 [e]	
		$E_{1/2}$ [c] (mV)	E_p [d] (mV)	$E_{1/2}$ [c] (mV)	E_p [d] (mV)
6	$[NEt_4][PF_6]$	+100	70	+770	70
6	$Li[ClO_4]$	+150	115	+810	75
6	$Na[PF_6]$	+180	160	+880	150
6	$K[PF_6]$	+170	150	+865	150
5	$[NEt_4][PF_6]$	+150	100	+815	70
5	$Na[PF_6]$	+220	180	+960	170

[a] The solvent in all cases was dry CH_3CN; the electrolyte concentration was 0.1 *M*. [b] Couple 1 refers to the first couple as described in the text (see also Fig. 1). [c] The ferrocene/ferrocenium couple was used as an internal reference [17]. Potential values are reported with respect to the standard calomel electrode (SCE); the ferrocene/ferrocenium couple was measured at 355 mV vs. SCE. [d] The voltammograms were recorded at a scan rate of 20 mV s^{-1} at ambient temperature. [e] Couple 3 refers to the third couple as described in the text (see also Fig. 1).

observed. In 0.1 *M* $Na[PF_6]$, the $E_{1/2}$ of the first couple increased by 80 mV; the peak separation also increased by 90 mV. The third couple exhibited similar shifts; the $E_{1/2}$ increasing by 110 mV and the peak separation increasing by 80 mV. In 0.1 *M* $K[PF_6]$, similar changes were observed. The changes with $Li[ClO_4]$ as supporting electrolyte were not as large; the $E_{1/2}$ of the first couple shifts by 50 mV, and the peak separation increases by 45 mV. The third couple shifts by only 40 mV and the peak separation is not perturbed. We also examined the electrolytic dependence of electrochemistry of **5**, and it was very similar to **6** (see Table 1).

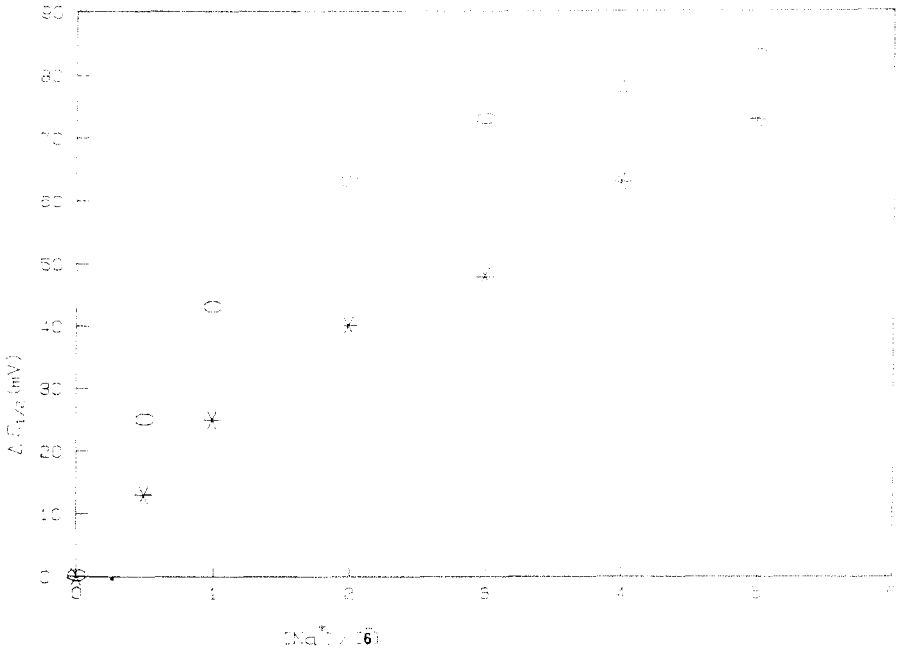

Fig. 2. Plot of the shift in $E_{1/2}$, $\Delta E_{1/2}$, of the first couple, ○, and third couple, ✶, vs. $[Na^+]/[\mathbf{6}]$.

Simple ion-pairing phenomena cannot explain these observations for two reasons. First, when the cation present is Li^+, which has the highest charge to radius ratio, we see the smallest effect. Secondly, when we prepared $[Mo(\eta\text{-}C_5H_5)_2\{4\text{-S-1,2-}(OMe)_2C_6H_3\}_2]$ (7) and examined its electrochemistry in CH_3CN with $[NEt_4][PF_6]$ and then with $Na[PF_6]$ as the electrolyte, no changes in the $E_{1/2}$ (> 10 mV) were observed. Upon titration of a 1.0 m*M* solution of **6** in $[NEt_4][PF_6]$ with $Na[PF_6]$, a smooth anodic shift in the $E_{1/2}$ for the first and third couple were observed, Fig. 2. Qualitatively, the first couple was more sensitive to small additions of Na^+ than the third couple. This is in contrast to the shifts observed when the electrolyte was changed from $[NEt_4][PF_6]$ to $Na[PF_6]$; here the first couple shifted 80 mV whereas the third couple shifted 110 mV. This is not surprising in view of the fact that the reduced species present in the third couple is most likely a multivalent cation and thus its affinity for Na^+ would be expected to be much lower than that of **6**.

We note that the changes observed upon addition of $Na[PF_6]$ to a solution of **6** in $[NEt_4][PF_6]$ can be reversed fully by the addition of benzo-15-crown-5. We conclude that in these systems involving bent metallocene derivatives of molybdenum(IV) and tungsten(IV), substantial changes in the two reversible couples observed for compounds **5** and **6** can be affected by ion binding in the crown ether ligands.

Acknowledgements

We wish to thank Genetics International (U.K.) Inc. for support (to S.R. Marder).

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16 Characterizing data for complex 6: ^{1}H NMR (300 MHz, CD_2Cl_2): 6.95 (d, *J* 2.0 Hz, 2H), 6.84 (dd, *J* 8.3, 2.0 Hz, 2H), 6.75 (d, *J* 8.3 Hz, 2H), 5.15 (s, 10H), 4.1 (m, 8H), 3.8 (m, 8H), 3.7 (m, 16H). Analysis: Found: C, 49.39, H, 5.31. $C_{38}H_{48}S_2O_{10}W$ calcd.: C, 50.00, H, 5.26%. Mass spectrum: (FAB^+) m/z 913 $(M + H)^+$.

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