Inorganica Chimica Acta, *185* (1991) 33–37

$\{\eta^6$-Phenylmethylsila-14-crown-5$\}$chromium tricarbonyl. Synthesis, characterization and electrochemical studies on the first example of an electroactive ionophore containing a silacrown

Moises Moran*, Carmen Ma. Casado, Isabel Cuadrado

Departamento de Química (Inorgánica), C-VIII Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049-Madrid (Spain)

and **Jose Losada***

Departamento de Ingeniería Química Industrial, Escuela Técnica Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28001-Madrid (Spain)

(Received January 4, 1990)

Abstract

$\{\eta^6$-Phenylmethylsila-14-crown-5$\}$chromium tricarbonyl has been prepared by thermal reaction of chromium hexacarbonyl with $(C_6H_5)(CH_3\overline{Si(OCH_2CH_2)_4O}$ in Bu_2O/THF (9/1, vol./vol.), being characterized by conventional spectroscopic techniques. The electrochemistry of this complex has been studied in acetonitrile and dichloromethane using cyclic voltammetry and coulometry. In CH_3CN the complex undergoes an irreversible one-electron oxidation and the redox potential is shifted anodically upon addition of alkali metal cations.

Introduction

Considerable attention in recent years has been focussed on the synthesis of redox-responsive macrocycles that contain redox-active functions, such as organometallic moieties, in close proximity to a cation binding site [1–6]. Interest in these molecules stems from their ability to complex metal cations, offering the possibility of studying mutual interactions (e.g. electron transfer) between the redox-active centre and a closely bound metal cation. In particular, such compounds have yielded redox-active host molecules for selective recognition and binding cations [1, 2, 6]. One application of such receptors lies in their potential development as components of new chemical sensory devices [1].

However the organometallic receptor molecules of this type that have been prepared were limited to organo–transition metal complexes (mainly ferrocene derivatives) containing macrocycles as crown ethers or cryptands [1–7]. Until now, there is no report of organometallic compounds in which the organic grouping attached to the transition metal contains a silacrown moiety.

Cyclic poly(alkyleneoxy)silanes, designated as silacrowns, are a new class of compounds that exhibit ionophoric properties that are comparable to crown ethers in both cation specificity and enhancement of anionic reactivities and which demonstrate phase transfer catalytic properties [8, 9]. For these compounds the presence of the silicon atom provides an opportunity to introduce organic moieties without precedent in other crown systems. Thus, the alkoxy functional silacrowns have been immobilized on siliceous supports; therefore the silacrowns are a new class of immobilizable phase transfer catalysts [9].

We report here the synthesis, characterization and electrochemical studies of $\{\eta^6$-phenylmethylsila-14-crown-5$\}$chromium tricarbonyl (**1**), a new complex, which to our knowledge is the first example of a redox-responsive complex containing a direct link between the organometallic redox-active centre and a silacrown. We also describe an analogous chromium tricarbonyl complex containing phenylmethyldimethoxisilane, $[\{\eta^6\text{-}C_6H_5(CH_3)Si(OCH_3)_2\}Cr(CO)_3]$ (**2**), i.e. a model compound for comparison with the complex containing a silacrown moiety.

Experimental

The reactions and manipulations were performed under an atmosphere of dry nitrogen by using con-

---

*Authors to whom correspondence should be addressed.

0020-1693/91/$3.50

ventional Schlenk techniques. Infrared spectra were recorded on a Nicolet 5DX-FT-IR spectrophotometer. Nuclear magnetic resonance spectra, ^1H and ^{13}C, were recorded on a Bruker WH-200-5Y (200 MHz, Fourier Transform mode) spectrometer. Chemical shifts (δ) are reported in ppm with reference to internal $SiMe_4$. Solvents used were dried by standard procedures [10] and stored under N_2; in particular Bu_2O was distilled from CaH_2. Phenylmethyldimethoxisilane (Petrarch Systems) was used as received. Tetrabutyl titanate and tetraethylene glycol purchased from Aldrich Chemical Co. and chromium hexacarbonyl (Strem) were used as received. Phenylmethylsila-14-crown-5 was prepared by reaction of tetraethylene glycol with phenylmethyldimethoxysilane according to the literature procedure [8, 9] and purified by distillation at reduced pressure (b.p. 178–185 °C at 0.1 mmHg).

For the purification of the compounds via column chromatography, silica pretreated with Me_3SiCl according to the literature procedure [11] was used. Commercial silical gel 60 silanized (Merck) for column chromatography has also been used.

The electrochemical apparatus, techniques and measurements have been described previously [12, 13]. Potentials were quoted versus the $[Fe(\eta^5\text{-}C_5H_5)_2]^+/[Fe(\eta^5\text{-}C_5H_5)_2]$ couple.

Synthesis of complexes

$[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]$ *(1)*

Chromium hexacarbonyl (4 g, 18.18 mm) and phenylmethylsila-14-crown-5 (1.89 g, 6.06 mm) in a solvent mixture of Bu_2O and THF (9/1, vol./vol.) were heated at 140 °C. The progress of the reaction was monitored by occasionally allowing the reaction to cool to room temperature and recording the IR spectrum of the supernatant solution. The heating was continued until the new carbonyl bands (ν(CO) at 1974 and 1902 cm^{-1}) stopped increasing in intensity. The final green–yellow mixture was cooled at −10 °C for 24 h and filtered from silanized silica to separate the unreacted $Cr(CO)_6$ and solid decomposition materials. The solvent was removed *in vacuo* and the residue redissolved with degassed dichloromethane and column chromatographied with CH_2Cl_2/petroleum ether (40–60 °C) 1/9 vol./vol. The yellow band was collected and the solvent was removed to give complex **1** as an air- and light-sensitive yellow oil, yield 70%. *Anal.* Calc. for $C_{18}H_{24}O_8SiCr$: C, 48.20; H, 5.35; Cr, 11.60. Found: C, 48.59; H, 5.71; Cr, 11.55%.

$\{\eta^6\text{-}C_6H_5(CH_3)Si(OCH_3)_2\}Cr(CO)_3]$ *(2)*

Following the procedure described above, complex **2** was prepared from $Cr(CO)_6$ (7 g, 31.80 mmol) and $C_6H_5CH_3Si(OCH_3)_2$ (1.90 g, 10.42 mmol). After purification by chromatography column (silanized silica, 3 × 30 cm) with CH_2Cl_2/petroleum ether (40–60 °C) 1/9 vol./vol. the complex was isolated as an air- and light-sensitive yellow oil. Yield 75%. *Anal.* Calc. for $C_{12}H_{14}O_5SiCr$: C, 45.24; H, 4.39; Cr, 16.34. Found: C, 45.47; H, 4.53; Cr, 16.29%.

Results and discussion

Phenylmethylsila-14-crown-5 was prepared by transesterification of phenylmethyldimethoxysilane with tetraethylene glycol, in the presence of tetrabutyltitanate as a catalyst (eqn. (1)), being the conditions of transesterification selected to promote cyclization in preference to polymerization [8, 9].

$$\begin{aligned}&(C_6H_5)(CH_3)Si(OCH_3)_2\\&\quad + OH(CH_2CH_2O)_4H \xrightarrow{Ti(OBu)_4}\\&(C_6H_5)(CH_3)\overline{Si(OCH_2CH_2)_4O} + 2CH_3OH\end{aligned} \tag{1}$$

The novel arene chromium tricarbonyl complex $[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]$ (**1**) containing an arene ring bound to a silacrown was conveniently prepared by thermal treatment of chromium hexacarbonyl and phenylmethylsila-14-crown-5 in Bu_2O/THF (9:1, vol./vol.) as solvent mixture, at temperatures around 140 °C (eqn. (2)).

$$\begin{aligned}&(C_6H_5)(CH_3)\overline{Si(OCH_2CH_2)_4O} + Cr(CO)_6 \xrightarrow[\Delta]{Bu_2O/THF}\\&[\{\eta^6\text{-}C_6H_5CH_3\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3] + 3CO\end{aligned} \tag{2}$$

The reaction takes place rapidly as indicated by an immediate color change from colorless to yellow. The progress of the reaction was accompanied by a slight decomposition, it being necessary to remove unreacted $Cr(CO)_6$ and greenish-grey decomposition solids by column chromatography. After chromatographic workup the metalla–silacrown complex (**1**) was obtained as an air-sensitive viscous oil, very soluble in common organic solvents such as CH_2Cl_2, CH_3CN, THF and sparingly soluble in n-hexane and n-pentane. Attempts to induce crystallization have not been successful. On the basis of analytical and spectroscopic data the complex was formulated as $[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]$.

On the other hand, phenylmethyldimethoxisilane reacts with $Cr(CO)_6$ to give the model complex $[\{\eta^6\text{-}C_6H_5(CH_3)Si(OCH_3)_2\}Cr(CO)_3]$ (**2**). Its purification can be accomplished via column chromatography on silica previously silanized. If normal silica or neutral alumina is used, the compound remains on the column

TABLE 1. Selected spectroscopic data (IR and NMR) for $C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}$ and complexes **1** and **2**

Compound	^1H NMR^a	^{13}C NMR^a				$\nu(CO)^b$
$C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}$	7.67–7.36 (m, 5H, C_6H_5)	135.23	C_6H_5	73.31	OCH_2	
	3.90–3.65 (m, 16H, OCH_2)	131.32		71.92		
	0.35 (s, 3H, CH_3)	129.15		71.43		
				63.85		
$\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}Cr(CO)_3$ (**1**)	5.62 (t, H, H_p, C_6H_5)	102.35	C_6H_5	73.17	OCH_2	1966 (A_1)
	5.60 (d, 2H, H_o, C_6H_5)	98.50		71.83		1869 (E)
	5.15 (t, 2H, H_m, C_6H_5)	92.97		71.49		
	3.90–3.60 (m, 16H, OCH_2)			64.31		
	0.38 (s, 3H, CH_3)					
$\{\eta^6\text{-}C_6H_5(CH_3)Si(OCH_3)_2\}Cr(CO)_3$ (**2**)	5.54 (d, 2H, H_o, C_6H_5)	103.10	C_6H_5			1971 (A_1)
	5.50 (t, H, H_p, C_6H_5)	98.00				1892 (E)
	5.14 (t, 2H, H_m, C_6H_5)	93.15				
	3.60 (s, 6H, OCH_3)					
	0.41 (s, 3H, CH_3)					

^{a}In CD_3CN solution; chemical shifts (δ) in ppm. ^{b}In cm^{-1}; in CH_2Cl_2 solution.

due to the attachment of the hydrolizable $Si(OCH_3)$ groups to the silica or alumina surfaces.

For compound **1** the IR spectra in the $\nu(CO)$ region show the two strong bands expected for $[(\eta^6\text{-arene})Cr(CO)_3]$ complexes (Table 1), corresponding to the A_1 and E IR active modes. The ^1H NMR spectral data of **1** exhibit upfield shifts for the aromatic protons of the $Cr(CO)_3$ coordinated ring (Table 1), a large upfield shift (30–40 ppm) of the ring carbon resonance also being detected upon complexation. These NMR data coupled with the IR spectra indicate the coordination of the chromium to the aromatic system rather than to a silacrown oxygen; therefore the complex possesses a piano-stool structure with the $Cr(CO)_3$ π-bonded to the arene ring as shown in Fig. 1.

Similarly, for complex **2** the analytical, ^1H and ^{13}C NMR, and IR spectral data (Table 1) confirm the formulation $[\{\eta^6\text{-}C_6H_5(CH_3)Si(OCH_3)_2\}Cr(CO)_3]$.

NMR spectroscopy [1, 5, 14–16] and electrochemical techniques [2, 6, 17–19] have been applied to investigate the complexation between alkali metal cations and crown ethers compounds. Therefore we have used ^{13}C NMR spectroscopy and cyclovoltammometric studies as a probe to monitor the interaction of the novel metalla–silacrown complex (**1**) with Li^+, Na^+ and K^+ cations.

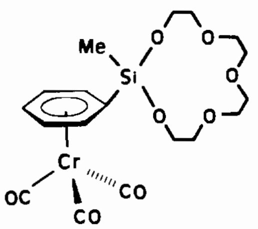

Fig. 1. $\{\eta^6$-Phenylmethylsila-14-crown-5$\}$chromium tricarbonyl.

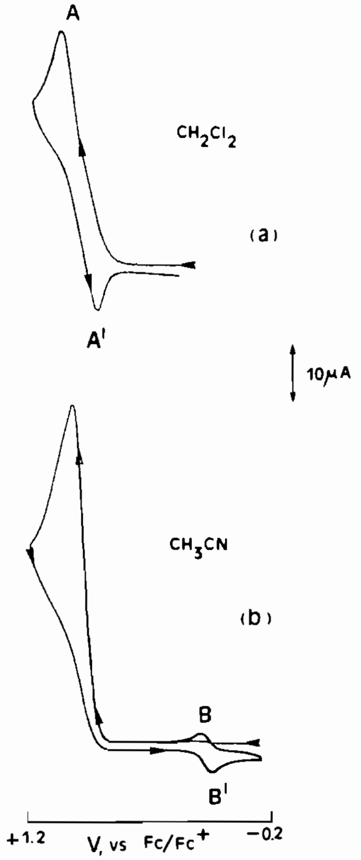

Fig. 2. Cyclic voltammograms of **1** (1×10^{-3} M) with $[n\text{-}Bu_4N][PF_6]$ (0.1 M): (a) in CH_2Cl_2, scan rate 500 mV/s; (b) in CH_3CN, scan rate 200 mV/s.

The ^{13}C NMR spectra of complex **1** were recorded in CD_3CN in the presence of various equivalents of

TABLE 2. Electrochemical data for complexes **1** and **2**

Electrolyte		$[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]$ (**1**)		$[\{\eta^6\text{-}C_6H_5(CH_3)Si(OMe)_2\}Cr(CO)_3]$ (**2**)	
		100 mV/s	20 mV/s	100 mV/s	20 mV/s
$[n\text{-}Bu_4N][PF_6]$	E_p[a]	+890	+880	+900	+875
$[n\text{-}Bu_4N][PF_6] + LiPF_6$	ΔE_p[b]	100	110	20	20
$[n\text{-}Bu_4N][PF_6] + NaPF_6$	ΔE_p[b]	70	65	20	25
$[n\text{-}Bu_4N][PF_6] + KPF_6$	ΔE_p[b]	45	50	20	25

[a] In mV. Obtained in CH_3CN solution containing 0.1 M $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte at a carbon glassy electrode. Solutions were c. 5×10^{-3} M in complexes and potentials were quoted vs. $[Fe(\eta^5\text{-}C_5H_5)_2]^+/[Fe(\eta^5\text{-}C_5H_5)_2]$ couple. [b] In mV. Shift in oxidation potential produced by presence of metal cation added as hexafluorophosphate salts in concentration 2×10^{-2} M.

$LiPF_6$, $NaPF_6$ or KPF_6. A shift in the $\delta(^{13}C)$ values for the ring methylene carbons implies significant metalla–silacrown–cation interaction. On adding one equivalent of $LiPF_6$, $NaPF_6$ and the $\delta(^{13}C)$ values of the OCH_2 carbon undergo an upfield shift of about 2–5 ppm, the shift detected being smaller when KPF_6 is added. Additions of Na^+ and Li^+ above one equivalent caused no further changes in $\delta(^{13}C)$. The results of these qualitative studies suggest that a 1:1 complexation for both Li^+ and Na^+ with the silacrown complex (**1**) takes place.

Similar additions of MPF_6 ($M^+ = Li^+$, Na^+ and K^+) to CD_3CN solutions of the model complex **2** did not change the $\delta(^{13}C)$ values of the OCH_3 and C_6H_5 carbons, and showed no evidence of interaction with MPF_6.

Electrochemistry

The electrochemistry of **1** was investigated in dichloromethane and acetonitrile solution with $(n\text{-}Bu_4N)PF_6$ as electrolyte.

In CH_2Cl_2 the cyclic voltammograms are characterized by an anodic peak (A) and a corresponding cathodic peak (A′) (Fig. 2). The peak separations, ΔE_p, were 70–200 mV, depending on concentration (*iR* compensation not applied) and i_c/i_a values are less than unity. Increasing the scan rate, v, from 0.1 to 1 V s^{-1}, increases i_c/i_a. For low values of v, E_p shifts anodically *c.* 30 mV per tenfold increase in v, with a smaller shift at higher values of v.

When CH_3CN is used as solvent the oxidation is irreversible as shown by the complete absence of a cathodic peak (Fig. 2). On the reverse sweep a new reversible wave, absent in the first scan in this region, can be detected (B/B′, $E_{1/2} = 40$ mV). This observed redox potential corresponds to that observed for $[(CH_3CN)_3Cr(CO)_3]^{+/0}$ chemically obtained.

In all cases the electron transfers are diffusion-controlled with the anodic current function ($i_p/v^{1/2}$) independent of scan rate. By comparison to ferrocene standards the oxidation of **1** was determined to involve one electron. These results are consistent with an EC mechanism in which an irreversible chemical reaction follows a reversible electrochemical oxidation.

$$\begin{tikzcd}
{[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]} \arrow[d, shift right] \\
{[\{\eta^6\text{-}C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}\}Cr(CO)_3]^+} \arrow[u, shift right] \arrow[d, "+3CH_3CN"] \\
{[(CH_3CN)_3Cr(CO)_3]^+ + C_6H_5(CH_3)\overline{Si(OCH_2CH_2)_4O}}
\end{tikzcd}$$

Cyclic voltammograms of **1** and **2** were also recorded after addition of $LiPF_6$, $NaPF_6$ and KPF_6 to the electrochemical solutions; the results obtained are collected in Table 2.

Only in the case of **1** are significant anodic shifts observed with the presence of cationic guests. The smaller changes in redox potential of compound **2** with supporting electrolyte variation indicate that the perturbations observed in **1** can be, mainly, due to specific ion binding by the silacrown functionality.

Nevertheless it is remarkable that the magnitude of the potential shifts is related to the charge/radius ratio of alkali metal cations, Li^+ causing the largest value and K^+ the smallest. These results suggest that the polarizing power of the cation is important in determining the magnitude of the anodic potential shift produced by cationic binding. Thus it can be proposed that the changes in electrochemistry of compound **1** arise from specific ion binding although the electrochemical data do not allow distinction of the relative contributions of the polarizing power and of ion binding to the observed modifications in redox potential.

Acknowledgements

We thank DGICYT (Dirección General de Investigación Científica y Técnica), project no. 87/0123 for the financial support of this work, and Professor E. Brunett for NMR assistance.

References

1 P. D. Beer, H. Sikanyika, A. M. Z. Slawin and D. J. Williams, *Polyhedron, 8* (1989) 879, and refs. therein.

2 P. D. Beer, H. Sikanyika, C. Blackburn and J. F. McAleer, *J. Organomet. Chem., 356* (1988) C19.

3 P. D. Beer, *J. Organomet. Chem., 297* (1985) 313.

4 C. D. Hall, I. P. Danks, S. C. Nyburg and A. N. Parkins, *Organometallics, 9* (1990) 1602, and refs. therein.

5 J. Powell, M. R. Gregg, A. Kuksis, C. J. May and S. J. Smith, *Organometallics, 8* (1989) 2918.

6 E. Fu, J. Granell, M. L. H. Green, V. J. Lowe, S. R. Marder, G. C. Saunders and M. Tuddenham, *J. Organomet. Chem., 355* (1988) 205.

7 K. J. Odell, E. M. Hyde and B. L. Shaw, *J. Organomet. Chem., 68* (1979) 103.

8 B. Arkles, K. King, R. Anderson and N. Peterser, *Organometallics, 2* (1983) 454.

9 B. Arkles, W. Peterson and K. King, in J. S. Miller (ed.), *Chemically Modified Surface's in Catalysis and Electrocatalysis,* ACS Symposium Series 192, Washington, DC, 1982, Ch. 17, p. 281.

10 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals,* Pergamon, Oxford, 2nd edn., 1980.

11 J. Wartmann and N. N. Deuel, *Helv. Chim. Acta, 42* (1959) 1166.

12 M. Morán, I. Cuadrado, C. Muñoz Reja, J. R. Masaguer and J. Losada, *J. Chem. Soc., Dalton Trans.,* (1988) 149.

13 M. Morán, I. Cuadrado, L. Pineda, J. R. Masaguer and J. Losada, *Inorg. Chim. Acta, 169* (1990) 119.

14 E. Amble and E. Amble, *Polyhedron, 2* (10) (1983) 1063.

15 J. M. Lehn, E. Sonveaux and A. K. Willard, *J. Am. Chem. Soc., 100* (1978) 4914.

16 M. Shampsipur and A. I. Popov, *J. Am. Chem. Soc., 101* (1979) 405.

17 A. Kaifer, L. Echegoyen, D. Gustowski, D. Goli and G. Gokel, *J. Am. Chem. Soc., 105* (1983) 7168.

18 D. Gustowski, M. Delgado, V. Gatto, L. Echegoyen and G. Gokel, *Tetrahedron Lett., 27* (1986) 3487.

19 L. Echeverria, M. Delgado, V. Gatto, G. Gokel and L. Echegoyen, *J. Am. Chem. Soc., 108* (1986) 6825.