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SYNTHESIS AND CHARACTERISATION OF THE MIXED SANDWICH CATIONS $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ (M = Ru, Os)

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Summary

The published reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ has been extended to other $[\{M(\eta\text{-arene})Cl_2\}_2]$ complexes to provide a convenient, high yield route to the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M= Ru; arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M = Os; arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$). Electrochemical studies and some reactions of these complexes are also described.

Since the preparation of the first mixed sandwich iron cation $[Fe(\eta\text{-}C_6H_3Me_3)(\eta\text{-}C_5H_5)]I$ by Coffield et al. in 1957 [1], a large number of publications on the synthesis and reactions of $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations have appeared in the literature [2].

In contrast, very few papers on the synthesis and reactions of their ruthenium and osmium analogues have been published. These consist of a very brief patent report on the preparation of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru, Os) via reaction of $[M(\eta\text{-}C_5H_5)(CO)_2]^+$ cations with the appropriate arene [3]; the synthesis of $[Ru(\eta^6\text{-}C_6H_5BPh_3)(\eta\text{-}C_5H_5)]$ via reaction of $[Ru(\eta\text{-}C_5H_5)(PPh_3)_2Cl]$ with $Na[BPh_4]$ [4]; a brief mention of the reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ to give $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ [5] and two recent preliminary notes [6,7] on the use of the well-known Nesmeyanov route ($M(C_5H_5)_2$, $AlCl_3$, Al, arene [2]) to synthesise various $[Ru(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations. Unfortunately, using ruthenocene the latter method requires long reaction times, high temperatures and only low yields are obtained (<10% in ref. 7). These yields can be increased to 30% (for arene = 1,3,5-$C_6H_3Me_3$) by addition of water to the reaction mixture [6] but with C_6Me_6 this also results in extensive demethylation and disproportionation of the aromatic ligand. Therefore, in this short paper we now report the results of an extension of Zelonka and Baird's route [5] to the synthesis of a series of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations (M = Ru; arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$, C_6H_5OMe, C_6Me_6; M = Os; arene = C_6H_6, p-

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$MeC_6H_4CHMe_2$) and also the electrochemical behaviour and some reactions [8] of these complexes.

Results and discussion

In 1972, Zelonka and Baird [5] briefly reported that reaction of $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ with $Tl[C_5H_5]$ in MeCN at ambient temperature gave a high yield (83%) of $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$. In view of the ready availability of other $[\{M(\eta\text{-arene})Cl_2\}_2]$ (M = Ru, Os) compounds [9], coupled with the alternative high temperature, low yield, Nesmeyanov route [6,7] we decided to investigate the possibility of synthesising a series of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations by reaction of $[\{M(\eta\text{-arene})Cl_2\}_2]$ with $Tl[C_5H_5]$.

Thus, reaction of $[\{M(\eta\text{-arene})Cl_2\}_2]$ with $Tl[C_5H_5]$ (1 : 2 molar ratio) in MeCN for several hours at ambient temperature gave a fine precipitate of TlCl which was removed by filtering through celite. Removal of solvent and treatment of the resulting solid or oil with a methanolic solution of $Na[BPh_4]$ produced the desired $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]BPh_4$ as greyish-white or pale brown solids. In the $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ reaction, treatment of the residue with a methanolic solution of $NH_4[PF_6]$ gave $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$ (cf. $[Ru(\eta\text{-}C_6H_6)Cl(NH_3)_2]_3(PF_6)_3NH_4PF_6$ [10]. For M = Ru, yields of 50—80% were obtained; for M = Os, lower yields of 20—40% were realised (see Experimental section). The compounds were characterised by elemental analyses, hydrogen-1 NMR (Table 1) and carbon-13 NMR (Table 2) spectroscopy and by conductivity measurements in $(CH_3)_2SO$ or CH_3NO_2.

As reported earlier for Fe and Ru analogues [7], the $\eta\text{-}C_5H_5$ protons shift to higher frequencies on descending the triad, e.g. for the $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cations, M = Fe, δ 5.23 [7]; M = Ru, 5.43; M = Os, 5.67 ppm. Conversely, the

TABLE 1

HYDROGEN-1 NMR DATA AT 301 K IN $(CD_3)_2SO$ FOR SOME $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ CATIONS (M = Ru, Os)

Compound	δ (ppm) [a, b]	
	η-arene	$\eta\text{-}C_5H_5$
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$	6.20(s)	5.43(s)
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c]	6.11s, 4 H); 2.22(s, CH_3); 1.15(d, CH_3 of $CHMe_2$, J 6.0 Hz)	5.31(s)
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)]BPh_4$	5.80—6.50(m, 5 H) 3.67(s, OMe)	5.34(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$ [d]	2.39(s)	4.96(s)
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	2.33(s)	5.09(s)
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]BPh_4$	6.14(s)	5.67(s)
$[Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c, d]	6.15(s, 4 H) 2.43(s, CH_3) 1.24(d, CH_3 of $CHMe_2$, J 6.0 Hz)	5.59(s)

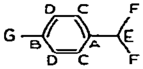
[a] Reference standard-internal Me_4Si lock. [b] Where appropriate BPh_4^- multiplets observed between δ 6.60—7.60 ppm. [c] *C*HMe$_2$ septet not observed due to low solubility of compound. [d] Measured in CD_3NO_2.

TABLE 2

CARBON-13 NMR DATA (PROTON NOISE DECOUPLED) AT 301 K IN $(CD_3)_2SO$ FOR SOME $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ CATIONS

Compound	δ ppm [a, b]	
	η-arene	η-C_5H_5
$[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2[PF_6]_2NH_4PF_6$	85.8	80.9
$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ [c]	111.7(A), 100.7(B) 86.0(C), 84.0(D), 31.2(E), 23.1(F), 19.6(G)	80.3
$[Ru(\eta\text{-}C_6H_5OMe)(\eta\text{-}C_5H_5)]BPh_4$	(85.8, 84.1, 82.9 80.0, 74.4) [d], 57.1 [e]	79.6
$[Os(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]BPh_4$	76.1; 76.5 [f]	
$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$	98.9 [g], 17.3 [h]	81.6

[a] Chemical shifts quoted to high frequency of $SiMe_4$ (internal lock). [b] Where appropriate BPh_4^- resonances observed between δ 120—140 ppm. [c] Labelling of *p*-cymene protons



[d] Aromatic carbons of C_6H_5OMe. [e] Methyl carbon of C_6H_5OMe. [f] Not possible to assign resonances unambiguously as they are so close together and similar in intensity. [g] Aromatic carbons of C_6Me_6. [h] Methyl carbons of C_6Me_6.

benzene protons shift to lower frequency, e.g. for the $[M(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cations, M = Fe δ 6.44 [7]; M = Ru, 6.20; M = Os, 6.14 ppm. As suggested earlier [7], this might indicate that the positive charge of the cations is delocalised onto the arene ligand in the order Fe > Ru > Os.

In support of this statement, attempted reactions of some of these $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations with various nucleophiles (Y) gave either no reaction (M = Ru; Y = various PR_3; M = Os, Y = various PR_3, H^-, CN^-, OH^-) or extensive decomposition which probably involved displacement of both carbocyclic rings (M = Ru; Y = CN^-, OH^-). This behaviour is to be contrasted with that of the $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations which react readily with various nucleophiles to give high yields of *exo*-substituted cyclohexadienyl complexes, $[Fe(\eta\text{-}C_6R_6Y)(\eta\text{-}C_5H_5)]$ etc. [2]. The only evidence we have found for nucleophilic attack on the arene ring occurred in the reaction of the $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$ cation with $Na[BH_4]$ in 1,2-dimethoxyethane from which $[Ru(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ could be isolated in very small yield (ca. 5%) by extraction with petroleum ether (b.p. 60—80°C). This compound exhibited a very similar hydrogen-1 NMR spectrum [11] and mass spectral fragmentation pattern [12] (see Experimental section) to that of $[Fe(\eta^5\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$.

A similar reduction of reactivity towards tertiary phosphines in the order Fe >> Ru > Os has been observed in the series $[M(\eta\text{-}C_6H_6)_2](PF_6)_2$, and this has been attributed to the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II} [13].

Finally, in view of the extensive studies on the electroreduction of various $[Fe(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations [14], an electrochemical study was carried out on the $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]BPh_4$ complexes. However, unlike the iron compounds, cyclic voltammetric and A.C. polarographic studies in CH_3NO_2 or

CH_3CN showed that all the ruthenium and osmium mixed sandwich compounds studied (see Experimental section) resisted reduction upto the solvent limit. The complexes $[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$, $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$ and $[Os(\eta\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ did undergo oxidation at fairly modest potentials (see Experimental section) (unlike $[Fe(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]PF_6$, which showed no oxidation wave upto the solvent limit) but unfortunately these processes remained irreversible in nature even at low temperatures (—40°C) and high scan rates (100 V s^{-1}).

It is likely that these disappointing electrochemical observations can also be correlated with the greater π-back-bonding ability of Ru^{II} and Os^{II} compared to Fe^{II}.

Experimental

Microanalyses were by the University of Edinburgh Chemistry Department. Infrared spectra were recorded in the region 4000—250 cm^{-1} on a Perkin Elmer 447 grating spectrometer using Nujol and hexachlorobutadiene mulls on caesium iodide plates. Hydrogen-1 NMR spectra were obtained on Varian Associates HA-100 and EM-360 spectrometers and $^{13}C\text{-}\{^1H\}$ NMR spectra on a Varian CFT-20 spectrometer operating at 20 MHz (^{13}C NMR chemical shifts quoted in ppm to high frequency of tetramethylsilane). Conductivity measurements were made at 303 K using a model 310 Portland Electronics conductivity bridge. The mass spectrum of $[Ru(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]$ was measured on an A.E.I. MS9 spectrometer. Melting points were determined with a Köfler hot stage microscope and are uncorrected.

Materials

Ruthenium trichloride trihydrate, sodium hexachloroosmate(IV) (Johnson-Matthey Ltd.), ammonium hexafluorophosphate, dicyclopentadiene, cyclohexa-1,3-diene (Aldrich Chemicals), α-phellandrene (5-isopropyl-2-methylcyclohexa-1,3-diene) (Eastman Chemicals), sodium tetraphenylborate, thallium(I)-sulphate (BDH). Various cyclohexa-1,4-dienes were prepared by the Birch reduction of the corresponding arene [15] and then $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, C_6H_5OMe, $p\text{-}MeC_6H_4CHMe_2$) and $[\{Os(\eta\text{-arene})Cl_2\}_2]$ (arene = C_6H_6, $p\text{-}MeC_6H_4CHMe_2$) were prepared as described elsewhere [9]. The compound $[\{Ru(\eta\text{-}C_6Me_6)Cl_2\}_2]$ was prepared by direct exchange of $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ with C_6Me_6 [16]. Thallium(I) cyclopentadienide was prepared from freshly cracked cyclopentadiene and thallium(I) sulphate [17].

Hydrogen-1 NMR and carbon-13 NMR data are given in Tables 1 and 2 respectively. All reactions were carried out in degassed solvents under an atmosphere of nitrogen.

Bis[η-benzene-η-cyclopentadienylruthenium(II) hexafluorophosphate](2/1)-[ammonium hexafluorophosphate]

The compound $[\{Ru(\eta\text{-}C_6H_6)Cl_2\}_2]$ (0.30 g; 0.60 mmol) was dissolved in acetonitrile (80 cm^3) and $Tl[C_5H_5]$ (0.32 g; 1.17 mmol) was added. The reaction mixture was stirred under nitrogen for four hours. The precipitated thallium(I) chloride was removed by filtration through celite. The resulting orange solution was evaporated to dryness on a rotary evaporator and the orange-brown residue redissolved in a small amount of methanol (3 cm^3). Addition of an excesss of $NH_4[PF_6]$ precipitated a light brown solid, m.p. 110—112°C (yield 0.28 g; 60%). Found: C, 29.3; H, 2.9; N, 1.5. Calcd. for $C_{22}H_{26}F_{18}NP_3Ru_2$; C, 28.1; H, 2.8; N, 1.5%. Λ_m (10^{-3} mol dm^{-3} in $(CH_3)_2SO$ at 303 K) = 40 S cm^2 mol^{-1}.

η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienylruthenium(II) tetraphenylborate

The compound $[\{Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.30 g; 0.49 mmol) was dissolved in acetonitrile (80 cm^3) and $Tl[C_5H_5]$ (0.29 g; 1.06 mmol) was added. The reaction mixture was stirred under nitrogen for two hours. The precipitated thallium(I) chloride was removed by filtration through celite and the resulting solution evaporated to dryness. The orange-brown residue was redissolved in methanol (3 cm^{-1}) and an excess of $Na[BPh_4]$ (0.20 g; 0.58 mmol) added to produce a pale greyish-brown precipitate which was filtered off, washed with methanol and diethyl ether and dried in vacuo at 56°C, m.p. 168—169°C (decomp.) (0.51 g; 82%) Found: C, 75.6; H, 6.5. Calcd. for $C_{39}H_{39}BRu$: C, 75.6; H, 6.3%.

η-Methoxobenzene-η-cyclopentadienylruthenium(II) tetraphenylborate (m.p. 123—125°C (0.26 g; 47%). Found: C, 72.1; H, 5.5 (calcd. for $C_{36}H_{33}BORu$: C, 74.8; H, 5.7%) and η-hexamethylbenzene-η-cyclopentadienylruthenium(II) tetraphenylborate (m.p. 252°C (decomp.) (0.15 g; 64%). Found: C, 75.8; H, 6.8 (calcd. for $C_{41}H_{43}BRu$: C, 76.0; H, 6.7%. Λ_m (10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 51 S cm^2 mol^{-1}) were also synthesised from the corresponding $[\{Ru(\eta\text{-arene})Cl_2\}_2]$ and $Tl[C_5H_5]$ followed by treatment with $Na[BPh_4]$. An impure sample of $[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]Cl$ (contaminated with excess TlCl) was also characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy (see Tables 1 and 2).

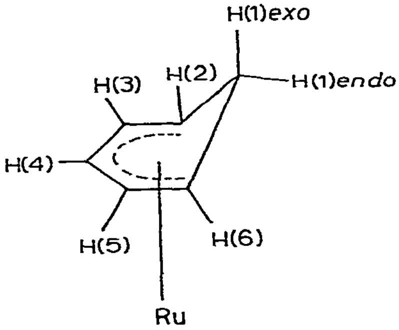
η-(5-Isopropyl-2-methylbenzene)-η-cyclopentadienylosmium(II) tetraphenylborate

The compound $[\{Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)Cl_2\}_2]$ (0.16 g; 0.20 mmol) was suspended in acetonitrile (50 cm^3) and $Tl[C_5H_5]$ (0.22 g; 0.82 mmol) was added. The reaction mixture was stirred under nitrogen for two hours and then filtered through celite to remove thallium(I) chloride. Removal of solvent gave a yellowish oil which was dissolved in methanol (3 cm^3) and treated with $Na[BPh_4]$ (0.20 g; 0.58 mmol) to give a greyish-white precipitate. This was filtered off, washed with methanol, chloroform and diethyl ether and dried in vacuo at 56°C, m.p. 245°C (decomp) (0.12 g; 43%). Found: C, 65.9; H, 5.5 (calcd. for $C_{39}H_{39}BOs$: C, 66.1; H, 5.6%. Λ_m (10^{-3} mol dm^{-3} in CH_3NO_2 at 303 K) = 48 S cm^2 mol^{-1}.

η-Benzene-η-cyclopentadienylosmium(II) tetraphenylborate (m.p. 125—126°C (0.12 g; 17%). Found: C, 63.1; H, 4.5. Calcd. for $C_{35}H_{31}BOs$: C, 64.4; H, 4.8%) was similarly prepared from $[\{Os(\eta\text{-}C_6H_6)Cl_2\}_2]$, $Tl[C_5H_5]$ and $Na[BPh_4]$.

η^5-Cyclohexadienyl-η-cyclopentadienylruthenium(II)

The complex $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]Cl$ [5] (0.20 g; 0.72 mmol) was dissolved in 1,2-dimethoxyethane (50 cm^3) and $Na[BH_4]$ (0.24 g; 6.30 mmol) added in small amounts over a 20 minute period while the reaction mixture was stirred under nitrogen. After 4 hours, water was added to destroy the excess of $Na[BH_4]$ and the solvent removed under vacuo to give a dark brown residue. On shaking this with petroleum ether (b.p. 60—80°C) a very small amount of the product was extracted and removal of solvent gave a yellow solid (ca. 5% yield). ^1H NMR in $CDCl_3$ at 301 K: 5.79 (m) (H_4), 4.72s (η-C_5H_5); 4.43(m), (H(3,5)); 2.25(m) (H(2,6), H(1) *exo* and *endo*)



Mass spectrum *m/e* (based on ^{102}Ru peak): 245 ($[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]^+$); 167 ($[Ru(\eta\text{-}C_5H_5)]^+$); 123 ($[Ru(\eta\text{-}C_6H_7)(\eta\text{-}C_5H_5)]^{2+}$). Trace amounts of this product were also obtained when $[Ru(\eta\text{-}C_6H_6)(\eta\text{-}C_5H_5)]_2(PF_6)_2NH_4PF_6$ was treated with $Na[BH_4]$ in various solvents (tetrahydrofuran, dioxane). No evidence however for even trace amounts of $[Os(C_6H_7)(C_5H_5)]$ was found on treatment of $[Os(\eta\text{-}C_6H_6)(C_5H_5)]BPh_4$ with $NaBH_4$ in various solvents.

Similarly, reaction of $[M(\eta\text{-arene})(\eta\text{-}C_5H_5)]^+$ cations with other nucleophiles (Y) such as CN^-, OH^- and various PR_3 gave either no evidence for reaction (M = Ru; Y = PR_3; M = Os, Y = PR_3, CN^-, OH^-) or extensive decomposition involving displacement of both carbocyclic rings (M = Ru; Y = CN^-, OH^-).

Electrochemical investigation

Electrochemical studies were carried out using a Princeton Applied Research (PAR 170) instrument. All solutions were degassed with argon prior to measurement to remove dissolved oxygen. The electrolyte solution was tetrabutylammonium tetrafluoroborate ($TBABF_4$) in either CH_2Cl_2, CH_3CN or CH_3NO_2 and the reference electrode was Ag/AgI (using this reference electrode, ferrocene is oxidised at +0.60 V).

$[Ru(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ in 0.25 M $TBABF_4/CH_3NO_2$. No cathodic response to —1.50 V; irreversible oxidation at $E_{1/2}$ + 0.58 V (100 mV s^{-1} scan rate) even at —24°C: remains irreversible at 100 V s^{-1} scan rate in 0.10 *M* $TBABF_4/CH_3CN$ but moves to +0.80 V in this solvent.

$[Ru(\eta\text{-}C_6Me_6)(\eta\text{-}C_5H_5)]BPh_4$; in 0.10 M $TBABF_4/CH_3CN$. No cathodic response to —2.60 V at —40°C. Irreversible oxidation at $E_{1/2}$ = +0.94 V (even at —40°C and 100 V s^{-1} scan rate).

$[Os(\eta\text{-}p\text{-}MeC_6H_4CHMe_2)(\eta\text{-}C_5H_5)]BPh_4$ in 0.10 M $TBABF_4/CH_3CN$. No cathodic response on scanning to —2.60 V at —40°C. Irreversible oxidation at $E_{1/2}$ = +0.56 V (100 mV s^{-1} scan rate). Remains irreversible at —40°C.

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