underwent room-temperature substitution reactions with PPh_3 to form compounds **2** and **3** (eq 2) and with dppm to form compound **4** (eq 3).

Compounds **1**, **3**, and **4** contain only 62 valence electrons each, and thus are formally electron deficient by 2 electrons, according to the 18-electron rule. They do however obey the PSEP theory,[10] according to which the core of each cluster (including the Te ligands) is an octahedron, requiring the presence of 14 cluster valence electrons. Compounds **1**, **3**, and **4**, have 7 SEPs required for the octahedral geometry. Compound **2** contains 50 electrons and to be electron precise, on the basis of the 18-electron rule, should contain only two metal–metal bonds, as observed. The PSEP theory also seems to apply well in the case of **2**. According to this theory the cluster core of **2**, including the Te ligands, has the form of a nido octahedron, requiring the presence of 7 SEPs, which this cluster has.

The known isoelectronic clusters $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu\text{-}PPh)_2$[11] and $Ru_4(CO)_{11}(\mu\text{-}CO)(\mu\text{-}PPh)_2$[12] contain square arrangements of the four metal atoms with quadruply bridging phosphinidene ligands on opposite sides of the cluster and have the bridging carbonyl ligand associated with the shortest metal–metal bond. It has been proposed that this shortening could be due to the influence of the bridging ligand. The unsaturation of the iron bis(phosphinidene) cluster was demonstrated by the ease with which it adds a two-electron ligand, L (L = CO, $P(OMe)_3$, *t*-BuNC), to form the saturated clusters $Fe_4(CO)_{11}L(\mu\text{-}PPh)_2$. The latter, however, are not significantly more stable because they quantitatively loss one CO under vacuum to give the substituted derivatives, $Fe_4(CO)_{10}L(\mu\text{-}PPh)_2$.[13] When **1** was treated with phosphines, we did not observe any addition products.

Although it is not possible at present to predict the mechanism of formation of **1** from $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$, a mixed-metal intermediate containing both iron and ruthenium atoms bridged by tellurium ligands may be involved. The involvement of such mixed-metal intermediates in the overall atom-transfer reactions has been observed in the formation of $Os_3(CO)_9(\mu_3\text{-}Te)_2$ from the reaction of $Fe_2(CO)_6(\mu_2\text{-}Te_2)$ and $Os_3(CO)_{11}(NCMe)$, which proceeds via an initial formation of $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$.[5] Attempts are presently being made to identify any such intermediates in the formation of compound **1**.

Acknowledgment. A.L.R. was supported in part by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

Supplementary Material Available: Tables of complete crystal, data collection, and refinement parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters for **1–4** (21 pages); tables of observed and calculated structure factors for **1–4** (121 pages). Ordering information is given on any current masthead page.

---

(10) Polyhedral skeletal electron pair theory: Wade, K. *Chem. Br.* **1975**, *11*, 177. Mingos, D. M. P. *Nature* **1972**, *236*, 99.

(11) Vahrenkamp, H.; Wolters, D. *J. Organomet. Chem.* **1982**, *224*, C17.

(12) Natarajan, K.; Zsolnai, L.; Huttner, G. *J. Organomet. Chem.* **1981**, *209*, 85.

(13) Jaeger, T.; Aime, S.; Vahrenkamp, H. *Organometallics* **1986**, *5*, 245.

Contribution from the Department of Chemical and Analytical Sciences, Deakin University, Geelong, Victoria 3217, Australia,
and Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia

Comparison of the $[M^{IV}(RR'dtc)_3]^+/M^{III}(RR'dtc)_3$ and $[M^{IV}(Et_2dsc)_3]^+/M^{III}(Et_2dsc)_3$ (M = Co, Rh, Ir; dtc = Dithiocarbamate; dsc = Diselenocarbamate) Redox Couples and the Reactivity of the Oxidation State IV Complexes in Solution and in the Gas Phase As Studied by Electrochemical and Mass Spectrometric Techniques

Alan M. Bond,*[1] Ray Colton,[2] and Desma R. Mann[1]

Received April 11, 1990

A range of $Ir^{III}(RR'dtc)_3$ complexes (RR'dtc = dithiocarbamate) and $Ir^{III}(Et_2dsc)_3$ (dsc = diselenocarbamate) have been synthesized. The $[Ir^{IV}(RR'dtc)_3]^+$ and $[Ir^{IV}(Et_2dsc)_3]^+$ oxidized species have been prepared and studied in solution by electrochemical techniques and in the gas phase by mass spectrometry. Voltammetric studies at platinum disk electrodes in dichloromethane, acetone, and acetonitrile enable the standard redox potentials ($E°$) for the $[Ir(RR'dtc)_3]^+/Ir(RR'dtc)_3$ couple (and the selenium analogue) to be calculated from the chemically reversible one-electron-oxidation process $Ir(RR'dtc)_3 \rightleftharpoons [Ir(RR'dtc)_3]^+ + e^-$. Comparison with data for the corresponding cobalt and rhodium complexes shows the $E°$ values to have the unexpected order Rh > Co > Ir with the rhodium couple being the most positive. Bulk electrolysis at platinum-gauze electrodes enables the Ir(IV) complexes to be characterized in dichloromethane solution. $[Ir(RR'dtc)_3]^+$ is stable on the synthetic time scale whereas $[Ir(Et_2dsc)_3]^+$ slowly dimerizes during the course of bulk electrolysis experiments and subsequently undergoes an internal redox reaction to give $[Ir_2(Et_2dsc)_5]^+$ and oxidized ligand, as previously observed for cobalt and rhodium dithiocarbamate and diselenocarbamate complexes. The order of the rates of these redox-based decomposition reactions is Rh ≫ Co ≫ Ir, which leads to the unusual result that Rh(IV) is considerably more reactive than Co(IV), with the high stability of Ir(IV) being as expected. That is, in this case, the thermodynamic and kinetic stabilities are parallel. The strong oxidizing power of the $[Ir(RR'dtc)_3]^+$ cations is illustrated by their oxidation of free dithiocarbamate ion to give thiuram disulfide and by the oxidation of elemental mercury to give mixed-metal complexes $Hg + 2[Ir(RR'dtc)_3]^+ \rightarrow [HgIr_2(RR'dtc)_6]^{2+}$. The mixed mercury/iridium complexes are also generated electrochemically at mercury electrodes by the reversible process $Hg + 2Ir(RR'dtc)_3 \rightleftharpoons [HgIr_2(RR'dtc)_6]^{2+} + 2e^-$. Generation of $[M(RR'dtc)_3]^+$ (M = Co, Rh, Ir) in the gas phase by positive ion mass spectrometry reveals the expected order of reactivity Ir < Rh < Co. The differences between the solution and gas-phase reactivities of the oxidation state IV complexes are explained by the presence of dimerization reactions in solution, which cannot occur under the conditions of mass spectrometry.

Introduction

Little is known about the quantitative aspects of the higher oxidation state solution chemistry of the group 9 metals (Co, Rh, Ir). Thus, in a very recent paper, Sykes et al.[3] noted the paucity of information about the solution chemistry of iridium in its higher oxidation states, despite the fact that numerous studies on the oxidation of Ir(III) complexes have been reported. Typically, the products of oxidation of Ir(III) complexes have not been well

---

(1) Deakin University.

(2) University of Melbourne.

(3) Castillo-Blum, S. E.; Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1989**, *28*, 954 and references cited therein.

0020-1669/90/1329-4665$02.50/0 © 1990 American Chemical Society

characterized and the chemistry is poorly defined.[3] However, those Ir(IV), Ir(V), and Ir(VI) compounds that have been prepared are noted for their strong oxidizing powers.[3-6] The situation for higher oxidation state solution studies on simple inorganic Co and Rh compounds is even less clear as such compounds are even more reactive than their iridium analogues,[4-6] although a number of well-characterized and relatively stable mononuclear and binuclear organometallic oxidation state IV compounds are known.[7-11] Despite a lack of definitive studies, the generally expected order of stabilities for the high oxidation states based upon available quantitative data would be Ir > Rh > Co.[6]

One important method of characterizing the chemistry of the higher valent complexes is to establish the thermodynamics of redox processes that involve electron transfer between complexes in different oxidation states. For example, Heath et al.[12,13] have used voltammetric measurements on reversible one-electron processes to establish relative values for the reversible half-wave potential, $E^r_{1/2}$, (approximately standard redox potential, E° value), of redox couples involving high-valent fluoro and chloro complexes of the second- and third-row transition metals and described systematic variations that occur with different metals. Unfortunately, studies of this kind are very few and in any case with the group 9 triad of metals usually involve comparisons of at least some potentials obtained from irreversible processes having no direct thermodynamic significance. For example, the oxidations of $M(acac)_3$ (M = Co, Rh, Ir; acac = acetylacetonate) give cyclic voltammetric peak potentials of 1.80 (Co), 1.74 (Rh), and 1.24 V (Ir) vs Ag/AgCl.[14] The potentials show the systematic trend expected, but only the E° value for the $[Ir(acac)_3]^{+/0}$ couple can be calculated since the oxidations of the Co and Rh complexes are irreversible under the conditions of cyclic voltammetry.

Certain ligands such as fluoride are well-known for their ability to stabilize high-oxidation-state complexes, with the second- and third-row transition metals usually existing in higher oxidation states than those of the first row. For example, oxidation state IV $[CoF_6]^{2-}$ is the highest oxidation state known for cobalt, whereas oxidation state VI MF_6 (M = Rh, Ir) species can be formed.[5]

The dithiocarbamate ligand (RR′dtc), like fluoride, also is effective in stabilizing high oxidation states; for example, Fe(IV), Ni(IV), and Cu(III) complexes are known.[15-17] Oxidation state III complexes $M(RR'dtc)_3$ are known for all the group 9 metals, and detailed studies on the electrochemical oxidation of $Co(RR'dtc)_3$[18-20] and $Rh(RR'dtc)_3$[21] have demonstrated some stability for $[Co(RR'dtc)_3]^+$ but only a transient existence of the Rh(IV) counterpart $[Rh(RR'dtc)_3]^+$. Thus, the relative order of stabilities (or reactivities) with respect to first- and second-row analogues is reversed from that expected. The electrochemical oxidation of the selenium analogues $Co(RR'dsc)_3$ and $Rh(RR'dsc)_3$ (RR′dsc = diselenocarbamate) have also been described,[21,22] and although they are easier to oxidize than the dithiocarbamates, they exhibit parallel behavior with regard to the relative reactivity of $[Co(RR'dsc)_3]^+$ and $[Rh(RR'dsc)_3]^+$. The majority of studies on iridium complexes concern the preparation, structural characterization, and spectroscopic properties of a very limited range of $Ir(RR'dtc)_3$ complexes,[23-27] and electrochemical studies are limited to reduction.[28] Apparently, there are no previous studies on iridium diselenocarbamates in any oxidation state, and no information is available on higher oxidation state iridium dithiocarbamate or diselenocarbamate complexes.

In the present paper, detailed studies on the electrochemical oxidation of $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$ enable the E° values for the $[Ir(RR'dtc)_3]^+/Ir(RR'dtc)_3$ and selenium analogue redox couples to be obtained. This completes the measurement of the triad of potentials for the M(IV)/M(III) couples and allows them to be compared for the first time in order to ascertain the order of redox stability. Studies on the reactivities of the electrochemically generated Ir(IV) complexes and their decomposition pathways also can be compared with those of their Co(IV) and Rh(IV) counterparts in an endeavor to understand the order of reactivity of the oxidation state IV species.

While voltammetric oxidation of $M(RR'dtc)_3$ complexes provides information on the reactivity of oxidation state IV complexes in solution, positive ion mass spectrometric studies on the complexes provide a complementary method of study of $[M(RR'dtc)_3]^+$ species in the gas phase. Information on the abundance of the parent ions and their gas-phase decomposition reactions can be compared with the solution studies. The present paper therefore provides a rare example where reactivity data concerning first-, second-, and third-row transition metals in high oxidation states becomes available in both the solution and gas phases.

Experimental Section

Abbreviations. Morphdtc = morpholine-*N*-carbodithioate; Pyrrdtc = pyrrolidine-*N*-carbodithioate.

Materials. All solvents and reagents used were of AR grade or better. The electrochemical supporting electrolyte Bu_4NClO_4 was obtained wet with water from Southwestern Analytical (Texas) and was dried under vacuum at 70 °C.

Preparations. $Ir(RR'dtc)_3$ complexes were prepared by modified literature methods.[24,29] Stoichiometric amounts of sodium hydroxide, carbon disulfide and the appropriate secondary amine were reacted in cold water to produce the sodium dithiocarbamate NaRR′dtc. An aqueous solution of Na_2IrCl_6 was added to an excess of the sodium dithiocarbamate in a water/methanol mixture, the excess of ligand being used to reduce Ir(IV) to Ir(III). The green-brown solution was stirred for several days, and an orange-yellow precipitate of crude $Ir(RR'dtc)_3$ slowly formed. It was filtered, washed well, and dried, and any further product that separated from the filtrate was also recovered. Purification was carried out by Soxhlet extraction using dichloromethane followed by chromatography through a very long alumina column using dichloromethane as eluant. Collection of the yellow portion of the broad yellow to orange band and evaporation of the solvent yielded a yellow-gold solid. Analyses were performed by the Australian Microanalytical Service AMDEL. Anal. Calcd percentage by mass for $Ir(Et_2dtc)_3$: C, 28.3; H, 4.7; N, 6.6. Found: C, 28.1; H, 4.4; N, 6.3. Calcd for $Ir(Morphdtc)_3$:

---

(4) Canterford, J. H.; Colton, R. *Halides of the Second and Third Row Transition Metals*; John Wiley: New York, 1968.

(5) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley: New York, 1987.

(6) *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D.; McCleverty, J., Eds.; Pergamon: Oxford, England, 1987; Vol. 4, Chapters 47–49.

(7) Vol'pin, M. F.; Levitin, I. Ya.; Sigan, A. L.; Nikitaev, A. T. *J. Organomet. Chem. Rev.* **1985**, *279*, 263 and references cited therein.

(8) Levitin, I.; Sigan, A. L.; Vol'pin, M. E. *J. Chem. Soc., Chem. Commun.* **1975**, 469.

(9) Isobe, K.; Vazquez de Miguel, A.; Bailey, P. M.; Okeya, S.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1441.

(10) Okeya, S.; Meanwell, N. J.; Taylor, B. F.; Isobe, K.; Vazquez de Miguel, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1453.

(11) Meanwell, N. J.; Smith, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1986**, 1419.

(12) Brownstein, S.; Heath, G. A.; Sengupta, A.; Sharp, D. W. A. *J. Chem. Soc., Chem. Commun.* **1983**, 669.

(13) Heath, G. A.; Moock, K. A.; Sharp, D. W. A.; Yellowlees, L. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1503.

(14) Tocher, J. H.; Fackler, J. P. Jr. *Inorg. Chim. Acta* **1985**, *102*, 211.

(15) Cauquis, G.; Lachenal, D. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 1095.

(16) Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Inorg. Chem.* **1975**, *14*, 2980.

(17) Chant, R.; Hendrickson, A. R.; Martin, R. L.; Rohde, N. M. *Aust. J. Chem.* **1973**, *26*, 2533.

(18) Bond, A. M.; Hendrickson, A. R.; Martin, R. L.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1983**, *22*, 3440.

(19) Bond, A. M.; Colton, R.; Moir, J. E.; Page, D. R. *Inorg. Chem.* **1985**, *24*, 1298.

(20) Bond, A. M.; Colton, R.; Ho, Y.; Mann, D. R.; Moir, J. E.; Stott, R. *Inorg. Chem.* **1985**, *24*, 4402.

(21) Bond, A. M.; Colton, R.; Mann, D. R. *Inorg. Chem.* **1989**, *28*, 54.

(22) Bond, A. M.; Colton, R.; Mann, D. R.; Moir, J. E. *Aust. J. Chem.* **1986**, *39*, 1385.

(23) De Croon, M. H. J. M.; van Gaal, H. L. M.; van der Ent, A. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 1081.

(24) Sceney, C. G.; Magee, R. J. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 595.

(25) Glen, K.; Swab, R. *Angew. Chem.* **1950**, *62*, 320.

(26) Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1976**, 32.

(27) Butcher, R. J.; Sinn, E. *J. Am. Chem. Soc.* **1976**, *98*, 2440.

(28) Budnikov, G. K.; Romanova, O. N.; Medyantseva, E. P. *J. Gen. Chem. USSR (Engl. Transl.)* **1987**, *57*, 1954.

(29) Coucouvanis, D. *Prog. Inorg. Chem.* (a) **1970**, *11*, 233; (b) **1979**, *26*, 301.

Table I. Electrochemical Data at a Platinum Electrode for Oxidation of 1.0×10^{-3} M $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$ Complexes in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

		(i_p^{ox}/i_p^{red})[a]			
compound	$E^r_{1/2}$, V[b]	v = 500 mV s^{-1}	v = 200 mV s^{-1}	v = 100 mV s^{-1}	v = 50 mV s^{-1}
$Ir(Et_2dtc)_3$	0.79	1.0	1.0	1.1	1.2
$Ir(i\text{-}Pr_2dtc)_3$	0.68	1.0	1.0	1.0	1.1
$Ir(Morphdtc)_3$	0.92	1.0	1.0	1.1	1.2
$Ir(Pyrrdtc)_3$	0.81	1.0	1.0	1.1	1.1
$Ir(Et_2dsc)_3$	0.56	1.0	1.1	1.1	1.2

[a] Calculated by using the semiempirical procedure of Nicholson[33] where $[i_p^{ox}/i_p^{red}]$ is the ratio of oxidation (i_p^{ox}) and reduction (i_p^{red}) peak currents. [b] Potential vs Ag/AgCl.

C, 26.6; H, 3.5; N, 6.2. Found: C, 26.2.; H, 3.5; N, 5.8. The remaining $Ir(RR'dtc)_3$ complexes were characterized by positive ion mass spectrometry and observation of the expected m/e value for $[Ir(RR'dtc)_3]^+$ and fragmentation pattern (see later).

A precipitate of crude $Ir(Et_2dsc)_3$ was prepared by adding an aqueous solution of Na_2IrCl_6 to a water/methanol solution of $(Et_2NH_2)(Et_2NCSe_2)$[30] followed by stirring for several days. Purification procedures were as for the dithiocarbamates, and collection of the yellow portion of the first chromatographic band followed by evaporation of the solvent yielded an orange solid. Anal. Calcd percentage by mass for $Ir(Et_2dsc)_3$: C, 19.6; H, 3.3; N, 4.6. Found: C, 19.4; H, 3.9; N, 3.9.

Iridium(IV) complexes were prepared by controlled-potential electrolysis of solutions of $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$ at a platinum-gauze electrode and characterized in solution by their voltammetric behavior and their visible spectra (see later).

Instrumentation. Voltammetric measurements were made with a Princeton Applied Research Corp. (PAR) (Princeton, NJ) Model 174A polarographic analyzer with a dropping mercury or a polished platinum disk working electrode. For experiments with a platinum rotating disk electrode either a Beckman or a Metrohm assembly was used. A platinum wire served as the auxiliary electrode while the reference electrode was Ag/AgCl (saturated LiCl in EtOH) separated from the test solution by a salt bridge. Unless otherwise stated, all measurements were made at 20 ± 1 °C with 0.1 M supporting electrolyte (Bu_4NClO_4) present.

Controlled-potential electrolysis experiments were performed at either a mercury-pool or a platinum-gauze working electrode with a PAR Model 173 potentiostat/galvanostat in conjunction with a PAR Model 179 digital coulometer. The platinum-gauze auxiliary electrode was isolated from the test solution via a salt bridge, and the reference electrode was that used for voltammetry.

Electron-impact positive ion mass spectra were obtained on a Finnigan 3200 series quadrupole mass spectrometer coupled to a Finnigan 6000 series interactive digital system. Spectra were obtained under the following conditions: electron energy 30–70 eV, filament emission current 0.5 mA, collector voltage 34.8 V, electron multiplier voltage 1.6 kV, and pressure (3–5) × 10^{-6} Torr. The compounds were introduced via a solids probe at temperatures of 200–350 °C.

Results and Discussion

Electrochemical Studies on Iridium Compounds. No reduction processes for $Ir(RR'dtc)_3$ or $Ir(Et_2dsc)_3$ were observed in dichloromethane (0.1 M Bu_4NClO_4) at either platinum or mercury electrodes. However, well-defined oxidation processes are found at both electrode surfaces and they have been characterized.

(a) Oxidation of $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$ at Platinum Electrodes. Electrochemical oxidation in dichloromethane (0.1 M Bu_4NClO_4) at a platinum disk electrode for each $Ir(RR'dtc)_3$ complex shows a single well-defined response (Figure 1a) corresponding to the chemically reversible process

$$Ir(RR'dtc)_3 \rightleftharpoons [Ir(RR'dtc)_3]^+ + e^- \qquad (1)$$

The reversible half-wave potentials, calculated as the average, $[(E_p^{ox} + E_p^{red})/2]$, of the oxidation, E_p^{ox}, and reduction, E_p^{red}, potentials by assuming equal diffusion coefficients for the oxidized and reduced species, are the $E°$ values for the $[Ir(RR'dtc)_3]^+/Ir(RR'dtc)_3$ redox couple. These values span the wide range of 0.68–0.92 V vs Ag/AgCl for the series of compounds studied. Data are summarized in Table I. The thermodynamic ($E°$) effects associated with change of the organic R group are essentially the same as for the cobalt and rhodium analogues[18-21] as well as for other metals.[29]

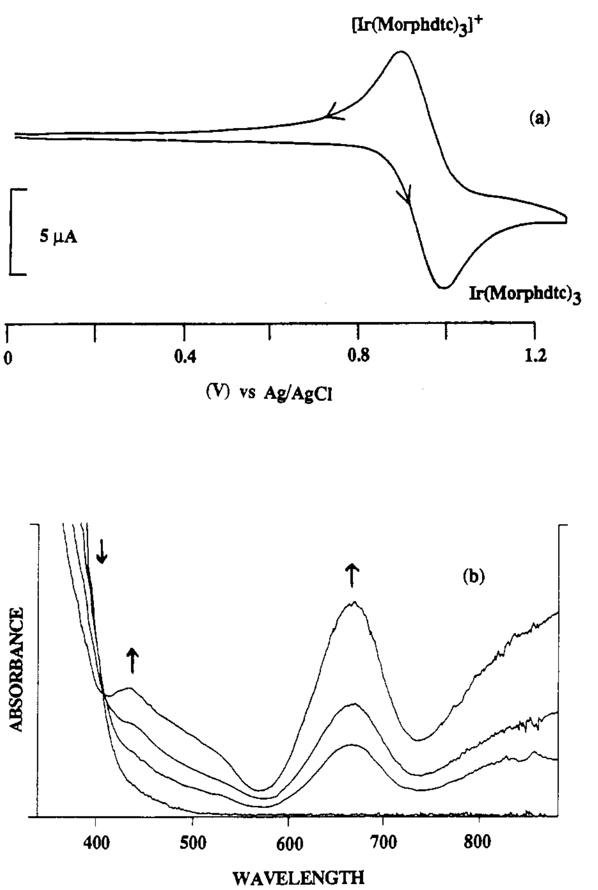


Figure 1. (a) Cyclic voltammogram (scan rate 200 mV s^{-1}) at a platinum electrode for oxidation of 1.0×10^{-3} M $Ir(Morphdtc)_3$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C. (b) Spectrophotometric monitoring of the oxidative controlled-potential electrolysis of $Ir(Morphdtc)_3$ in dichloromethane (0.1 Bu_4NClO_4) at a platinum gauze electrode at 20 °C.

Bulk oxidative controlled-potential electrolysis of $Ir(RR'dtc)_3$ at a potential of 1.0 V vs Ag/AgCl at a platinum-gauze electrode occurs with the transfer of (1.0 ± 0.1) electron per molecule (coulometric data), and the color of the solution changes from yellow to green. After the bulk electrolysis, as expected for a reversible process, reductive cyclic voltammograms commenced at a potential of 1.2 V vs Ag/AgCl and recorded at the platinum disk electrode show the same response as for the original solution. Monitoring of the solution during the course of the bulk electrolysis by the use of a platinum rotating disk electrode shows the original sigmoidal-shaped reversible oxidation process changing to a reversible reduction response as defined by a change in sign of the limiting current, but no change in $E^r_{1/2}$. Controlled-potential bulk reductive electrolysis of the green solution at 0.0 V vs Ag/AgCl is a one-electron process (coulometry), regenerating yellow $Ir(RR'dtc)_3$ at its original concentration (voltammetric monitoring).

Spectrophotometric measurements on a solution of $Ir(Et_2dtc)_3$ in dichloromethane during the course of the bulk oxidation and reduction experiments at platinum electrodes produce isosbestic points near 405 nm (Figure 1b) and confirm the complete chemical reversibility of the process on the synthetic time scale. All the data are consistent with the existence of a simple one-electron Ir(III)/Ir(IV) reversible process with the Ir(IV) complex having considerable stability. This stability of Ir(IV) is in marked contrast to the corresponding Co(IV) and Rh(IV) complexes, which rapidly undergo dimerization and internal redox reactions to yield $[M_2(RR'dtc)_5]^+$ complexes as the isolable products on the synthetic time scale.[18-21,31] Even on the time scale of days there is no

---

(30) Jensen, K. A.; Krishnan, V. *Acta Chem. Scand.* **1967**, *21*, 2904.

(31) Hendrickson, A. R.; Martin, R. L.; Taylor, D. *Aust. J. Chem.* **1976**, *29*, 269.

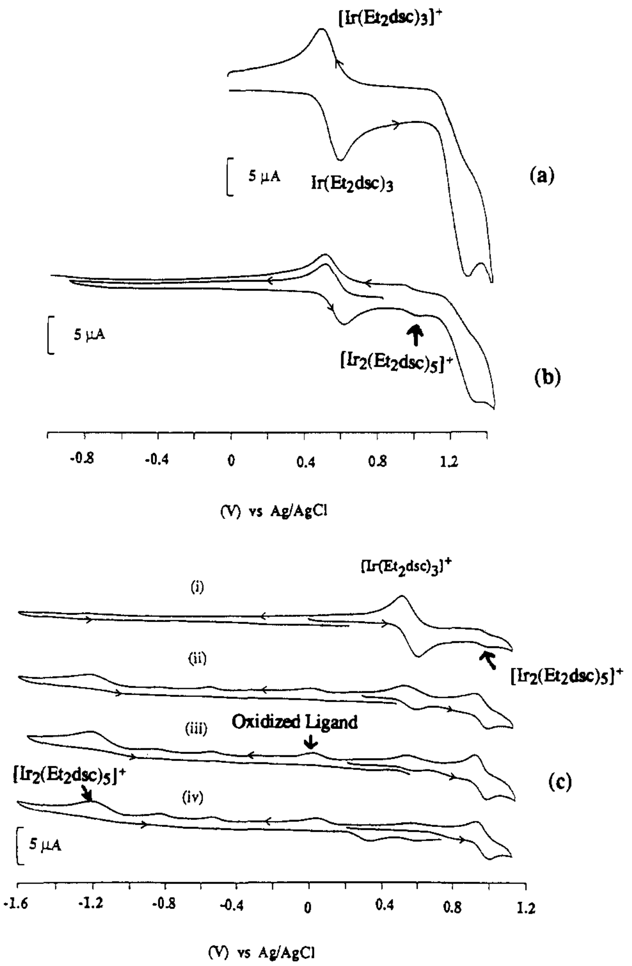


Figure 2. Cyclic voltammograms (scan rate 200 mV s^{-1}) at a platinum electrode for (a) oxidation of 1.0×10^{-3} M $Ir(Et_2dsc)_3$ in dichloromethane (0.1 M Bu_4NClO_4) at 20 °C (b) for the same solution immediately after bulk oxidative electrolysis of the same solution, (c) and for the same solution on standing after bulk electrolysis for (i) 0, (ii) 2, (iii) 4, and (iv) 8 h.

indication of a dimerization reaction for $[Ir(RR'dtc)_3]^+$. Initial studies[32] on the oxidation of $M(RR'dtc)_3$ (M = Co, Rh) complexes incorrectly identified the final product as being $[M(RR'dtc)_3]^+$ rather than $[M_2(RR'dtc)_5]^+$. The voltammetric and spectra data in Figure 1 unambiguously identify the oxidation product in the iridium case to be $[Ir(RR'dtc)_3]^+$ and reflect the considerably greater stability of the Ir(IV) complex relative to the Co(IV) and Rh(IV) analogues.

Similar data are obtained in acetone and acetonitrile solutions to that presented in dichloromethane, showing that the process for oxidation of $Ir(RR'dtc)_3$ is essentially independent of solvent. In acetonitrile, which has a wider available positive potential range, there is also an irreversible one-electron oxidation with a half-wave potential of about +1.5 V vs Ag/AgCl. This result suggests that iridium(V) is accessible as a short-lived species. However whether this second oxidation process is metal based or ligand based in the overall sense is unknown but it corresponds to eq 2. Since

$$[Ir(RR'dtc)_3]^+ \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Ir(RR'dtc)_3]^{2+} \rightarrow \text{products} \qquad (2)$$

the major theme of this paper concerns the $[M(RR'dtc)_3]^{+/0}$ redox couples, the process in eq 2 was not investigated further.

Cyclic voltammograms over the scan rate range 20–500 mV s^{-1} for the oxidation of $Ir(Et_2dsc)_3$ in dichloromethane at a platinum disk electrode show a well-defined reversible one-electron-oxidation process with an $E^r_{1/2}$ value of 0.56 V vs Ag/AgCl

$$Ir(Et_2dsc)_3 \rightleftharpoons [Ir(Et_2dsc)_3]^+ + e^- \qquad (3)$$

Table II. Polarographic Data obtained at 20 °C at a Mercury Electrode in the Presence of 1.0×10^{-3} M $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$ Complexes in Dichloromethane (0.1 M Bu_4NClO_4)

compound	dc[a] $E_{1/2}$, V[c]	dpp[b] E_p, V[c]	
$Ir(Et_2dtc)_3$	0.48	0.46	0.73[d]
$Ir(i\text{-}Pr_2dtc)_3$	0.43	0.41	0.70[d]
$Ir(Morphdtc)_3$	0.51[e]	0.50[f]	0.70[d]
$Ir(Pyrrdtc)_3$	0.40[e]	0.41[f]	0.78[d]
$Ir(Et_2dsc)_3$	0.25[e]	0.25[f]	

[a] Dc polarogram ($E_{1/2}$ = half-wave potential), drop time 0.5 s. [b] Differential-pulse polarogram (E_p = peak potential), drop time 0.5 s, pulse amplitude 50 mV. [c] Potential vs Ag/AgCl. [d] Small wave present as a shoulder on the mercury electrode oxidation process. [e] Maxima present. [f] Presence of absorption indicated.

A second one-electron process at 1.3 V vs Ag/AgCl remains irreversible over the temperature range +20 to −70 °C for a scan rate of 200 mV s^{-1}. Figure 2a shows a typical cyclic voltammogram for this complex. The potential of the reversible response, which is due to the $Ir(Et_2dsc)_3/[Ir(Er_2dsc)_3]^+$ oxidation process, is considerably less positive than that for the $Ir(Et_2dtc)_3/[Ir(Et_2dtc)_3]^+$ one, and this marked difference between dithiocarbamate and diselenocarbamate complexes has been observed before.[21,22] The second oxidative response parallels that seen only in acetonitrile for the $Ir(RR'dtc)_3$ complexes and is not considered further.

Bulk oxidative-controlled potential electrolysis of $Ir(Et_2dsc)_3$ in dichloromethane at a platinum-gauze electrode at a potential of 0.8 V vs Ag/AgCl occurs with the transfer of 1.0 ± 0.1 electron per molecule, and the solution changes from yellow to brown. However, cyclic voltammograms (Figure 2b) and rotating disk voltammograms recorded during the course of the electrolysis show that $[Ir(Et_2dsc)_3]^+$ is not the only product produced on the longer synthetic time scale. Another chemically reversible oxidation process becomes evident at about 1.0 V vs Ag/AgCl in addition to the expected Ir(III)/Ir(IV) reversible process (now reduction) at 0.56 V vs Ag/AgCl and irreversible oxidation process at 1.3 V vs Ag/AgCl. In addition, ligand-based processes around 0 V and a well-defined reduction process at −1.2 V vs Ag/AgCl are observed (Figure 2c). We have previously observed exactly analogous electrochemical behavior for the cobalt and rhodium dithiocarbamate and diselenocarbamate complexes, and in these cases, we have shown[20,21] by isolating authentic samples that these processes are associated with the formation of the oxidation state III binuclear species $[M_2(RR'dtc)_5]^+$ (eq 4), which is oxidized at positive potentials as in eq 5. The reduction response at −1.2

$$2[Ir(Et_2dsc)_3]^+ \rightarrow [Ir_2(Et_2dsc)_6]^{2+} \rightarrow [Ir_2(Et_2dsc)_5]^+ + \text{oxidized ligand} \qquad (4)$$

$$[Ir_2(Et_2dsc)_5]^+ \rightleftharpoons [Ir_2(Et_2dsc)_5)^{2+} + e^- \qquad (5)$$

V vs Ag/AgCl is due to the reduction of $[Ir_2(Et_2dsc)_5]^+$. When allowed to stand for many hours, all of the $[Ir(Et_2dsc)_3]^+$ is converted to $[Ir_2(Et_2dsc)_5]^+$ via the process given in eq 4 (Figure 2c).

(b) Oxidation Processes at Mercury Electrodes in the Presence of $Ir(RR'dtc)_3$ and $Ir(Et_2dsc)_3$. Electrochemical oxidation processes observed at dropping mercury electrodes in the presence of $Ir(RR'dtc)_3$ also are chemically reversible, but they occur at potentials much less positive than at platinum electrodes. They are complicated by adsorption effects, but approximate reversible $E_{1/2}$ values were obtained from dc and differential-pulse polarograms (Table II). Significantly, the oxidation potentials at mercury do not vary over as wide a range as they do at platinum (Table I) and cyclic voltammograms at hanging mercury drop electrodes are not as simple as those at platinum, with adsorption effects again being evident. Depending upon the ligand, the wave shape and the number of waves on the reverse scans of cyclic voltammograms all vary considerably.

Oxidative controlled-potential electrolysis in dichloromethane at a mercury-pool electrode is very slow because adsorption onto the surface causes inhibition of the process by blocking the

---

(32) Gahan, L. R.; O'Connor, M. J. *J. Chem. Soc., Chem. Commun.* **1974**, 68.

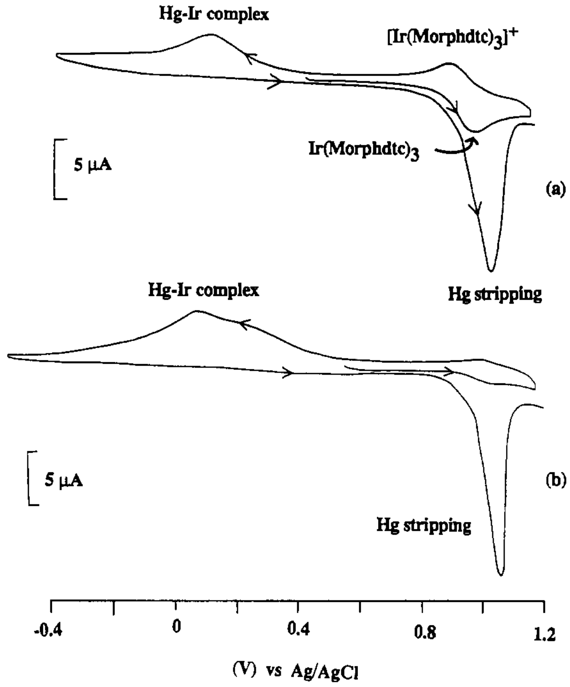


Figure 3. (a) Cyclic voltammogram (scan rate 200 mV s^{-1}) at a platinum electrode following oxidative controlled-potential electrolysis of Ir(Morphdtc)$_3$ in dichloromethane (0.1 M Bu_4NClO_4) at a mercury pool electrode at +0.60 V vs Ag/AgCl at 20 °C showing the mercury stripping peak on the second scan. (b) Cyclic voltammogram (scan rate 200 mV s^{-1}) at a platinum electrode at 20 °C of [Ir(Morphdtc)$_3$]$^+$ after reaction with Hg.

electrode. The color of the solution changes from yellow to orange rather than to green as is the case in the equivalent experiment at a platinum electrode. Coulometric determinations of the *n* value (*n* = number of electrons transferred per molecule) range from 0.5 to 0.8 when the current flow ceases, but the electrolyses are not exhaustive. Electrochemical measurements at a dropping mercury electrode during the course of the electrolysis show a significant amount of Ir(RR′dtc)$_3$ remains after the electrolysis, but on the basis of the amount of material actually oxidized, an *n* value of 1.0 ± 0.1 is always calculated for the number of electrons transferred per molecule of Ir(RR′dtc)$_3$ initially present. Figure 3a shows a cyclic voltammogram at a platinum electrode for a partially oxidized (mercury-pool electrode) solution of Ir(Morphdtc)$_3$. On the first scan, in addition to the oxidation of the residual Ir(Morphdtc)$_3$ at about 0.95 V vs Ag/AgCl, there is an irreversible reduction process at about 0.0 V vs Ag/AgCl. Scanning past this reduction wave at 0.0 V followed by scanning in the positive direction gives a large peak at about +1.0 V vs Ag/AgCl, which is attributable to the stripping of elemental mercury from the platinum electrode. The stripping peak is observed only after scanning past the reduction wave at 0.0 V vs Ag/AgCl. These results show that a mercury complex must be formed during the oxidative electrolysis at the mercury electrode, and the reduction peak at 0 V vs Ag/AgCl is due to the reduction of this complex.

Bulk reductive controlled-potential electrolysis at a large platinum-gauze electrode of the partially oxidized (mercury-pool electrode) solution results in the transfer of the same number of coulombs as for the original oxidation, and the color of the solution reverts back to yellow. The platinum electrode used in the reductive electrolysis becomes coated with mercury and its weight corresponds to a stoichiometry of Hg:Ir(Morphdtc)$_3$ = 1:2 for the oxidized product. Cyclic voltammograms at a platinum disk electrode show Ir(Morphdtc)$_3$ to be regenerated at its original concentration, and no extra responses are observed.

It is now clear that it is the mercury electrode which is oxidized during the oxidative electrolysis at mercury. The equation for the reaction is

$$2\mathrm{Ir(RR'dtc)_3} + \mathrm{Hg} \rightleftharpoons [\mathrm{HgIr_2(RR'dtc)_6}]^{2+} + 2e^- \quad (6)$$

and the mixed-metal complex is reduced at a platinum electrode according to

$$[\mathrm{HgIr_2(RR'dtc)_6}]^{2+} + 2e^- \rightarrow \mathrm{Hg(plated)} + 2\mathrm{Ir(RR'dtc)_3} \quad (7)$$

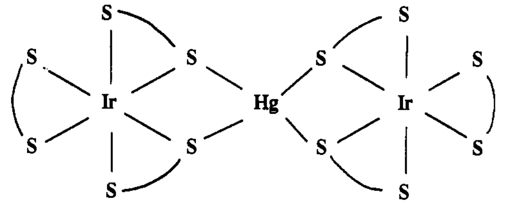
A much better electrochemical method of preparing this mixed mercury/iridium complex, which avoids the adsorption problems associated with electrolysis at a mercury-pool electrode, is to quantitatively generate green [Ir(RR′dtc)$_3$]$^+$ at a platinum electrode by bulk electrolysis of Ir(RR′dtc)$_3$ and then to react this Ir(IV) complex with elemental mercury. The solution immediately turns orange, and cyclic voltammograms (Figure 3b) show that the response due to the [Ir(Morphdtc)$_3$]$^+$/Ir(Morphdtc)$_3$ couple is now almost completely absent on the initial positive direction scan, indicating that the mercury complex is extremely strong. All steps are now quantitative on the synthetic time scale and reduction of the orange mercury/iridium complex at platinum gives a molar ratio of mercury to Ir(Morphdtc)$_3$ of exactly 1:2. The reaction between [Ir(RR′dtc)$_3$]$^+$ and Hg is a simple redox reaction

$$2[\mathrm{Ir(RR'dtc)_3}]^+ + \mathrm{Hg} \rightarrow [\mathrm{HgIr_2(RR'dtc)_6}]^{2+} \quad (8)$$

indicating that the iridium(IV) complex is a strong oxidant. This conclusion is further confirmed by demonstrating that the reaction with dithiocarbamate ion to give thiuram disulfide (tds) is quantitative

$$2[\mathrm{Ir(RR'dtc)_3}]^+ + 2[\mathrm{RR'dtc}]^- \rightarrow 2\mathrm{Ir(RR'dtc)_3} + \mathrm{tds} \quad (9)$$

While the detailed structure of the mixed iridium/mercury complex is unknown, it is presumably a bridged complex of the kind shown in structure I. The electrochemical oxidation processes at mercury electrodes in the presence of M(RR′dtc)$_3$ and M(RR′dsc)$_3$ complexes (M = Co, Rh) were noted to be different to those at platinum electrodes, but the products were unstable. The data on iridium now suggests that unstable [HgM$_2$(RR′dtc)$_6$]$^{2+}$ and [HgM$_2$(RR′dsc)$_6$]$^{2+}$ species are formed at mercury electrodes.



I

Mass Spectrometric Studies. Data from positive ion mass spectrometry for a range of Ir(RR′dtc)$_3$ complexes are given in Table III, and the parent ion corresponding to the formation of [Ir(RR′dtc)$_3$]$^+$ is observed. Unfortunately, the molecular weight of Ir(RR′dsc)$_3$ is above the maximum value of 800 available with the instrument used in this work so that its parent ion could not be observed.

The positive ion mass spectra of M(RR′dtc)$_3$ (M = Co, Rh, Ir) all show similar fragmentation patterns, although the relative abundances of the fragments varies with the metal. The fragmentation pattern is simple, generally only involving loss of ligand, CS_2, S_2, CS, or R(R′) and is similar to that found in other studies of metal dithiocarbamate compounds.[33-35] Table IV lists the fragments for the M(Et$_2$dtc)$_3$ compounds recorded under identical instrumental conditions. The molecular ion [M(Et$_2$dtc)$_3$]$^+$ is observed for all the compounds but at varying abundances, being most abundant for iridium and least abundant for cobalt, and this order is observed for all the dithiocarbamate derivatives studied. It is obvious that peaks due to [M(RR′dtc)$_2$]$^+$ and [M(RR′dtc)]$^+$

---

(33) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406.

(34) Matsumura-Inoue, T.; Kuroda, K.; Umezawa, Y.; Achiba, Y. *J. Chem. Soc., Faraday Trans. 2* **1989**, 857.

(35) Denisovich, L. I.; Peterleitner, M. G.; Kravtsov, D. N.; Kreindlin, A. Z.; Fadeeva, S. S.; Rybinskaya, M. I. *Organomet. Chem. USSR* (*Engl. Transl.*) **1988**, *1*, 166; *Metalloorg. Khim.* **1988**, *1*, 301.

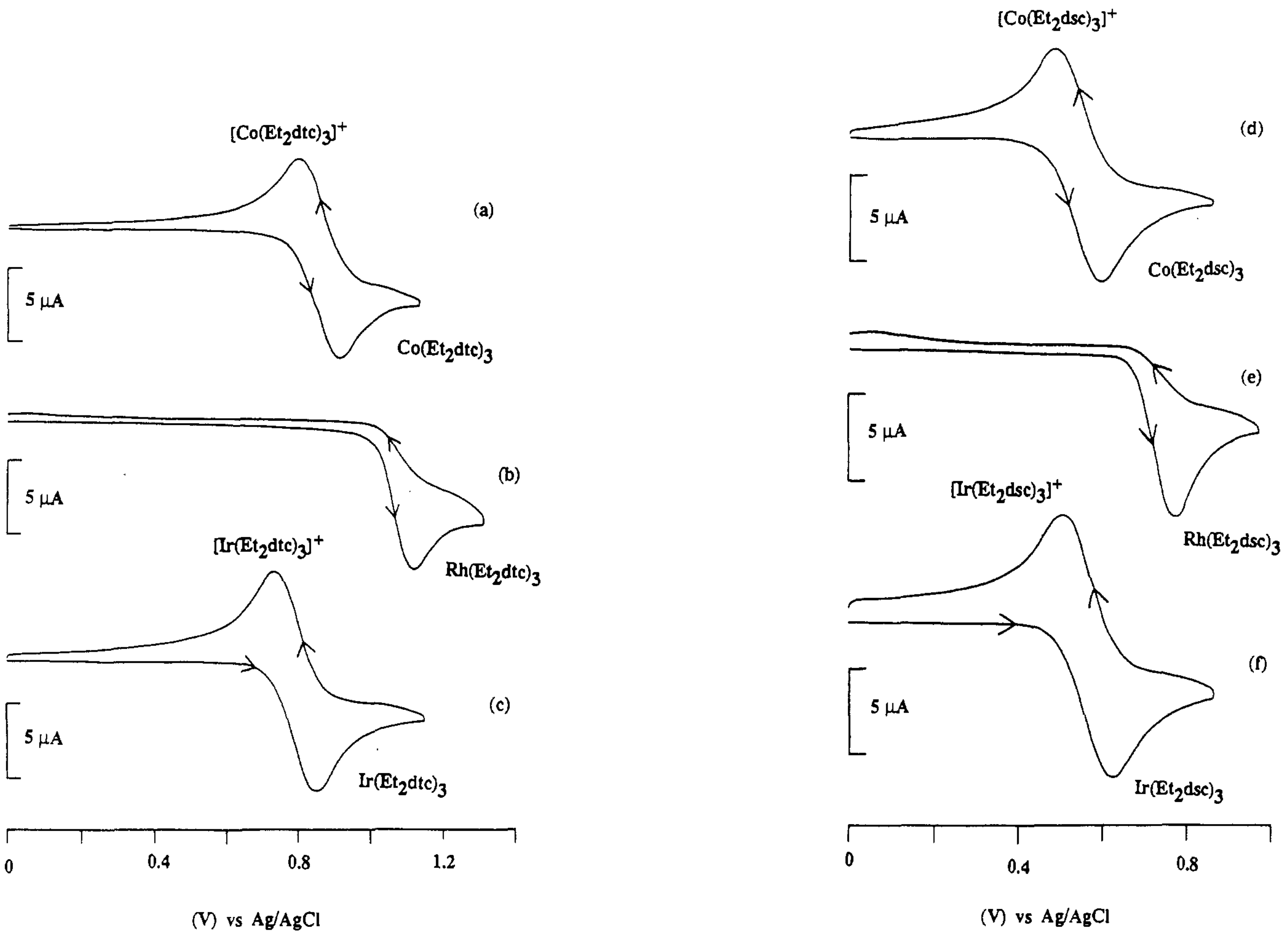


Figure 4. Cyclic voltammograms (scan rate 200 mV s^{-1}) for the oxidation of $M(Et_2dtc)_3$ and $M(Et_2dsc)_3$ in dichloromethane (0.1 M Bu_4NClO_4) at a platinum electrode at 20 °C: (a) $Co(Et_2dtc)_3$; (b) $Rh(Et_2dtc)_3$; (c) $Ir(Et_2dtc)_3$; (d) $Co(Et_2dsc)_3$; (e) $Rh(Et_2dsc)_3$; (f) $Ir(Et_2dsc)_3$.

Table III. Major Positive Ion Mass Spectral Fragments for $Ir(RR'dtc)_3$ Complexes[a]

	RR'							
	Et$_2$		*i*-Pr$_2$		Morph		Pyrr	
probable ion	*m/e*	% *I*	*m/e*	% *I*	*m/e*	% *I*	*m/e*	% *I*[b]
$[IrL_3]^+$	637	80	721	35	679	25	631	33
$[IrL_3 - S_2R]^+$	544	10	614	1				
$[IrL_2CS]^+$	533	7	589	1	561	3	529	3
$[IrL_2]^+$	489	31	545	13	517	9	485	16
$[IrL_2 - S]^+$	457	29	513	22	485	14	453	22
$[IrL_2 - S_2]^+$	425	52	481	8	453	31	421	46
$[IrLS_2]^+$	405	13	433	14	419	1		
$[L(\pm H)]^+$	148	5	176	7	162	2	146	2
$[L - S]^+$	116	69	144	14	130	37	114	63
$[L - SR(\pm H)]^+$	87	100	102	100				
$[L - S_2]^+$	84	8	112	3	98	4	82	5
$[L - CS_2]^+$	72	14	100	34	86	100	70	27
$[R]^+$	29		43	48				
$[H_2NCS]^+$	60	67	60	47	60	17	60	3

[a] *m/e* = mass to charge ratio; % *I* = % abundance; L = RR'dtc. [b] 100% abundance for unknown ion with *m/e* value of 72.

decrease in intensity as the metal changes from cobalt to iridium, suggesting that oxidation states III and II are much more stable for cobalt. The mass spectrometric data provide information on the reactivity of $[M(RR'dtc)_3]^+$ and $[M(RR'dsc)_3]^+$ species in the gas phase but none on the thermodynamics of redox processes in the gas phase.

General Summary and Conclusions

The oxidation of $M(RR'dtc)_3$ (M = Co, Rh, Ir) at a platinum electrode in dichloromethane solution produces an order of reactivity for the resultant $[M(RR'dtc)_3]^+$ species that is surprising. Co(IV) compounds are generally unstable. In the case of $[Co(RR'dtc)_3]^+$, they decompose on the synthetic time scale via an internal redox reaction to give the cobalt(III) complex $[Co_2(RR'dtc)_5]^+$ and an oxidized form of the ligand.[18-20] In contrast, $[Ir(RR'dtc)_3]^+$ compounds are stable, even on the synthetic time scale, and this order of stabilities is as expected from general trends in the relative stabilities of oxidation states of the transition metals.[4-6] It is the behavior of the rhodium complexes that is anomalous in the electrochemical studies in that Rh(IV) is much more reactive than Co(IV) and the rates of the dimerization reactions for rhodium, which preceed the internal redox reactions that form the dimeric oxidation state III binuclear complexes, are on the order of 1000 times greater than those for cobalt.[21]

Figure 4 shows the oxidative cyclic voltammograms for the $M(Et_2dtc)_3$ and $M(Et_2dsc)_3$ compounds. Although the oxidation response for $Rh(Et_2dtc)_3$ is irreversible at conventional scan rates, studies at very fast rates have shown[21] that the process becomes reversible under these conditions so that the $E°$ value of the $[Rh(RR'dtc)_3]^+/Rh(RR'dtc)_3$ couple can be calculated from the cyclic voltammograms. The order of $E°$ values is Rh(IV)/Rh(III) > Co(IV)/Co(III) > Ir(IV)/Ir(III) (Rh being most positive) and data are summarized in Table V. In the case of the diethylselenocarbamate complexes, the Co and Ir values are similar but much less positive than the value for rhodium. The substituent effects on the $E°$ values caused by varying the R groups are similar for all the metals. Clearly, the potential required to oxidize $Rh(Et_2dtc)_3$ is more positive than that required to oxidize either $Co(Et_2dtc)_3$ or $Ir(Et_2dtc)_3$. Since the decomposition reactions of the $[M(RR'dtc)_3]^+$ species to generate $[M_2(RR'dtc)_5]^+$ and oxidized ligand are redox-based, the more positive potential of the Rh(IV)/Rh(III) couple may explain why the Rh(IV) complexes are much more reactive than their Co(IV) analogues if kinetic terms parallel thermodynamic ones, which of course need not be the case. The reactivities of $[Ir(RR'dtc)_3]^+$ are far less, in accord

Table IV. Major Positive Ion Mass Spectral Fragments for $M(Et_2dtc)_3$ Complexes[a]

probable ion[b]	Co *m/e*	Co *% I*	Rh *m/e*	Rh *% I*	Ir *m/e*	Ir *% I*
$[ML_3]^+$	503	7	547	42	637	80
$[ML_3 - S_2R]^+$	410		454		544	10
$[ML_2CS]^+$	399		443		533	7
$[ML_2S]^+$	387	10	431		521	1
$[ML_2]^+$	355	100	399	100	489	31
$[ML_2 - S]^+$	323	5	367	34	457	29
$[ML_2 - S_2]^+$	291	17	335	86	425	52
$[MLS_2]^+$	271		315	2	405	13
$[ML_2 - S_2R]^+$	262	3	306	1	396	1
$[MLS]^+$	239	3	283	6	373	8
$[ML]^+$	207	20	251	11	341	2
$[ML - S(\pm H)]^+$	175	12	219	30	309	1
$[MRNCS]^+$	146	11	190	4	280	
$[ML - CS_2(\pm H)]^+$	131	1	175	3	265	
$[L(\pm H)]^+$	148	10	148	16	148	5
$[MS_2]^+$	123	4	167	14	257	
$[L - S]^+$	116	39	116	41	116	69
$[L - SR(\pm H)]^+$	87	36	87	66	87	100
$[L - S_2]^+$	84		84	4	84	8
$[L - CS_2]^+$	72	6	72	12	72	14
$[H_2NCS]^+$	60	14	60	26	60	67

[a] *All spectra recorded under identical instrumental conditions.* [b] L = Et_2NCS_2, R = Et; Other symbols are defined in Table III.

with both expectation and the electrochemical redox data.

In contrast, the mass spectrometric studies do show the expected trend for the reactivity of the M(IV) state of Co(IV) > Rh(IV) > Ir(IV) (based on the relative abundances of $[M(RR'dtc)_3]^+$) and the inverse order for the reactivities of the lower oxidation states (based on the relative abundances of $[M(RR'dtc)_2]^+$ and $[M(RR'dtc)]^+$). It is believed that the major reason for the differences in the reactivity trends between the electrochemical studies in the solution phase and mass spectrometric studies in the gas phase is that second-order gas-phase dimerization reactions are unfavorable under the conditions of mass spectrometry. Without this pathway, the rhodium(IV) dithiocarbamate complexes have their expected relative reactivities with respect to those of their Co(IV) and Ir(IV) counterparts.

Table V. Reversible Half-Wave Potentials ($\approx E^\circ$ values) Calculated from Cyclic Voltammetric Data Obtained at Platinum Electrodes at 20 °C for the Oxidation of 1.0×10^{-3} M $M(RR'dtc)_3$ and $M(Et_2dsc)_3$ in Dichloromethane (0.1 M Bu_4NClO_4)

ligand	$E^r_{1/2}$, V[b] Co	Rh[a]	Ir
Et_2dtc	0.86	1.12	0.79
i-Pr_2dtc	0.74	1.02	0.68
Morphdtc	1.01	1.22	0.92
Pyrrdtc	0.90	1.11	0.81
Et_2dsc	0.54	0.78	0.56

[a] Data obtained at very fast scan rate.[21] [b] Potential vs Ag/AgCl.

The gas-phase mass spectrometric data as obtained in this work do not provide thermodynamic information that can be correlated with the solution E° data obtained from electrochemical measurements. That is, all the above discussion concerning the comparison between gas and solution results refers to the kinetic reactivity of the $[M(RR'dtc)_3]^+$ and $[M(RR'dsc)_3]^+$ species. In other studies,[34] it has been demonstrated by photoelectron spectroscopy that gas-phase ionization energies of ferrocene derivatives may be correlated with the voltammetric data obtained in the range of solvents. Unfortunately, no ionization potential data are available for the compounds considered in this work, and a thermodynamic correlation cannot be considered.

However, a very recent report[35] has described a correlation between electrochemical oxidation in solution and ionization potential in the gas phase for $(C_5R_5)_2M$ compounds (M = Fe, Ru, Os; R = H, Me). Interestingly, both techniques show the order Fe < Os < Ru for these compounds.

Contribution from the Department of Chemistry,
University of British Columbia, Vancouver, BC, Canada V6T 1Y6

Independence of the Ethylene Ligands in Bis(η^2-ethene)rhodium(I) Complexes

Eugene B. Wickenheiser and William R. Cullen*

Received December 11, 1989

A ^1H NMR study of bis(η^2-ethene)(2'-acetylphenoxy-*O,O'*)rhodium(I) reveals two separate types of exchange processes, namely, ethylene rotation and ethylene dissociation. The exchange processes are studied by using a variety of NMR techniques that allow the calculation of the activation parameters: the ethylene ligands behave independently with respect to both types of exchange.

Introduction

The study of fluxionality in organometallic molecules provides useful information about the strength and type of interaction between ligand and metal, steric interactions between ligands, and preferred geometries and can lead to predictions of reactivity. NMR studies have revealed a variety of fluxional processes and techniques are available to correlate exchanging nuclei and, more importantly, determine rates of exchange.[1-7] Determination of the exchange rates at a range of temperatures allows the calculation of the activation parameters for the fluxional processes.

Data for the simplest calculation of $\Delta G^\ddagger$ can be acquired from the NMR spectrum at the temperature at which the resonances due to the exchanging nuclei coalesce.[4] More sophisticated methods determine the rate constant k for the fluxional process; the activation parameters can then be calculated by using the Eyring equation. A useful, and more accurate, technique for determining $\Delta G^\ddagger$, first described by Forsen and Hoffman,[8] is spin saturation transfer. In their method a resonance absorption due to one set of the exchanging nuclei is saturated and the decrease in intensity of the resonances due to the nuclei with which it is exchanging is monitored. A disadvantage of this spin saturation

---

(1) Cramer, R. *J. Am. Chem. Soc.* **1964**, *86*, 217.
(2) Vrieze, K.; Van Leeuwen, P. W. N. M. *Prog. Inorg. Chem.* **1974**, *14*, 1.
(3) Noggle, J. H.; Shirmer, R. E. *The Nuclear Overhauser Effect, Chemical Applications*; Academic: New York, 1971.
(4) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.
(5) Martin, M. L.; Martin, G. J.; Delpuech, J. *Practical NMR Spectroscopy*; Heyden and Son: London, 1980.
(6) Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.
(7) Stengle, T. R.; Langford, C. H. *Coord. Chem. Rev.* **1967**, *2*, 349.
(8) Forsen, S.; Hoffman, R. A. *J. Chem. Phys.* **1966**, *45*, 2059.

0020-1669/90/1329-4671$02.50/0 © 1990 American Chemical Society