atom, can be classified from the structural point of view according to the rules of classical complex chemistry, interesting transition-metal ring and cage systems are found in compounds containing metals with closed d shells. Especially remarkable are compounds with Cu^+ and Ag^+ (being very soft acids and having a high tendency to form metal–sulfur bonds), toward which MoS_4^{2-} and WS_4^{2-} act preferably as terdentate or tetradentate ligands.

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Registry No. $\{Mo_2S_8Ag_4\}(PPh_3)_4$, 70368-92-2; $(NH_4)_2MoS_4$, 15060-55-6.

Supplementary Material Available: Listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Notes

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Electrochemical Investigations of Some Azo Macrocyclic Ligands and Their Nickel(II) Complexes

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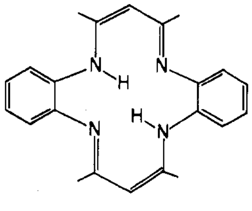
Introduction

The redox properties of transition-metal complexes containing synthetic macrocyclic ligands have been actively investigated.[1–9] Unlike the porphyrins, synthetic cyclic structures, especially those based on a Schiff-base reaction, offer a wide assortment of macrocyclic ring sizes, with a variety of types and degrees of unsaturation. These features, combined with the fact that macrocyclic complexes are generally more resistant toward demetallation than are their acyclic counterparts, make this class of compounds useful agents for exploring the relationship between ligand structure and metal oxidation state. Redox transformations which are necessary to explore this relationship do not normally lead to complex decomposition. We reported earlier[8] on a series of Mn(III) complexes containing the macrocyclic Schiff base **1**. Electrochemical oxidation of compounds having stoichiometry Mn^{III}–**1**(X), where X is Cl^-, Br^-, SCN^-, and N_3^-, did not lead to Mn(IV) complexes but lead instead to cation radicals containing an oxidized form of the ligand. Ligand oxidation also occurs if the bound metal ion is Ni(II), but in this case the cation radical which is formed rapidly dimerizes to form a dinuclear macrocyclic complex.[9] The dimer contains two macrocyclic units which are joined via the γ position of the diiminate framework. Although ligand oxidation has been observed for other tetraaza diiminate frameworks,[3,4] at least one group of diiminate compounds similar in structure to **1** sustain a metal-centered oxidation in preference to a ligand oxidation.[1,5] In an attempt to more clearly define the various factors which influence the site at which a redox process will take place within this type of macrocyclic structure, we have examined the electrochemical properties of the two methine-substituted macrocyclic ligands **2** and **3** and their nickel complexes Ni^{II}–**2** and Ni^{II}–**3**.[10] Since the latter two compounds contain three distinct groups, which are potentially polarographically active, the metal ion, the macrocyclic ligand, and the azo chromophore, we have also investigated the electro-



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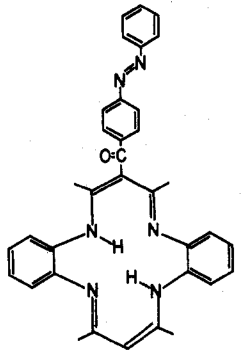

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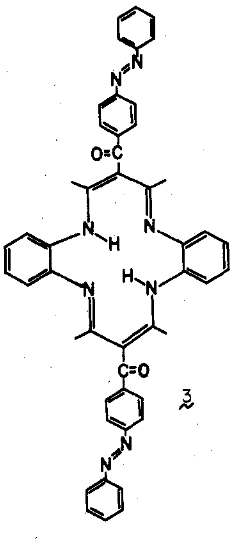

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chemistry of **1** and its Ni(II) complex, Ni^{II}–**1**, and have reinvestigated the electrochemistry of azobenzene itself.[11,12] Our findings form the basis of this report.

Experimental Section

Physical Measurements. All solutions for electrochemical and ESR measurements were prepared under nitrogen in an inert-atmosphere box. Proton magnetic resonance data were obtained in $CDCl_3$ solution with a Varian T-60A spectrometer. All shifts are reported relative to Me_4Si. Low-resolution mass spectra were provided by the Mass Spectroscopy Facility, Department of Chemistry, Cornell University, Ithaca, NY. Elemental analyses were performed by Galbraith Laboratories, Nashville, TN. All of the compounds gave satisfactory elemental analyses.

ESR spectra were obtained on a Varian Associates E-9 dual-cavity electron spin resonance spectrometer operating at ca. 9.4 GHz with 100 kHz modulation. Room-temperature electrochemical generation of redox products in the ESR cavity was done with a Varian Associates V-4556 three-electrode electrolytic cell suitably modified for nonaqueous use.

The electrochemical solvents acetonitrile and methylene chloride were purified in the previously described manner.[13,14] Unless otherwise noted acetonitrile was used as the electrochemical solvent. Tetraethylammonium tetrafluoroborate ($TEABF_4$) and tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$), at 0.1 M, were used as supporting electrolytes in the electrochemical studies.

A microprocessor electrochemical station was used to collect the electrochemical data.[15] In-phase ac polarograms were obtained with the aid of a Princeton Applied Research Model 121 lock-in amplifier. Positive *IR* compensation was employed where necessary, and a Hewlett-Packard Model 7001-A X-Y recorder was used to obtain permanent records of the polarographic traces. A conventional H-cell was used for all voltammetric measurements. The aqueous Ag/AgCl/saturated NaCl reference electrode was isolated from the background solution by an ultrafine-porosity glass frit, which in turn was further isolated from the depolarizer solution by another fine-porosity glass disk within the H-cell. This reference electrode has a potential of −0.047 V vs. SCE and +0.194 V vs. NHE at 25 °C.[16] Unless otherwise stated, all measurements were made by using a mercury working electrode.

All controlled-potential electrolysis experiments for the determination of coulometric *n* values were carried out in the H-cell by using a platinum gauze working electrode and a Ag/AgCl wire as the reference electrode. The coulometric *n* values found were the following [compound (couple, *n* value)]: Ni^{II}–**1** ($0 \rightarrow +1$, 0.97; $0 \rightarrow -1$, 1.04), Ni^{II}–**2** ($0 \rightarrow +1$, 0.94; $0 \rightarrow -1$, 1.00; $-1 \rightarrow -2$, 1.07), Ni^{II}–**3** ($0 \rightarrow +1$, 1.01), **2** ($0 \rightarrow -1$, 1.05; $-1 \rightarrow -2$, 0.95).

Syntheses. Preparation of 2 and 3. An acetonitrile solution of *p*-phenylazobenzoyl chloride (0.142 g, 0.58 mmol) was added, dropwise, to a hot (65 °C) acetonitrile solution containing the macrocyclic Schiff base **1** (2.9 mmol). The pale yellow solution which resulted was allowed to cool for 5–10 min. The small amount of the white dihydrochloride, **1**·2HCl, which formed was removed by filtration. The flask containing the filtrate was stoppered and allowed to stand for 1 day. The red crystalline solid which formed, crude **2**, was removed by filtration and washed three times with 40 ml of hot (60 °C) methanol to remove unreacted **1** and its dihydrochloride. After the solid was washed, the free ligand was dried over P_4O_{10} overnight under vacuum (0.01 mm). The yield of **2**, based on the *p*-phenylazobenzoyl chloride, was 53%. ^1H NMR ($CDCl_3$): δ 2.02 (s, 6 H), 2.16 (s, 6 H), 4.90 (s, 1 H), 7.0–8.3 (m, 17 H), 12.25 (s, 1 H), 13.88 (s, 1 H). Mass spectrum, *m/e*: calcd 553; obsd 553. Silica gel (C_6H_6) R_f(*trans*-**2**): 0.54.

The synthesis of **3** was identical with that used for **2**. However, in this case the synthesis required 1.0 g (2.9 mmol) of **3** and 0.71 g (2.9 mmol) of the acid chloride. The yield of **3** was 45%. ^1H NMR ($CDCl_3$): δ 2.00 (s, 12 H), 7.0–8.33 (m, 17 H), 14.67 (s, 2 H). Silica gel (C_6H_6) R_f: 0.36.

Preparation of Ni^{II}–2. The following synthesis was carried out in a dry nitrogen atmosphere. Nickel(II) acetate tetrahydrate (0.58 g, 2.3 mmol) was added to 0.26 g (0.47 mmol) of **2**, which had been dissolved in a 1:1 mixture of tetrahydrofuran and methanol. The reaction mixture was warmed to 35 °C and stirred.

The progress of the reaction could be conveniently checked by monitoring the ratio of the intensity of the absorption bands which occurred at 3.05 and 2.57 μm^{-1} in the spectrum of the reaction mixture. After 2 days, the ratio of the absorbances at 3.05 and 2.57 μm^{-1} was 1.1:1.0, and the reaction was judged to be complete. The resulting mixture was filtered, and the solvent was removed from the filtrate. For removal of any remaining nickel(II) acetate tetrahydrate, the residue was dissolved in 200 mL of CH_2Cl_2, and the solution was filtered. The resulting filtrate was again taken to dryness, leaving a deep green solid residue, Ni^{II}–**2**. The compound was recrystallized from acetonitrile and was dried over P_4O_{10} under vacuum (0.01 mm). The compound is best stored under nitrogen in the dark. The yield was 30%. ^1H NMR ($CDCl_3$): δ 1.83 (s, 6 H), 2.05 (s, 6 H), 4.83 (s, 1 H), 6.5–8.5 (m, 17 H). Mass spectrum, *m/e*: calcd 609; obsd 609. Silica gel (C_6H_6) R_f(*trans*-Ni^{II}–**2**): 0.55.

Preparation of Ni^{II}–3. The following procedure was also carried out in a dry nitrogen atmosphere. Five milliliters of triethylamine was added to a suspension of **3** (0.2 g, 0.26 mmol) and $Ni^{II}(CH_3CN)_6(BF_4)_2$ (0.63 g, 1.3 mmol) in 350 mL of a 1:1 mixture of THF and acetonitrile. The suspension was stirred in the dark at 40 °C for 1 day. After this time the solution was filtered to remove the deep green insoluble solid, crude Ni^{II}–**3**. The crude complex was washed with 20 mL of acetonitrile and dried under a stream of nitrogen gas. The complex was further dried over P_4O_{10} under vacuum (0.01 mm). The yield was 30%. The complex is best stored under nitrogen in the dark. ^1H NMR ($CDCl_3$): δ 2.06 (s, 12 H), 6.97–8.36 (m, 17 H). Silica gel (C_6H_6) R_f: 0.39.

Results and Discussion

The cyclic voltammograms of Ni^{II}–**1**, Ni^{II}–**2**, and Ni^{II}–**3** are shown in Figure 1, and the electrochemical data are collected in Table I. Ni^{II}–**1** exhibits a one-electron reversible reduction at −1.714 V. In order to establish the electron-density distribution of the one-electron reduction product, controlled-potential electrolyses at −1.9 V followed by ESR measurements were undertaken. The liquid-nitrogen ESR spectrum of the complex obtained from reduction exhibited three transitions at $g_x = 2.137$, $g_y = 2.03$, and $g_z = 2.02$ (Table II) which were characteristic of a d^9 transition-metal ion in a rhombic crystal field.[17] Thus, the reduction is metal centered, and the product is Ni^{I}–**1** and not an anion radical. Axial ligation by the acetonitrile solvent, as has occurred for other Ni(I) complexes,[1] apparently does not happen with Ni^{I}–**1**. None of the ESR transitions exhibited superhyperfine structure. Since the third-reduction process of Ni^{II}–**2** occurred at the same potential (−1.71 V) and possessed essentially the same electrochemical characteristics as did the first-reduction wave of Ni^{II}–**1**, it is probably associated with the production of Ni^{I}–**2**. Because of its limited solubility in acetonitrile, the metal-centered reduction of Ni^{II}–**3** could not be observed.

Both Ni^{II}–**2** and Ni^{II}–**3** exhibit two one-electron reduction processes in the potential range −1.0 to −1.3 V. Since the free

Table I. Voltammetric Data for the Compounds

compd couple	$E_{1/2}$, V[a]	ΔE_p, mV[b]	half-width,[c] mV
1			
$+1 \rightarrow +2$[d]	+1.39	NRP	
$0 \rightarrow +1$[d]	+0.67	NRP	
2			
$+1 \rightarrow +2$[d]	+1.36	NRP	
$0 \rightarrow +1$[d]	+0.939	NRP	
$0 \rightarrow -1$	−1.084	60	95
$-1 \rightarrow -2$	−1.383	60	97
3			
$+1 \rightarrow +2$[d]	+1.351	NRP	
$0 \rightarrow +1$[d]	+0.934	NRP	
$0 \rightarrow -2$	−1.056	60	98
$-2 \rightarrow -4$	−1.316	60	95
azobenzene			
$0 \rightarrow +1$[d]	+1.856	NRP	
$0 \rightarrow -1$	−1.360	69	90
$-1 \rightarrow -2$	−1.717	NRP	120
Ni^{II}–**1**			
$+1 \rightarrow +2$[d]	+0.97	NRP	
$0 \rightarrow +1$	+0.434	840	92
$0 \rightarrow -1$	−1.714	65	92
$-1 \rightarrow -2$	−2.240	140	91
Ni^{II}–**2**			
$+1 \rightarrow +1$[d]			
$0 \rightarrow +1$[d]	+1.15	NRP	
$0 \rightarrow -1$	+0.556	1430	96
$-1 \rightarrow -2$	−1.032	65	92
$-2 \rightarrow -3$	−1.350	190	200
Ni^{II}–**3**	−1.710	92	92
$+1 \rightarrow +2$[d]			
$0 \rightarrow +1$	+1.264	95	
$0 \rightarrow -2$	+0.709	68	92
$-2 \rightarrow -4$	−1.116	90	111
	−1.382	140	146

[a] The half-wave potential as determined by dc polarography is given. [b] The cyclic voltammetric peak-to-peak separation in mV is given. NRP means no reverse peak. [c] The peak width at half-height in mV of the ac polarogram is given. Applied frequency, 30 Hz. [d] At a rotating platinum electrode.

Table II. ESR Data for the Macrocyclic Complexes and Free Ligands[a]

compd	couple	g[b]	oxidn state characterizn
Ni^{II}–**2**	$0 \rightarrow -1$	2.005 (19)	ligand radical
Ni^{II}–**3**	$0 \rightarrow +1$	2.005 (65)	ligand radical
	$0 \rightarrow -1$	2.003 (19)	ligand radical
2	$0 \rightarrow -1$	2.004 (18)	ligand radical
3[c]	$0 \rightarrow -1$	2.004 (17)	ligand radical
azobenzene	$0 \rightarrow -1$	2.004 (10)	ligand radical
Ni^{II}–**1**[d]	$0 \rightarrow -1$	$g_x = 2.137$, $g_y = 2.03$, $g_z = 2.02$	Ni^{I}

[a] Unless otherwise noted all spectra were determined at room temperature in acetonitrile by using $TEABF_4$ as a supporting electrolyte. [b] The peak to peak width in gauss is given in parentheses. [c] Done in CH_2Cl_2 by using $TBAPF_6$ as the background electrolyte. [d] Done with $TBAPF_6$ at 77 K.

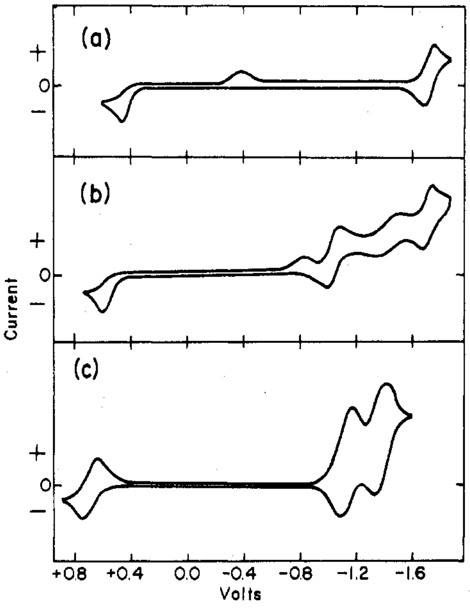

Figure 1. Cyclic voltammograms of Ni^{II}–**1** (a), Ni^{II}–**2** (b), and Ni^{II}–**3** (c).

ligands **2** and **3** as well as azobenzene also reduce in this region, the reductions in the metal complexes must be associated with the azo chromophores. As a check, the first-reduction products of Ni^{II}–**2**, Ni^{II}–**3**, the free ligands **2** and **3**, and azobenzene were generated by constant-potential electrolysis. In every case, ESR studies showed the electrogenerated products to be free radical in nature and to give g values of ~2.0 (Table II). The radical nature of the first one-electron reduction product of azobenzene has been previously reported.[11]

Consideration of the diffusion currents for Ni^{II}–**3** and **3** relative to those of Ni^{II}–**2** and **2** shows that both azo linkages in the bis(azo) analogues sustain reduction. The diffusion currents of Ni^{II}–**3** and **3** were approximately twice those of the monoazo analogues. Thus, reduction of Ni^{II}–**3** and its free ligand leads to ESR-active diradical dianions. The similarity in reduction behavior and ESR properties of **2** and **3** and their Ni(II) complexes shows that the two azo linkages in the bis(azo) adducts act independently of one another.

Constant-potential electrolysis to generate the second-reduction product of all of the compounds yielded diamagnetic species. By analogy with azobenzene, these compounds probably contain a protonated form of the azo dianion.[18]

Earlier chemical[19] and electrochemical[9] studies of Ni^{II}–**1** have shown that the oxidation of this complex results in a compound containing an oxidized form of the ligand. The radical cation initially produced in the reaction is unstable, and it rapidly dimerizes to form a dinuclear macrocyclic complex. Examining this oxidation with cyclic voltammetry has shown that the system is electrochemically irreversible, the observed CV peak splitting being ~800 mV (Table I and Figure 1). Similar oxidation behavior also occurs for Ni^{II}–**2**; however, examining the 0 → +1 couple by using ac polarography revealed that the oxidations of Ni^{II}–**1** and Ni^{II}–**2** are reversible. Under ac conditions, the cation radical generated is apparently reduced before it has any opportunity to dimerize. Since the first-oxidation process of the diazo complex Ni^{II}–**3** is electrochemically reversible at all CV scan rates employed, it apparently oxidizes to an anion which does not dimerize. The presence of free radical for [Ni^{II}–**3**]$^+$ was confirmed via ESR of the oxidized species (Table II).

It thus appears that for these compounds dimer formation depends on the nature of and/or the presence of a substituent at the γ position of the macrocyclic framework. If the substituent is a hydrogen atom, dimer formation occurs. If it is a benzoyl group, as it is in this case, oxidation occurs, but the radical which is formed is stable and it does not dimerize. The origins of this contrasting behavior are not yet clear. However, in an effort to understand the various electronic and/or steric effects which control this interesting reaction, we are synthesizing and intend to examine the electrochemical properties of a series of systematically substituted macrocyclic compounds.

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Registry No. **1**, 56276-51-8; **2**, 70320-24-0; **3**, 70320-25-1; Ni^{II}–**1**, 51223-51-9; Ni^{II}–**2**, 70354-80-2; Ni^{II}–**3**, 70320-77-3; Ni^{II}(CH$_3$CN)$_6$(BF$_4$)$_2$, 15170-11-3; *p*-phenylazobenzoyl chloride, 104-24-5; azobenzene, 103-33-3.

Supplementary Material Available: An extended version of Table I containing additional polarographic and voltammetric data (2 pages). Ordering information is given on any current masthead page.

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Complexes of the Platinum Metals. 16.[1] New Carboxylato Derivatives of Ruthenium(III) and Osmium(III)

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Received November 27, 1978

Since their discovery over ten years ago, the ruthenium(II) triphenylphosphine complexes RuX$_2$(PPh$_3$)$_n$ (X = Cl or Br; n = 3 or 4)[2] and, to a lesser degree, their osmium analogues[3] have attracted much attention. Their structures,[4,5] dissociative behavior,[5,6] chemical reactivity,[7] and catalytic activity[8] have all been intensively studied, and their aerobic oxidation in organic media has been well documented.[6,9] However, the nature of the ruthenium and osmium species present in the dark colored solutions after oxidation has not been properly elucidated. Moreover, aerobic oxidation of the complexes MX$_2$(PPh$_3$)$_3$ in organic media has attracted little attention as a possible route to ruthenium(III) and osmium(III) derivatives.

We now find that under aerobic conditions the complexes MX$_2$(PPh$_3$)$_3$ react with carboxylic acids, RCO$_2$H (R = alkyl or aryl), in benzene to afford red-brown solutions from which air-stable carboxylato derivatives MX$_2$(O$_2$CR)(PPh$_3$)$_2$ rapidly crystallize (R = aryl) or may be precipitated with petroleum ether (R = alkyl). In the absence of air, unchanged ruthenium(II) and osmium(II) complexes are recovered in good yield.

Experimental Section

The ruthenium and osmium halide complexes MX$_2$(PPh$_3$)$_n$ (M = Ru, X = Cl or Br; M = Os, X = Br; n = 3 or 4) were prepared by standard literature procedures[2,3] with platinum metal salts obtained from Johnson Matthey and Co., Ltd. Benzene, petroleum ether (bp 40–60 °C), and carboxylic acids were used as purchased. All reactions were performed in open conical flasks over a steam bath situated in an efficient fumehood. Infrared spectra were taken on a Perkin-Elmer 621 grating spectrometer by using KBr disks, and molecular weights were determined with a Perkin-Elmer Hitachi osmometer. Analyses were performed by the microanalytical laboratories at University College, London, and the School of Pharmacy, London. Melting points were taken in sealed tubes under nitrogen with a Buchi melting point apparatus.

Dichloro(benzoato)bis(triphenylphosphine)ruthenium(III) was prepared by the following two methods.

Method a. Dichlorotris(triphenylphosphine)ruthenium (0.48 g, 0.5 mM) and benzoic acid (0.12 g, 1.0 mM) were warmed together in benzene (15 mL) at ca. 70 °C for 15 min. The resultant red-brown solution was then filtered, cooled to room temperature, and set aside to crystallize. After ca. 24–48 h the precipitated solid was filtered off, washed with petroleum ether (bp 40–60 °C), and dried in vacuo to yield the required product as red-brown platelets (0.389 g, 95%).

Method b. Dichlorotris(triphenylphosphine)ruthenium (0.48 g, 0.5 mM) and benzoyl peroxide (0.125 g, 0.5 mM) were warmed together in benzene (15 mL) at ca. 70 °C for 15 min. The resultant red-brown solution was worked up as described above to yield the required product as red-brown platelets (0.372 g, 90%). The following were prepared by method a with the appropriate carboxylic acid; where necessary, crystallization of the required product from the benzene solution was induced by addition of petroleum ether (bp 40–60 °C): **dichloro(acetato)bis(triphenylphosphine)ruthenium(III)** as flesh pink needles (41%), **dichloro(propionato)bis(triphenylphosphine)ruthenium(III)** as flesh pink microcrystals (62%), **dichloro(chloroacetato)bis(triphenylphosphine)ruthenium(III)** as cream needles (57%), **dichloro(*p*-chlorobenzoato)bis(triphenylphosphine)ruthenium(III)** as flesh pink platelets (38%), **dichloro(*o*-bromobenzoato)bis(triphenylphosphine)ruthenium(III)** as red-brown platelets (55%), **dichloro(*p*-bromobenzoato)bis(triphenylphosphine)ruthenium(III)** as orange-brown platelets (60%), **dichloro(*p*-methoxybenzoato)bis(triphenylphosphine)ruthenium(III)** as orange-brown platelets (84%), **dichloro(*o*-toluato)bis(triphenylphosphine)ruthenium(III)** as red-brown platelets (56%), **dichloro(*p*-toluato)bis(triphenylphosphine)ruthenium(III)** as orange-brown microcrystals (52%), **dichloro(*p*-nitrobenzoato)bis(triphenylphosphine)ruthenium(III)** as red-brown platelets (63%).

The following were prepared by method a with dibromotris(triphenylphosphine)ruthenium and the appropriate carboxylic acid: **dibromo(acetato)bis(triphenylphosphine)ruthenium(III)** as lustrous brown platelets (62%), **dibromo(benzoato)bis(triphenylphosphine)ruthenium(III)** as dark brown microcrystals (58%), **dibromo(*p*-bromobenzoato)bis(triphenylphosphine)ruthenium(III)** as brown rhombic crystals (40%), **dibromo(*p*-toluato)bis(triphenylphosphine)ruthenium(III)** as yellow-brown rhombic crystals (44%).

Dibromo(benzoato)bis(triphenylphosphine)ruthenium(III), as dark brown microcrystals (65%), was prepared by method b with dibromotris(triphenylphosphine)ruthenium.

The following were prepared by method a with dibromotris(triphenylphosphine)osmium: **dibromo(benzoato)bis(triphenylphosphine)osmium(III)** as bright yellow microcrystals (31%), **dibromo(*p*-bromobenzoato)bis(triphenylphosphine)osmium(III)** as bright yellow microcrystals (40%), **dibromo(*p*-toluato)bis(triphenylphosphine)osmium(III)** as bright yellow microcrystals (40%).

Results and Discussion

The ruthenium and osmium complexes MX$_2$(PPh$_3$)$_3$ dissolve in warm benzene under aerobic conditions and in the presence of carboxylic acids to afford dark red-brown (M = Ru) or yellow-brown (M = Os) solutions from which products of