Table I. Fixation of Nitrogen in Aqueous Solution at 25° and 1 Atm (N_2 + $3H_2$) Catalyzed by Platinum Group Metal Ions

No.	Catalyst	Reducing agent	[Catalyst], *M*	Yield of NH_3, mol/mol of catalyst
1	Ru(II)	$TiCl_3$	1.6×10^{-3}	0.40
2	Ru(III)	$SnCl_2$	1.6×10^{-3}	0.07
3	Ru(III)	$(CH_3)_2SnCl_2$	4.0×10^{-4}	0.05
4	Rh(III)	$TiCl_3$	1.0×10^{-3}	0.36
5	Rh(III)	$SnCl_2$	5.0×10^{-4}	0.40
6	Rh(III)	$SnCl_2$ + PPh_3	5.0×10^{-4}	0.06
7	Rh(III)	$SnCl_2$ + $TiCl_3$	1.0×10^{-3}	0.36
8	Ir(III)	$SnCl_2$	2.7×10^{-3}	0.10
9	Ir(III)	$TiCl_3$	2.7×10^{-3}	0.20
10	Os(II)	$TiCl_3$	2.7×10^{-3}	0.10
11	Os(III)	$SnCl_2$	2.7×10^{-3}	0.12

In the above solutions the active reducing agent seems to be molecular hydrogen since no ammonia was obtained when gaseous nitrogen alone was passed through the catalytic solution.

Isotopic Analysis. An isotopic mixture of $^{15}N_2$ (25% enrichment) and H_2 in the ratio of 1:3 was circulated through a catalyst solution containing Ru(II) + $TiCl_3$ or Rh(III) + $SnCl_2$. The liberated ammonia was absorbed in the Kjeldahl apparatus and the resulting NH_4NO_3 and $^{15}NH_4NO_3$ solution was carefully dried and examined with a mass spectrometer. The mass spectrograms of N_2O obtained by the decomposition of NH_4NO_3 and $^{15}NH_4NO_3$ gave relative peak intensities of 4:1 for mass 44 and 45, respectively, indicating enrichment of ^{15}N in the reaction product.

Results

The yield of ammonia obtained in the catalytic runs varied from 0.05 to 0.4 mol/mol of catalyst, as indicated in Table I. The best catalysts were found to be Ru(II) + $TiCl_3$ and Rh(III) + $SnCl_2$. $TiCl_3$ and $SnCl_2$ alone or combined were inactive in the fixation of nitrogen under the same experimental conditions.

Fixation of nitrogen from the reaction mixture consisting of nitrogen and hydrogen was further established by isotopic analysis. Prominent peaks of N_2O at mass numbers 44 and 45 ($^{14}N_2O$ and $^{14}N^{15}NO$) established nitrogen fixation in catalyst systems no. 1 and 5 of Table I (Ru(II) + $TiCl_3$ and Rh(III) + $SnCl_2$). These were the systems which gave the highest yields of ammonia. The ratio of the intensities obtained for N_2O of mass numbers 44 and 45 confirm that the nitrogen fixed was produced from the nitrogen gas circulated through the catalytic solution.

Discussion

Fixation of molecular nitrogen in aqueous solution containing molybdenum,[7] molybdenum and iron,[8] and iron compounds[9] in the presence of thiol groups and a reducing agent like borohydride or dithionite had been previously reported. In all these cases, the maximum yield of ammonia reported[2-9] varied from 0.05 to 0.15 mol/mol of the catalyst. These systems are of some theoretical interest because they serve as models of nitrogenase.

Although a truly catalytic system for the fixation of molecular nitrogen at ambient conditions is yet to be developed,[6] the reactions carried out in the present investigation are significant as the first catalysis by platinum group metal ions in aqueous solution. Of the nitrogen fixation systems tabulated in Table I, the maximum yield of ammonia was obtained with solutions of the metal ions ruthenium(II) and rhodium(III) having the $4d^6$ electronic configuration. The metal ions iridium(III) and osmium(II) with the $5d^6$ configuration were far less reactive than the $4d^6$ systems. The observed catalytic reactivity of these metal ions is thus in accord with the reported stability[6] of their stable dinitrogen complexes which decreases in the order 5d > 3d > 4d. The ruthenium(II) and rhodium(III) solutions employed in the present investigation are expected to form reactive dinitrogen complexes in the absence of stabilizing ligands such as ammonia or tertiary phosphines. These complexes are thus readily reduced to ammonia. It is interesting to note that no stable dinitrogen complex of rhodium(III) has been reported thus far.

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Registry No. N_2, 7727-37-9; Ru(II), 22541-59-9; Ru(III), 22541-88-4; Ir(III), 22555-00-6; Os(II), 22542-07-0; Os(III), 22542-06-9; $TiCl_3$, 7705-07-9; $SnCl_2$, 7772-99-8; $(CH_3)_2SnCl_2$, 753-73-1.

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Preparation of $[diphosMo(CO)_4SnCl_3]^+[SnCl_5OH_2]^-$ and Related Derivatives

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There is kinetic[1-3] and synthetic[4,5] evidence that the reaction of metal carbonyl complexes with SnX_4 or HgX_2 (X = halogen) proceeds in a stepwise fashion. The first step (or steps) involves donor–adduct formation, and the second, oxidation, *e.g.*

$$L_2M(CO)_4 + nTX \rightarrow \underset{1}{L_2M(CO)_4 \cdot nTX} \rightarrow \underset{2}{L_2M(CO)_3(T)X} + CO + (n-1)TX$$

L_2 = for example $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (diphos) or 2,2'-dipyridyl; TX = HgX_2 or SnX_4.

Depending on the nature of the metal carbonyl compounds of either type **1** or type **2** may be isolated. However, the $SnCl_4$ derivatives of type **1** have not been fully characterized because of their air-sensitive nature.[6]

Herein we report the characterization of the products of the reaction of 2 mol of $SnCl_4$ with $L_2M(CO)_4$ (L_2 = diphos or diars [1,2-($(CH_3)_2As)_2C_6H_4$]; M = Mo or W). An X-ray crystallographic study[7] of one of these has shown that it should be formulated as $[diphosMo(CO)_4SnCl_3]^+[SnCl_5OH_2]^-$.

Table I. Analytical Data for New Complexes[a]

Compd	% calcd C	% calcd H	% calcd Cl	% found C	% found H	% found Cl
$[\text{diphosMo(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]\cdot\text{C}_6\text{H}_6$	35.34	2.64	23.18	35.41	2.55	23.63
$[\text{diphosW(CO)}_4\text{SnCl}_3[\text{SnCl}_5\text{OH}_2]\cdot\text{C}_6\text{H}_6$	32.96	2.46	21.62	32.72	2.41	22.00
$[\text{diarsMo(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	16.28	1.76	27.46	16.80	1.81	27.49
$[\text{diarsW(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	15.00	1.62	25.30	15.96	1.66	25.71
$[(\text{H}^3)\text{As}_2\text{Mo(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	12.31	1.88	26.43	12.33	1.91	26.08
$[(\text{H}^3)\text{As}_2\text{W(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	13.42	2.05	28.80	14.03	2.01	28.75

[a] diphos = $((\text{C}_6\text{H}_5)_2\text{PCH}_2)_2$, diars = 1,2-$((\text{CH}_3)_2\text{As})_2\text{C}_6\text{H}_4$, $(\text{H}^3)\text{As}_2 = (\text{CH}_3)_2\text{As}(\text{CH}_2)_3\text{As}(\text{CH}_3)_2$.

Table II. Representative Mössbauer ^{119}Sn Parameters

Compd	IS[a]	QS[b]
$[\text{diphosMo(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	1.22	1.60
	0.95	0
$[\text{diphosW(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$	1.18	1.62
	0.87	0

[a] Isomer shift in mm sec^{-1} relative to Ba^{119}SnO$_3$. [b] Quadrupole splitting in mm sec^{-1}.

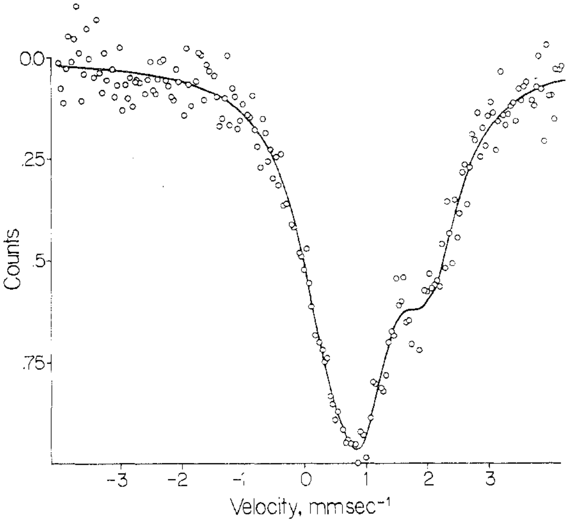

Figure 1. Mössbauer spectrum of $[\text{diphosMo(CO)}_4\text{SnCl}_3]$-$[\text{SnCl}_5\text{OH}_2]$.

Experimental Section

Materials. Hydrocarbon solvents were dried using CaH_2. They were stored under N_2 and over sodium before use. Stannic chloride was obtained commercially and used without further purification. The following complexes were prepared by literature methods (or using minor variations thereof): diphosM(CO)$_4$,[8] diarsM(CO)$_4$,[9] and $[(\text{CH}_3)_2\text{As}(\text{CH}_2)_3\text{As}(\text{CH}_3)_2]\text{M(CO)}_4$[10] (M = Mo or W). All new complexes were prepared under a nitrogen atmosphere using Schlenk tube techniques. Other manipulations were carried out in a dry (over P_4O_{10}) glove bag, under nitrogen.

Preparation of $[\text{diphosMo(CO)}_4\text{SnCl}_3]^+[\text{SnCl}_5\text{OH}_2]^-\cdot\text{C}_6\text{H}_6$. To a solution of diphosMo(CO)$_4$ (0.606 g, 1 mmol) in 25 ml of benzene was added SnCl_4 (1 ml, 8.5 mmol). The color of the solution immediately deepened to a yellow-orange. The solution was stirred and after a short induction period (*ca.* 7 min) a yellow precipitate formed. Stirring was allowed to continue for 45 min. The benzene and excess SnCl_4 were then removed and the precipitate washed several times with petroleum ether (bp 50–60°) and dried under vacuum. The yield (1.10 g) of $[\text{diphosMo(CO)}_4\text{SnCl}_3]^+[\text{SnCl}_5\text{OH}_2]^-\cdot\text{C}_6\text{H}_6$ was 90%.

By carrying out the reaction at 6° without stirring, the product was deposited as yellow crystals suitable for crystallographic study. The preparation of the other derivatives (Table I) was essentially the same. With the di(tertiary arsine) complexes precipitation of the product was immediate upon addition of SnCl_4. The chromium compound diphosCr(CO)$_4$ did not give a precipitate with SnCl_4 although a color change was observed.

In air the diphos derivatives began to show signs of decomposition after 2–3 min; with the arsenic derivatives it was faster, obvious signs of decomposition appearing after only 30 sec. In both cases the tungsten complexes appeared more robust than the molybdenum analogs.

Microanalyses (Table I) were carried out by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, West Germany.

Mössbauer spectra were recorded as previously described.[11] In all cases the spectra were similar (Figure 1). Difficulty was experienced in fitting the spectra so the complete analysis was done only for the diphos derivatives (Table II).

Results and Discussion

As found previously[6] diphosM(CO)$_4$ or diarsM(CO)$_4$ (M = Mo or W) reacts rapidly with SnCl_4 at room temperature to give yellow, air-sensitive products. The analytical data indicate their formation involves the reaction of 2 mol of SnCl_4/mol of $\text{L}_2\text{M(CO)}_4$ (Table I).

The crystal structure[7] of the diphosMo(CO)$_4$ derivative shows that it should be formulated as the ionic compound $[\text{diphosMo(CO)}_4\text{SnCl}_3]^+[\text{SnCl}_5\text{OH}_2]^-\cdot\text{C}_6\text{H}_6$ and not as a 2:1 Lewis acid–Lewis base adduct. Thus the structure consists of well-separated seven-coordinate molybdenum cations (a capped octahedron with the SnCl_3 group in the capping position), $[\text{SnCl}_5\text{OH}_2]^-$ anions, and benzene of crystallization.

The origin of the water is not clear, but since the benzene was dried before use, it is most probable that it was present in the SnCl_4 which was used in a large excess. The water present in these compounds could not be detected from the analytical results.

The Mössbauer spectra of these compounds (see Figure 1) give an indication of their constitution. The spectra can each be resolved into two signals: a single line arising from a tin atom in a symmetric environment and a doublet similar to that found for a range of M–SnCl_3 compounds.[12] Mössbauer spectra thus provide a useful tool in the characterization of these compounds. This has proved difficult in the past because of both their air-sensitive properties and their dissociation in solution.

It has been noticed[13] in a qualitative fashion that the formation of type **2** derivatives (T = SnX_3) appeared to proceed faster in more polar solvents suggesting that an ionic intermediate is involved. Similar observations have been made regarding the reaction of $\text{L}_2\text{W(CO)}_4$ with HgCl_2[2] and some evidence has been presented that the intermediate in this case is $[\text{L}_2\text{W(CO)}_4\text{HgX}]^+[\text{HgX}_3]^-$.[4] The characterization of the title compounds seems to add support to these suggestions.

However, it should be pointed out that attempts to induce $[\text{diphosMo(CO)}_4\text{SnCl}_3]^+$ to lose CO were unsuccessful. In solution the complex reverts to diphosMo(CO)$_4$ as reported previously.[5]

Acknowledgment. We thank Mr. T. B. Tsin for running the Mössbauer spectra. We also thank the National Research Council of Canada for financial support in the form of a fellowship to R.K.P. and an operating grant to W.R.C. We are grateful to an anonymous referee for comments.

Registry No. $[\text{diphosMo(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$, 53849-29-9; $[\text{diphosW(CO)}_4\text{SnCl}_3][\text{SnCl}_5\text{OH}_2]$, 53849-31-3; [diarsMo-

$(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-33-5; $[diarsW(CO)_4SnCl_3]$-$[SnCl_5OH_2]$, 53849-35-7; $[(H^3)As_2Mo(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-37-9; $[(H^3)As_2W(CO)_4SnCl_3][SnCl_5OH_2]$, 53849-39-1; diphos$Mo(CO)_4$, 15444-66-3; $SnCl_4$, 7646-78-8.

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Electrochemical Investigation of the Dichlorobis(1,10-phenanthroline)chromium(III) Complex Ion

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In a recent paper describing the results of an electrochemical investigation of tris(1,10-phenanthroline)chromium(III) ion, we reported briefly on the electrochemical behavior of a bis complex that was prepared *in situ via* the catalytic elimination of a phenanthroline molecule.[1] From that brief study it appeared that the reduced complex was not behaving in a straightforward manner and that oxidation of the reduced complex produced a substance quite different from the starting material. Similar behavior was noted in a complemental study of the tris-[2] and bis(2,2'-bipyridine)chromium(III)[3] systems.

This study was initiated to determine if the behavior of the bis(1,10-phenanthroline) complex would parallel that of its 2,2'-bipyridine analog and to clarify further the somewhat unusual behavior of the chromium(II) complex.[1,3] This study, like those previous, is based on the polarographic and cyclic voltammetric behavior of the bis system at various stages of reduction, where the reductions were performed by controlled-potential electrolysis at a mercury cathode.

Experimental Section

Apparatus. The electrochemical apparatus and electrolysis cell used were the same as described in previous studies.[2]

Solutions. Except where otherwise stated, solutions were about 10^{-3} *M* in the complex and 10^{-1} *M* in potassium chloride as the supporting electrolyte. All solutions contained 0.01% Triton X-100 as a maximum suppressor. Stock solutions were stable for at least 1 month as indicated by periodic comparisons of their ultraviolet and visible absorption spectra.

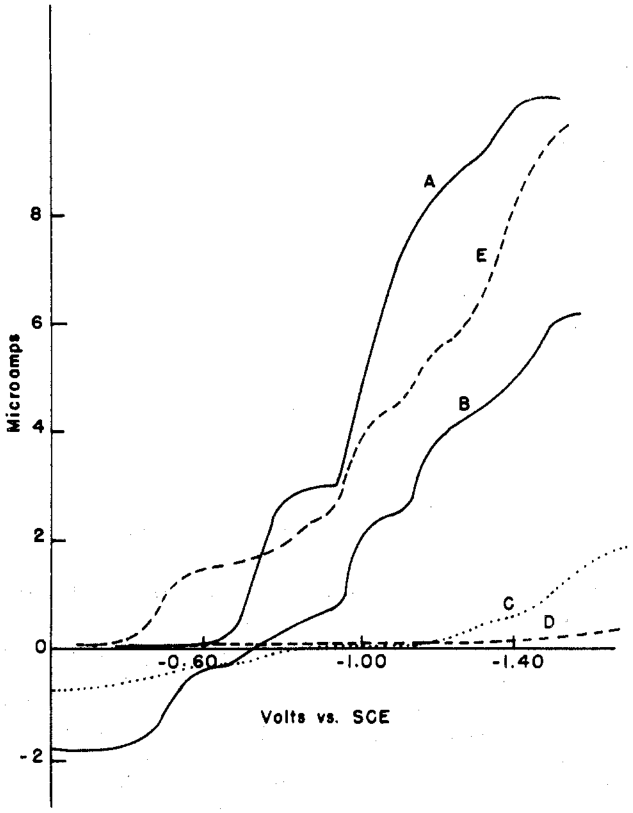

Figure 1. Polarograms of 1.34×10^{-3} *M* $[Cr(phen)_2Cl_2]^+$ and of products of successive coulometric reductions in 0.1 *M* KCl at pH 4.3 and 26°: (A) unreduced complex; (B) complex reduced one electron/molecule at −0.78 V ($n = 1$); (C) complex reduced a second electron/molecule at −1.06 V ($n = 2$); (D) complex reduced a third electron/molecule at −1.30 V ($n = 3$); (E) complex reduced a total of three electrons/molecule and rapidly oxidized with oxygen gas.

Dichlorobis(1,10-phenanthroline)chromium(III) Chloride Dihydrate. This cis[4] complex was prepared according to the method of Burstall and Nyholm[5] except that 1,10-phenanthroline was substituted for 2,2'-bipyridine. After recrystallization from hot water, the solid product was suspended in chloroform to remove any unreacted 1,10-phenanthroline.

Anal. Calcd for $[Cr(C_{12}H_8N_2)_2Cl_2]Cl \cdot 2H_2O$: C, 51.95; H, 3.61; N, 10.10; total Cl, 19.18. Found: C, 51.20; H, 3.45, N, 9.79; total Cl, 18.97.

Procedures. The general procedures used have been described previously.[3]

Results and Discussion

Polarograms of the solution initially containing $[Cr(phen)_2Cl_2]^+$ taken at various stages of the coulometric electrolysis are shown in Figure 1. The polarogram of the unreduced complex (Figure 1A) contains two major waves with $E_{1/2}$ values of −0.73 and −1.02 V *vs.* the sce. The second wave, whose diffusion current is about twice that of the first wave, probably consists of two closely spaced waves. Curtis has reported a similar polarogram for this complex.[6]

A cyclic voltammogram of a solution of the unreduced bis complex, taken over a voltage range of −0.20 to −0.85 V and at a scan rate of 0.1 V/sec, contained a single cathodic wave (1) at −0.80 V on the first cathodic sweep. On the reverse anodic sweep, two anodic waves were observed, one at −0.68 V (2) and the other at −0.43 V (3). On the second and all subsequent scans, a second cathodic wave (4) appeared at −0.54 V. The ratio of peak currents between waves 3 and 1 was affected only slightly by temperature but significantly by pH (see Figure 2). This behavior was remarkably similar to that observed for the $[Cr(bipy)_2Cl_2]^+$ complex[3] and is typical

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