Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE CHEMISTRY OF THE DINUCLEAR CARBONYL ANIONS
VI. ANIONIC METAL CARBONYL CARBOXYLATES*

W. JOSEPH SCHLIENTZ**, Y. LAVENDER, N. WELCMAN***, R. B. KING AND J. K. RUFF****
Department of Chemistry, University of Georgia, Athens, Georgia 30601 (U.S.A.)

(Received June 14th, 1971)

SUMMARY

Anionic metal carbonyl carboxylates $[RCO_2M(CO)_5]^-$ ($M = Cr$, $R = CF_3$, C_2F_5, and C_6F_5; $M = Mo$, $R = C_6F_5$; $M = W$, $R = H$, CH_3, C_2H_5, C_6H_5, CF_3, C_2F_5, and C_6F_5) may be obtained as their bis(triphenylphosphine)iminium (Ppn) salts by reactions of the appropriate $[Ppn]_2[M_2(CO)_{10}]$ salt with the corresponding silver(I) or mercury(II) carboxylate in dichloromethane at room temperature. The tungsten carbonyl trifluoroacetate $[CF_3CO_2W(CO)_5]^-$ may also be obtained as its tetraethylammonium salt by the thermal reaction of $W(CO)_6$ with tetraethylammonium trifluoroacetate in diglyme solution at 120°. The infrared spectra of these new compounds are discussed. Ultraviolet irradiation of $[Ppn][CF_3CO_2W(CO)_5]$ with triphenylphosphine in tetrahydrofuran solution results in the replacement of one carbonyl group by a triphenylphosphine ligand to give $[Ppn][CF_3CO_2W(CO)_4P(C_6H_5)_3]$.

INTRODUCTION

The hexacarbonyls of chromium, molybdenum, and tungsten react upon heating or ultraviolet irradiation with many anions containing non-bonded electron pairs such as halides[2], pseudohalides[3], trichlorostannate(II)[4], difluorothiophosphate[5] and alkylacetylides[6] to give anionic complexes of the type $[M(CO)_5X]^-$ ($M = Cr$, Mo, and W; $X = Cl$, Br, I, CN, SCN, $SnCl_3$, PF_2OS, $C{\equiv}CR$, etc.). More recently an alternate preparative route to certain $[M(CO)_5X]^-$ anions has been developed[7] which uses the following reactions of the bimetallic anions $[M_2(CO)_{10}]^{2-}$ ($M = Cr$, Mo, and W) with mercury(II) or silver(I) derivatives.

$$[M_2(CO)_{10}]^{2-} + HgX_2 \rightarrow 2\,[M(CO)_5X]^- + Hg$$

$$[M_2(CO)_{10}]^{2-} + 2\,AgX \rightarrow 2\,[M(CO)_5X]^- + 2\,Ag$$

The syntheses of these $[M(CO)_5X]^-$ anions from the $[M_2(CO)_{10}]^{2-}$ anions have

---

* For Part V of this series see ref. 1.

** NDEA Title IV Fellow, 1968–1971.

*** Post-doctoral Research Associate, 1968–1969.

**** Fellow of the Alfred P. Sloan Foundation, 1969–1971.

TABLE 1

NEW COMPOUNDS PREPARED IN THIS WORK

Compound[a]	M.p. (°C)	Yield[b] (%)	Analyses, found (calcd.) (%)						Conductivity[c]	
			C	H	N	O	F	M	c ($\times 10^{-3}$ *M*)	Λ ($cm^2/equiv^{-1}\cdot ohm^{-1}$)
[Ppn][$CF_3CO_2Cr(CO)_5$]	142–144	36 (Ag)	61.2	3.7			7.4	6.3	1.01	74.3
			(61.2)	(3.6)			(6.8)	(6.2)		
[Ppn][$C_2F_5CO_2Cr(CO)_5$]	114–116	67 (Ag)		3.6			10.6	6.0	0.99	69.0
				(3.4)			(10.6)	(5.8)		
[Ppn][$C_6F_5CO_2Cr(CO)_5$]	115–117	21 (Ag)	61.0	3.2			10.5	5.5	1.10	64.5
			(61.2)	(3.2)			(10.1)	(5.5)		
[Ppn][$C_6F_5CO_2Mo(CO)_5$]	116–118	51 (Ag)	58.9	3.1			9.3	9.1		[d]
			(58.5)	(3.1)			(9.6)	(9.7)		
[Ppn][$HCO_2W(CO)_5$]	130 (dec.)	86 (Ag)	55.6	3.9		11.9		20.6	1.10	62.0
			(55.9)	(3.4)		(12.3)		(20.3)		
[Ppn][$CH_3CO_2W(CO)_5$]	125–128	58 (Hg)	55.7	3.6	1.4	11.8			1.53	78.1
	(dec.)		(56.0)	(3.6)	(1.5)	(12.2)				
[Ppn][$C_2H_5CO_2W(CO)_5$]	113–117	22 (Hg)	56.5	3.7		12.0		19.9	1.25	65.3
		45 (Ag)	(56.5)	(3.8)		(12.0)		(19.7)		
[Ppn][$C_6H_5CO_2W(CO)_5$]	137–140	20 (Ag)	59.0	3.9		11.8		18.6	0.98	65.0
			(58.6)	(3.6)		(11.4)		(18.7)		
[Ppn][$CF_3CO_2W(CO)_5$]	135 (dec.)	59 (Hg)	53.4	3.1			6.2	19.7	1.72	66.2
		51 (Ag)	(53.0)	(3.1)			(5.8)	(18.8)		
[Et_4N][$CF_3CO_2W(CO)_5$]	56	31	31.5	4.1	2.7		10.5	31.8		
			(31.7)	(3.5)	(2.5)		(10.0)	(32.4)		
[Ppn][$C_2F_5CO_2W(CO)_5$]	114–116	77 (Ag)	51.4	3.2	1.4		9.3	18.1	0.88	78.5
	(dec.)		(51.5)	(2.9)	(1.4)		(9.3)	(17.9)		
[Ppn][$C_6F_5CO_2W(CO)_5$]	105–110	27 (Ag)	53.7	3.0			9.1	16.9	1.03	60.0
			(53.7)	(2.8)			(8.8)	(17.1)		
[Ppn][$CF_3CO_2W(CO)_4PPh_3$]	101–103	96	58.5	3.8			4.9	16.4	0.70	68.6
			(59.6)	(3.7)			(4.7)	(15.2)		

[a] The following abbreviations are used: Ppn = bis(triphenylphosphine)iminium; Ph = phenyl; Et = ethyl. [b] The indicated yields were obtained from preparations described in the Experimental Section. The use of the silver or mercury(II) carboxylates in the redox reactions is indicated in parentheses. [c] These equivalent conductance values were determined in nitromethane solutions of the indicated concentrations using the procedure described in the Experimental Section. [d] This compound decomposed too rapidly in solution for a meaningful conductance value to be obtained.

the advantage of utilizing milder reaction conditions than the syntheses of $[M(CO)_5X]^-$ anions directly from the metal hexacarbonyls $M(CO)_6$.

Recently[8] several neutral metal carbonyl carboxylates were prepared by reactions of metal carbonyl halides with silver carboxylates. This paper describes preparations of anionic metal carbonyl carboxylates of chromium, molybdenum, and tungsten using the following substitution and redox reactions cited above:

$$M(CO)_6 + [Et_4N][RCO_2] \xrightarrow{\text{Diglyme}} [Et_4N][RCO_2M(CO)_5] + CO \qquad (1)$$

$$[Ppn]_2[M_2(CO)_{10}] + (RCO_2)_2Hg \xrightarrow{CH_2Cl_2} 2\,[Ppn][RCO_2M(CO)_5] + Hg \qquad (2a)$$

$$[Ppn]_2[M_2(CO)_{10}] + 2\,RCO_2Ag \xrightarrow{CH_2Cl_2} 2\,[Ppn][RCO_2M(CO)_5] + 2\,Ag \qquad (2b)$$

Ppn = bis(triphenylphosphine)iminium, $[(C_6H_5)_3PNP(C_6H_5)_3]^+$.

EXPERIMENTAL

Microanalyses (Table 1) were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany, and by Mr. M. L. Kshatriya of this Department. Melting points were taken in capillaries and are uncorrected.

Materials

The bimetallic metal carbonyl anions $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, and W) were prepared as described previously[9] in the literature. They were isolated as their bis(triphenylphosphine)iminium, $[(C_6H_5)_3PNP(C_6H_5)_3]^+$ (hereafter abbreviated Ppn) salts using [Ppn]Cl as the counterion source.

The carboxylates $(CH_3CO_2)_2Hg$, CH_3CO_2Ag, CF_3CO_2Ag, $C_2F_5CO_2Ag$, HCO_2Ag and $C_2H_5CO_2Ag$ were obtained from commercial sources. The carboxylates $(CF_3CO_2)_2Hg$, $(C_2H_5CO_2)_2Hg$, and $(C_2F_5CO_2)_2Hg$ were prepared by addition of the anhydrous carboxylic acid to red mercuric oxide. The arenecarboxylates $(C_6H_5CO_2)_2Hg$, $C_6H_5CO_2Ag$, and $C_6F_5CO_2Ag$ were prepared by boiling under reflux the corresponding metal oxide with the appropriate arenecarboxylic acid in benzene solution. These arenecarboxylates were isolated by removal of benzene in vacuum from the filtered hot benzene solutions. The pentafluorobenzoic acid was purchased from Peninsular Chem. Research, Inc.

Tetraethylammonium trifluoroacetate was prepared by neutralization of a 10% aqueous solution of tetraethylammonium hydroxide with the stoichiometric quantity of trifluoroacetic acid. The resulting solution was concentrated as much as possible at 25°/0.1 mm. The remaining water was removed in a vacuum desiccator over phosphorus pentoxide to give a white hygroscopic solid which was used directly for the reactions with the metal hexacarbonyls.

Preparation of $[(C_2H_5)_4N][CF_3CO_2W(CO)_5]$ *directly from* $W(CO)_6$

A mixture of 6.85 g (28.2 mmoles) of tetraethylammonium trifluoroacetate, 9.61 g (27.3 mmoles) of hexacarbonyltungsten, and 100 ml of diglyme (diethylene glycol dimethyl ether; redistilled over $LiAlH_4$) was heated under nitrogen for 20 h at 80–90° and then for 48 h at 120°. After cooling to room temperature the reaction mixture was filtered under nitrogen. The filtrate was treated with a large excess

(~ 500 ml) of pentane and the mixture then shaken vigorously in a separatory funnel. The lower orange oily layer was separated and treated with excess anhydrous diethyl ether. A yellow crystalline solid remained. This was filtered from the diethyl ether and then heated at 50°/0.1 mm for several hours to remove unreacted hexacarbonyltungsten. The residue consisted of 4.87 g (31% yield) of yellow to yellow-green $[(C_2H_5)_4N][CF_3CO_2W(CO)_5]$, m.p. 56°.

Preparations of $[Ppn][RCO_2M(CO)_5]$ derivatives from the $[M_2(CO)_{10}]^{2-}$ anions

All reactions of this type were carried out in an analogous manner. In a typical reaction a solution of 1.7 g (1.0 mmoles) of $[Ppn]_2[W_2(CO)_{10}]$ and 0.54 g (2.0 mmoles) of silver(I) pentafluoropropionate in 25 ml of dichloromethane was treated with 100 ml of diethyl ether. The mixture was then kept for 30 to 60 min at −10° and then filtered. The filtrate was slowly treated with 100 ml of pentane. The resulting yellow precipitate was filtered and dried to give 1.29 g (77% yield) of $[Ppn][C_2F_5CO_2W(CO)_5]$.

Preparation of $[Ppn][CF_3CO_2W(CO)_4P(C_6H_5)_3]$

A mixture of 1.2 g (1.2 mmoles) of $[Ppn][CF_3CO_2W(CO)_5]$, 5.0 g (38 mmoles) of triphenylphosphine, and 150 ml of redistilled tetrahydrofuran was exposed for 2 h to the ultraviolet irradiation from a General Electric H44–46S type mercury spotlight placed 3 cm from the glass reaction vessel. The resulting solution was decanted from insoluble by-products. The solvent was then removed at 25°/20 mm. The residue was dissolved in 25 ml of dichloromethane. The filtered dichloromethane solution was then

TABLE 2

INFRARED AND NMR SPECTRA OF COMPOUNDS PREPARED IN THIS WORK

Compound[a]	Infrared, ν(CO) frequencies[b]		NMR spectrum[c]	
	Metal carbonyl groups	Carboxylate	Nucleus[d]	Resonances[e]
$[Ppn][CF_3CO_2Cr(CO)_5]$	2062 w, 1918 s, 1844 m	1681 m	F	74.2 s
$[Ppn][C_2F_5CO_2Cr(CO)_5]$	2061 w, 1918 s, 1854 m	1686 m	F	83,2, 119.2
$[Ppn][C_6F_5CO_2Cr(CO)_5]$	2061 w, 1920 s, 1855 m	1646 w	F	143, 160, 164
$[Ppn][C_6F_5CO_2Mo(CO)_5]$	2068 w, 1923 s, 1853 m	1645 m	F	143, 160, 165
$[Ppn][HCO_2W(CO)_5]$	2060 w, 1900 s, 1837 m	1612 m	H	[g]
$[Ppn][CH_3CO_2W(CO)_5]$	2059 w, 1907 s, 1835 m	1600 m	H	8.37 s
$[Ppn][C_2H_5CO_2W(CO)_5]$	2065 w, 1915 s, 1845 m	1640 m	H	7.91 q (7), 8.97 t (7)
$[Ppn][C_6H_5CO_2W(CO)_5]$	2060 w, 1908 s, 1833 m	1603 m	H	[g]
$[Ppn][CF_3CO_2W(CO)_5]$	2066 w, 1917 s, 1844 m	1683 m	F	74.4 s
$[Et_4N][CF_3CO_2W(CO)_5]$[f]	2060 w, 1902 vs, 1858 s	1684 s	F	74.5 s
$[Ppn][C_2F_5CO_2W(CO)_5]$	2068 w, 1909 s, 1835 m	1684 m	F	83.4, 119.2
$[Ppn][C_6F_5CO_2W(CO)_5]$	2068 w, 1915 s, 1842 m	1640 m	F	142, 159, 164
$[Ppn][CF_3CO_2W(CO)_4PPh_3]$	2007 m, 1880 s(sh), 1868 s, 1812 m	1682 m	F	74.7 s

[a] The same abbreviations as in Table 1 were used. [b] These infrared spectra were obtained in dichloromethane solution as described in the Experimental Section; cm^{-1}. [c] The NMR resonances from the Ppn and Et_4N cations were also observed, but are not listed here. [d] The τ scale is used for the proton chemical shifts. The φ scale (ppm upfield from internal CCl_3F) is used for the ^{19}F chemical shifts. [e] s=Singlet; t=triplet; q=quartet; coupling constant in Hz given in parentheses; RCO_2 group only. [f] This infrared spectrum was obtained in a KBr pellet rather than in CH_2Cl_2 solution. [g] The phenyl resonances from the Ppn cation prevented observation of the carboxylate proton resonances.

treated with 150 ml of diethyl ether. The resulting precipitate was filtered and dried to give 1.39 g (96% yield) of yellow crystalline [Ppn][$CF_3CO_2W(CO)_4P(C_6H_5)_3$].

The compound [Ppn][$CF_3CO_2W(CO)_4P(C_6H_5)_3$] could also be prepared in the absence of ultraviolet irradiation by boiling the reactants under reflux in tetrahydrofuran solution for 12 h. The quantities of reactants used and the product isolation procedure in this thermal reaction were identical to those used in the photochemical reaction described above.

Infrared spectra

The infrared spectra in the ν(CO) region of the compounds prepared in this work (Table 2) were obtained on a Perkin–Elmer Model 621 spectrometer with grating optics. Dichloromethane solutions were used with a concentration of 5 to 15 mg/ml and a 0.2 mm path length. The spectrometer was calibrated with indene.

NMR spectra

All NMR spectra (Table 2) were determined on a Perkin–Elmer–Hitachi Model R-20 spectrometer at ambient temperature. Tetramethylsilane was used as an internal standard for the proton spectra. Trichlorofluoromethane was used as the internal standard for the ^{19}F NMR spectra.

Conductivity

Conductance measurements (Table 1) were made in nitromethane solution using a standard type conductivity cell with a cell constant of $0.1792\ cm^{-1}$. The conductivity bridge was a model 31 instrument by Yellow Springs Mfg. Co. The specific conductance of the nitromethane was $5.7 \times 10^{-7}\ ohm^{-1}$.

DISCUSSION

The reaction between tetraethylammonium trifluoroacetate and hexacarbonyltungsten to give [$(C_2H_5)_4N$][$CF_3CO_2W(CO)_5$] is completely analogous to the reported[2] reactions between tetraethylammonium halides and the metal hexacarbonyls. The presence of the trifluoroacetate ion in [$(C_2H_5)_4N$][$CF_3CO_2W(CO)_5$] is demonstrated by the ν(CO) frequency of the trifluoroacetate group at 1684 cm^{-1} and the ^{19}F NMR resonance of the trifluoroacetate fluorine atoms at φ 74.5. Both of these values fall into the ranges previously observed for related neutral trifluoroacetate derivatives[8].

Attempts to prepare analogous anionic metal carbonyl trifluoroacetates of chromium and molybdenum by thermal reactions of tetraethylammonium trifluoroacetate with the corresponding metal hexacarbonyls were unpromising apparently because of limited stability of the products under the necessary reaction conditions. Therefore, the redox method[7] starting with the corresponding $[M_2(CO)_{10}]^{2-}$ anion and the silver or mercury(II) carboxylate was investigated for the preparation of other anionic metal carbonyl carboxylates of the type $[RCO_2M(CO)_5]^-$. This redox method has the advantage of proceeding rapidly at room temperature in contrast to the much more vigorous conditions required for direct substitution of one carbonyl group in a metal hexacarbonyl by a carboxylate anion. In the work with the redox reaction, the bis(triphenylphosphine)iminium (Ppn) salts were used because of their greater stability, ease of handling, and ease of crystallization. Using the redox method anionic metal carbonyl carboxylates of the type $[RCO_2M(CO)_5]^-$ could be prepared as their Ppn salts with formate ($R=H$), acetate ($R=CH_3$), propionate ($R=C_2H_5$), benzoate ($R=C_6H_5$), trifluoroacetate ($R=CF_3$), pentafluoropropionate ($R=C_2F_5$), and pentafluorobenzoate ($R=C_6F_5$) as ligands. The tungsten carbonyl derivatives were studied most extensively because of their greater stability.

The infrared spectrum of each $[RCO_2M(CO)_5]^-$ derivative in the metal $\nu(CO)$ region exhibits the expected three infrared-active metal $\nu(CO)$ frequencies for an $LM(CO)_5$ derivative[10,11]. The strong band at 1912 ± 12 cm^{-1} may be assigned to the E mode and the weaker bands at 2063 ± 5 and 1844 ± 11 cm^{-1} may be assigned to the two A_1 modes. These metal $\nu(CO)$ frequencies fall in the ranges previously[2] observed for the halopentacarbonylmetallates (*e.g.*, for $[(C_2H_5)_4N][W(CO)_5Cl]$ $\nu(CO)$ 2061 w, 1904 s and 1869 m cm^{-1}) but occur 90–140 cm^{-1} below the corresponding $\nu(CO)$ frequencies of isoelectronic neutral derivatives such as $CF_3CO_2Re(CO)_5$ because of increased retrodative bonding to the CO π^* antibonding orbitals which arises from the negative charge on the metal atom in the anionic derivative.

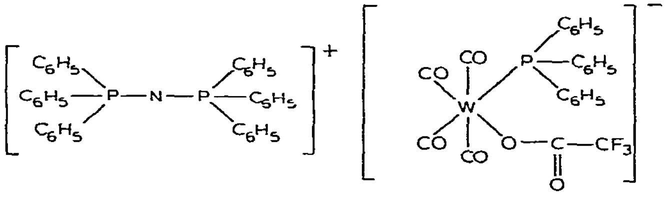
The infrared spectrum of each $[RCO_2M(CO)_5]^-$ derivative also exhibited an additional $\nu(CO)$ frequency in the range 1600–1684 cm^{-1} arising from the carbonyl group of the carboxylate ligand. The position of this carboxylate $\nu(CO)$ frequency is rather sensitive to the nature of the R group in the carboxylate (RCO_2) ligand but is rather insensitive to other types of structural changes. Thus the carboxylate $\nu(CO)$ frequency in all of the perfluoroalkanecarboxylate derivatives studied in this work (*e.g.* trifluoroacetates and pentafluoropropionates) appeared in the narrow range 1683 ± 3 cm^{-1}. Similarly, the carboxylate $\nu(CO)$ frequencies in the three pentafluorobenzoate derivatives studied in this work appeared in the narrow range 1643 ± 3 cm^{-1}. The relative insensitivity of the position of the carboxylate $\nu(CO)$ frequency to structural changes in portions of the molecule more remote than the R group is most clearly demonstrated by the proximity of the carboxylate $\nu(CO)$ frequencies in the neutral rhenium carbonyl derivatives $R_FCO_2Re(CO)_5$ [$R_F=CF_3$, C_2F_5, and C_3F_7; $\nu(CO)$ of the perfluorocarboxylate 1693 ± 1 cm^{-1}] to those in the anionic tungsten carbonyl derivatives $[Ppn][R_FCO_2W(CO)_5]$ [$R_F=CF_3$ and C_2F_5; $\nu(CO)$ of the perfluorocarboxylate 1683 ± 1 cm^{-1}]. Major changes in the retrodative bonding of the metal atom to the carbonyl groups in metal carbonyl carboxylate derivatives thus have a very small effect on the position of the $\nu(CO)$ carboxylate frequency. This is consistent with a low π-acceptor strength of the carboxylate ligands which is expected if the carboxylates bond to the metal atom through oxygen, an atom which has no empty orbitals of appropriate energies and symmetries to accept electron density from the metal atom. Because of this low π-acceptor strength of the carboxylate groups, the extra electron density in anionic derivatives of the type $[RCO_2M(CO)_5]^-$ relative to isoelectronic neutral derivatives of the type $RCO_2M(CO)_5$ ($M=Mn$ and Re) is nearly all transferred to the carbonyl groups. However, the small effect of changes in the negative charge on the central metal atom on the $\nu(CO)$ frequency of the carboxylate group is also undoubtedly partly due to the fact that neither atom of the carboxylate carbonyl group is bonded directly to the metal atom.

The anionic metal carbonyl carboxylates prepared in this work were also characterized by their NMR spectra and their equivalent conductances. In all of the carboxylates except the benzoate and formate, the expected proton or fluorine NMR resonances corresponding to the alkyl group in the carboxylate could be observed. The proton NMR resonances of the protons in the benzoate and formate ligands could not be observed because of interference from the phenyl protons of the Ppn cation. The relative intensities of the Ppn and carboxylate proton resonances in the hydrogen derivatives [Ppn][$RCO_2W(CO)_5$] ($R=CH_3$ and C_2H_5) were consistent with the proposed formulations. The ionic natures of the new compounds prepared in this work were confirmed by conductivity measurements on approximmately 0.001 *M* solutions in nitromethane which gave values between 60 to 80 $cm^2 \cdot equiv^{-1} \cdot ohm^{-1}$ for the equivalent conductance. This is consistent with 1/1 electrolyte behavior. The molybdenum compound [Ppn][$C_6F_5CO_2Mo(CO)_5$] was too unstable in solution for a meaningful conductivity measurement. The lower stability of molybdenum compounds as compared with analogous chromium and tungsten compounds is in accord with the past experience[12].

In order to assess the reactivity of the new anionic metal carbonyl carboxylates towards Lewis bases, the photochemical reaction of [Ppn][$CF_3CO_2W(CO)_5$] with triphenylphosphine was investigated. This reaction proceeded according to the following equation with replacement of a carbonyl group rather than the trifluoroacetate group by the triphenylphosphine:

$$[\mathrm{Ppn}][CF_3CO_2W(CO)_5] + (C_6H_5)_3P \rightarrow [\mathrm{Ppn}][CF_3CO_2W(CO)_4P(C_6H_5)_3] + CO$$

The infrared spectrum of [Ppn][$CF_3CO_2W(CO)_4P(C_6H_5)_3$] exhibited four metal $\nu(CO)$ frequencies indicating it to be the *cis*-isomer (I). The presence of the trifluoroacetate group in (I) was shown by a carboxylate $\nu(CO)$ frequency at 1682 cm^{-1} and by the ^{19}F NMR resonance of the CF_3 group at φ 74.7. The equivalent conductance of (I) was consistent with formulation as a 1/1 electrolyte.



(I)

ACKNOWLEDGEMENT

We are indebted to the National Institute of General Medical Sciences grant GM-14664-02 and the Petroleum Research Fund grant 4346-A3 for partial support of this work.

REFERENCES

1 J. K. Ruff and R. B. King, *Inorg. Chem.*, 8 (1969) 108.
2 (a) E. W. Abel, M. A. Bennett and G. Wilkinson, *Chem. Ind. (London)*, (1960) 442;
(b) E. O. Fischer and K. Öfele, *Chem. Ber.*, 93 (1960) 1156;
(c) E. W. Abel, I. S. Butler and J. G. Reid, *J. Chem. Soc.*, (1963) 2068;

(d) J. K. RUFF, *Inorg. Chem.*, 7 (1968) 1821.
3 (a) H. BEHRENS AND J. KOHLER, *Z. Naturforsch.*, *B*, 14 (1959) 462;
(b) H. BEHRENS AND J. KOHLER, *Z. Anorg. Allg. Chem.*, 306 (1960) 94;
(c) A. WOJCICKI AND M. F. FARONA, *J. Inorg. Nucl. Chem.*, 26 (1964) 2289;
(d) R. B. KING, *Inorg. Chem.*, 6 (1967) 25;
(e) J. K. RUFF, *Inorg. Chem.*, 8 (1969) 86.
4 J. K. RUFF, *Inorg. Chem.*, 6 (1967) 1502.
5 J. K. RUFF AND M. LUSTIG, *Inorg. Chem.*, 7 (1968) 2171.
6 W. J. SCHLIENTZ AND J. K. RUFF, *J. Chem. Soc. A*, (1971) 1139.
7 W. J. SCHLIENTZ AND J. K. RUFF, *Syn. Inorg. Metal-org. Chem.*, 1 (1971) 215.
8 R. B. KING AND R. N. KAPOOR, *J. Organometal. Chem.*, 15 (1968) 457.
9 R. G. HAYTER, *J. Amer. Chem. Soc.*, 88 (1966) 4376.
10 L. E. ORGEL, *Inorg. Chem.*, 1 (1962) 25.
11 J. B. WILFORD AND F. G. A. STONE, *Inorg. Chem.*, 4 (1965) 389.
12 R. B. KING, *Inorg. Nucl. Chem. Lett.*, 5 (1969) 905.