

Contribution from the School of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom, and Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

Infrared Spectroelectrochemistry of η^3 -Allyl Dicarbonyl Complexes of Molybdenum(II) and Tungsten(II)

Brian J. Brisdon,^{1a} Starla K. Enger,^{1b} Michael J. Weaver,^{1b} and Richard A. Walton*^{1b}

Received February 18, 1987

The technique of FTIR spectroscopy has been coupled with an optically transparent thin-layer electrode (OTTLE) cell to enable in situ monitoring of the intermediates and final products in the electrooxidation of $(\eta^3\text{-all})\text{MX}(\text{CO})_2(\text{L-L})$, where $\text{M} = \text{Mo}$ or W , $\text{X} = \text{Cl}$, Br , or O_2CCF_3 , all = allyl, and $\text{L-L} = 2,2'$ -bipyridyl (bpy), 4,4'-dimethyl-2,2'-bipyridyl (Me_2bpy), 1,10-phenanthroline (phen), di-2-pyridylamine (dpa), N,N' -di-*tert*-butylethylenediimine (dab), bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), or 1,2-bis(diphenylarsino)ethane (dpae). The N-ligand complexes for $\text{M} = \text{Mo}$ undergo a one-electron oxidation to form the paramagnetic monocations $[(\eta^3\text{-all})\text{MoX}(\text{CO})_2(\text{L-L})]^+$, which are generally stable in solution and are identified from the shift of the $\nu(\text{CO})$ modes upon oxidation. The monocations $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{bpy})]^+$, $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{phen})]^+$, and $[(\eta^3\text{-all})\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{bpy})]^+$ have been isolated as their PF_6^- salts. The P/As-ligand complexes undergo one-electron oxidation to give unstable monocations. In the case of $\text{M} = \text{Mo}$ and $\text{L-L} = \text{dppm}$ or dppe , the monocations decompose rapidly through CO scavenging to give $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ as the predominant final product, together with $\text{Mo}(\text{IV})$ and/or $\text{Mo}(\text{V})$ carbonyl-containing species. The cations $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dpae})]^+$ and $[(\eta^3\text{-all})\text{WCl}(\text{CO})_2(\text{dppe})]^+$ also decompose, but in these instances it is believed that seven-coordinate $(\eta^3\text{-all})\text{MCl}(\text{CO})_3(\text{L-L})$ is the major product upon the basis of an examination of the $\nu(\text{CO})$ modes in the FTIR spectra of the electrolyzed solutions.

Introduction

Although the chemistry of metal dicarbonyls of the type $(\eta^3\text{-all})\text{MX}(\text{CO})_2\text{L}_2$ ($\text{M} = \text{Mo}$ or W , all = allyl) has been examined extensively,²⁻⁹ their redox behavior has been largely unexplored. It has been found that these complexes possess a reversible or irreversible one-electron oxidation if L_2 is a bidentate ligand or a pair of monodentate ligands, respectively.¹⁰ Upon further investigation, it has become apparent that the identity of the bidentate ligand greatly affects the stability of the 17-electron monocation. The structural variance between the 2,2'-bipyridyl and similar α -diimine complexes and the $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (dppm), $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), and $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (dpae) complexes has been recognized,¹¹ and a corresponding difference in electrochemical behavior has now been determined. All of the complexes studied exhibit reversibility on the time scale of cyclic voltammetry, but upon bulk electrolysis the phosphorus- and arsenic-containing complexes decompose.

These differences are examined here through the use of infrared spectroelectrochemistry. Fourier transform infrared spectroscopy, which has rarely been used in this role to study organometallics and coordination complexes,¹² has been coupled with an optically transparent thin-layer electrode (OTTLE) to allow for the in situ monitoring of the electrolysis processes as well as identification of intermediates and final products.

Experimental Section

Starting Materials. The η^3 -allyl dicarbonyl $\text{Mo}(\text{II})$ and $\text{W}(\text{II})$ compounds of the type $(\eta^3\text{-C}_3\text{H}_5)\text{MX}(\text{CO})_2(\text{L-L})$, where $\text{M} = \text{Mo}$ or W , $\text{X} = \text{Cl}$, Br , or O_2CCF_3 , and $\text{L-L} =$ a bidentate ligand (see text), were synthesized as previously reported,¹³⁻¹⁵ as were the η^3 -allyl tricarbonyl perchlorate derivatives $[(\eta^3\text{-C}_3\text{H}_5)\text{Mo}(\text{CO})_3(\text{L-L})]\text{ClO}_4$, where $\text{L-L} =$

dppm, dppe, or dpae, and $[(\eta^3\text{-C}_3\text{H}_5)\text{W}(\text{CO})_3(\text{dppe})]\text{ClO}_4$.¹⁶ The spectroscopic grade Burdick and Jackson solvents used in the spectroelectrochemical measurements were vacuum-distilled over CaH_2 , by utilizing three freeze-pump-thaw cycles. The supporting electrolyte, tetra-*n*-butylammonium hexafluorophosphate (TBAH), was prepared from tetra-*n*-butylammonium bromide and KPF_6 in hot acetone and recrystallized several times from absolute ethanol.

Electrochemical Syntheses. The complex $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{bpy})]\text{PF}_6$ and its 1,10-phenanthroline analogue were prepared by a bulk electrolysis of 5 mM solutions of the neutral complexes in dichloromethane at 25 and 0 °C, respectively. Under these conditions, the salts are insoluble and precipitate as olive green solids. These were filtered off and recrystallized from absolute ethanol/dichloromethane; yield ca. 80%. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{ClF}_6\text{MoN}_2\text{O}_2\text{P}$: C, 36.86; H, 2.35; N, 5.06. Found: C, 36.39; H, 2.67; N, 5.41. Calcd for $\text{C}_{15}\text{H}_{13}\text{ClF}_6\text{MoN}_2\text{O}_2\text{P}$: C, 34.00; H, 2.47; N, 5.29. Found: C, 33.26; H, 2.64; N, 5.13. The salt $[(\eta^3\text{-all})\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{bpy})]\text{PF}_6$ was isolated in a similar manner, with the exception that precipitation was initiated by adding 0.5 mL of petroleum ether to 20 mL of solution and cooling this mixture to 0 °C. Cyclic voltammetry and IR and ESR spectroscopies confirmed the identity of these complexes.

Physical Measurements. Routine electrochemical measurements were made by using a PAR 173 potentiostat, a PAR 175 universal programmer, and a PAR 179 coulometer. Measurements were carried out in 0.1 M TBAH solutions at 25 °C by using either a Pt-bead or Pt-gauze working electrode, which was pretreated in boiling nitric acid. A three-electrode configuration was employed along with a double-fritted SCE reference cell, which hindered diffusion of water into the working compartment of the cell. Under our experimental conditions the formal potential of the ferrocenium/ferrocene couple is +0.40 V vs. SCE in 0.1 M TBAH/ CH_2Cl_2 . The cell volume was ca. 10 mL, and electrolysis times were usually 15-30 min. X-Band ESR spectra of such electrolyzed solutions were recorded as dichloromethane glasses at -150 °C with a Varian E-109 spectrometer.

Infrared spectra were recorded on an IBM/Bruker FTIR Model 98-4A spectrometer, using KBr pellets for solids and an OTTLE for all solution measurements (Figure 1). Because of the solubility of epoxy resins in nonaqueous solvents, the cell was constructed so that only Teflon and the CaF_2 windows come in contact with the solution. The cell, which is modeled after Heineman's "optically thick" thin-layer arrangement,¹⁷ consists of a modified Perkin-Elmer 1005 liquid IR cell. This construction provides a fairly short electrolysis time and an optical path length of 0.2 mm.

Electrolyses in the OTTLE cell were carried out in 0.5 M TBAH at 25 °C and were assumed complete (a few minutes) when the current reached less than 3% of its initial value. The working electrode consisted of 100 wires/in. gold mesh (Buckbee-Mears) that extended beyond the cell and was protected with Pt foil at the potentiostat lead contact. The auxiliary electrode, a thin strip of Pt foil (0.06 mm), was sandwiched

- (1) (a) University of Bath. (b) Purdue University.
- (2) Tom Dieck, H.; Friedel, H. J. *J. Organomet. Chem.* **1968**, *14*, 375.
- (3) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1.
- (4) Hull, C. G.; Stiddard, M. H. B. *J. Organomet. Chem.* **1967**, *9*, 519.
- (5) Murdoch, H. D.; Henzi, R. J. *J. Organomet. Chem.* **1966**, *5*, 552.
- (6) Paddick, K. E.; Brisdon, B. J. *J. Organomet. Chem.* **1978**, *149*, 113.
- (7) Cartwright, M.; Hodson, A. G.; Brisdon, B. J. *J. Organomet. Chem.* **1984**, *277*, 85.
- (8) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1977**, *99*, 1654.
- (9) Hsieh, A. T. T.; West, B. O. *J. Organomet. Chem.* **1976**, *112*, 285.
- (10) Brisdon, B. J.; Conner, K. A.; Walton, R. A. *Organometallics* **1983**, *2*, 1159.
- (11) Faller, J. W.; Haitko, D. A.; Adams, R. D.; Chodosh, D. F. *J. Am. Chem. Soc.* **1979**, *101*, 865 and references cited therein.
- (12) For a recent example see: Enger, S. K.; Weaver, M. J.; Walton, R. A. *Inorg. Chim. Acta* **1987**, *129*, L1.
- (13) King, R. B.; Saran, M. S. *Inorg. Chem.* **1974**, *13*, 74.
- (14) Brisdon, B. J.; Cartwright, M. *J. Organomet. Chem.* **1979**, *164*, 83.
- (15) Powell, P. *J. Organomet. Chem.* **1977**, *129*, 175.

- (16) Faller, J. W.; Haitko, D. A. *J. Organomet. Chem.* **1978**, *149*, C19.
- (17) Heineman, W. R.; Burnett, J. M.; Murray, R. W. *Anal. Chem.* **1968**, *40*, 1974.

Table I. Cyclic Voltammetric and Coulometric Parameters for Molybdenum(II) and Tungsten(II) Dicarbonyls^a

compd	solvent ^b	n_{app} ^c	$E_{p,a}(2)$	$E_{p,a}(1)$	$E_{1/2}$	$E_{p,c}(1)$	$E_{p,c}(2)$
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{bpy})$ (I)	A	1.0		+1.48	+0.53	-1.60	-1.90
	B	1.0	+2.10	+1.39	+0.55	-1.55	-1.90
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{Me}_2\text{bpy})$ (II)	A	0.9	+2.20	+1.53	+0.50	-1.64	
	B	1.0	+2.20	+1.52	+0.50	-1.80	-2.00
$(\eta^3\text{-all})\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{bpy})$ (III)	A	1.0	+2.20	+1.64	+0.61		
	B	1.0		+1.60	+0.58	-1.44	
$[(\eta^3\text{-all})\text{Mo}(\text{py})(\text{CO})_2(\text{bpy})]\text{PF}_6$ (IV)	A	1.0 ^d		+1.58	+1.05	-1.25	
$(\eta^3\text{-2-Me-all})\text{MoCl}(\text{CO})_2(\text{bpy})$ (V)	A	1.0		+1.50	+0.47	-1.63	
	B	1.0		+1.35	+0.48	-1.55	
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{phen})$ (VI)	A	1.0	+2.00	+1.56	+0.54	-1.72	
	B	1.1	+2.25	+1.35	+0.53	-1.55	-1.80
$(\eta^3\text{-all})\text{MoBr}(\text{CO})_2(\text{dpa})$ (VII)	A	1.0	+2.20	+1.57	+0.55	-2.34	
	B	1.0	+1.75	+1.30	+0.51	-1.85	
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dab})$ (VIII)	A	1.1	+1.85	+1.73	+0.48	-1.27	
	B	1.1		+1.70	+0.52	-2.40	
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dppm})$ (IX)	A	1.9	+2.15	+1.45	+0.60	-2.15	
	B	1.8	+2.10	+1.40	+0.60	-2.00	
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dppe})$ (X)	A	2.0	+1.68	+1.40	+0.62	-2.20	
	B	1.9	+1.50	+1.35	+0.60	-2.05	
$(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dpae})$ (XI)	A	2.0		+1.58	+0.68		
	B	1.9		+1.70	+0.60	-1.78	
$(\eta^3\text{-all})\text{WCl}(\text{CO})_2(\text{dppe})$ (XII)	A	1.9	+2.00	+1.38	+0.58	-2.25	
	B	2.1		+1.50	+0.69	-2.10	

^a Voltammograms (E in volts) recorded on solutions that contained 0.1 M TBAH as supporting electrolyte at $v = 200$ mV/s vs SCE. Ligand abbreviations are as follows: all = allyl, py = pyridine, bpy = 2,2'-bipyridyl, Me₂bpy = 4,4'-dimethyl-2,2'-bipyridyl, phen = 1,10-phenanthroline, dpa = di-2-pyridylamine, dab = *N,N'*-di-*tert*-butylethylenediamine, dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dpae = 1,2-bis(diphenylarsino)ethane. ^b Legend: A = CH₂Cl₂, B = CH₃CN. ^c For electrolysis at +0.75 V, i.e. anodic of the +1/0 couple. ^d Solution electrolyzed at +1.2 V.

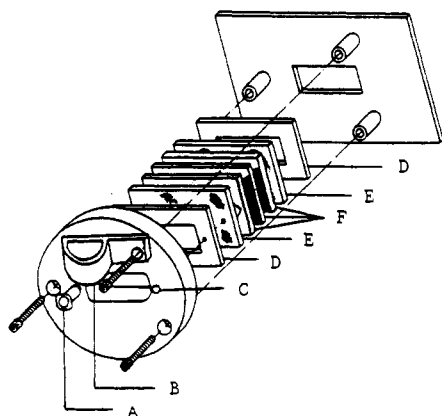


Figure 1. Construction of the OTTLE cell. The key is as follows: (A) inlet; (B) reservoir; (C) connection to reservoir; (D) Teflon gasket; (E) CaF₂ window; (F) gold minigrids (82% transmission) with spacers.

between the salt plates and also extended beyond the cell. Working electrode potentials were controlled vs. a Bioanalytical Systems Inc. 3 M Ag/AgCl reference electrode. The solutions to be electrolyzed, 5 mM, were saturated with N₂(g) prior to being introduced into the cell. The sample chamber of the instrument was flushed with N₂(g) during electrolysis.

Ferrocene was used to determine the optimum minigrad pretreatment and to confirm the electrochemical applicability of the OTTLE cell design. The utility of acetone, HNO₃, H₂SO₄, and HClO₄ as cleaning agents was investigated. The most reversible behavior was exhibited by ferrocene when the minigrad was pretreated with warm H₂SO₄ for 2 min.¹⁸ Initially the auxiliary electrode was placed in the reservoir cup along with the reference electrode, but resistive effects were prohibitively large. Satisfactory cyclic voltammograms were recorded when the auxiliary electrode was moved inside the cell but outside the optical pathway. Diffusion of products formed at the counter electrode into the optical pathway was not significant on the experimental time scale.

Results and Discussion

The electrochemical behavior of the complexes studied can be divided into two groups, comprising nitrogen (N) ligand and phosphorus/arsenic (P/As) ligand complexes. The anodic/

cathodic cyclic voltammograms (CV's) of the complexes ($\eta^3\text{-all})\text{MX}(\text{CO})_2(\text{L-L})$ exhibit a reversible +1/0 redox couple in the potential range +0.47 to +0.69 V with a peak current ratio $i_{p,c}/i_{p,a} \approx 1$ for scan rates greater than 100 mV/s. At slower scan rates, the presence of a following chemical step was apparent for the P/As complexes, but not for the N complexes, in that the cathodic/anodic current ratio for the former became less than unity, with the peak separation, $E_{p,a} - E_{p,c}$, remaining constant at about 70 mV.

The dependence of the stability of the metal(III) moiety on the ligand was demonstrated further by using coulometry. Upon exhaustive bulk electrolysis at +0.75 V, the N-ligand complexes undergo a one-electron oxidation to form the monocations $[(\eta^3\text{-all})\text{MoX}(\text{CO})_2(\text{L-L})]^+$, which are generally quite stable. The P/As complexes do not produce solutions that contain these cations but instead generate an ESR-active decomposition product(s) for which the apparent number of electrons transferred, determined from the Faradaic charge passed, is greater than 1. A representative single-scan cyclic voltammogram is shown (Figure S1, supplementary material), and half-wave and peak potentials of each complex studied are listed (Table I). Ligand abbreviations are summarized in the footnotes in Table I. In an earlier study,¹⁰ only the $E_{1/2}$ values for the one-electron oxidation at ca. +0.6 V were reported for complexes I, III, V, IX, and XI. These values occur at potentials slightly lower (by 0.03–0.08 V) than those reported in the present work due to differences in cell configuration and referencing procedures.

(i) **Nitrogen Donor Complexes.** Controlled-potential electrolysis of solutions of the bpy and phen complexes I–VI in CH₂Cl₂ and CH₃CN converted the red neutral complexes to the yellow-green monocations. However, the isolation of solid PF₆⁻ salts was not always successful due to their subsequent decomposition in solution during workup. The ions $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{bpy})]^+$, $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{phen})]^+$, and $[(\eta^3\text{-all})\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{bpy})]^+$ gave the most stable complexes and are fairly easily isolated as their PF₆⁻ salts in CH₂Cl₂. The solid salts were relatively insensitive to oxygen and to light, but over a period of months, they decomposed. While the phen-containing monocation of VI is formed upon electrolyzing solutions of this complex in both solvents, its yellow-green CH₂Cl₂ solutions slowly turn orange and exhibit two new CV reduction waves at -0.30 and -0.75 V. The X-band ESR spectra of CH₂Cl₂ solutions of the PF₆⁻ salts of the 17-electron monocations I⁺, III⁺, and VI⁺ were essentially the

(18) For further details see: Enger, S. K. M.S. Thesis, Purdue University, 1986.

Table II. Infrared Spectral Data for Metal(II) Dicarboxyls before and after Electrolysis in the OTTLE

compd	$\nu(\text{CO}), \text{cm}^{-1}$ ^a	
	before ^b	after ^c
I	1933, 1838	<i>d</i> (2059, 2010) ^e
II	1944, 1859	2065, 2014.
III	1951, 1863	2075, 2025
IV	1947, 1863	2064, 2013
V	1956, 1875	2079, 2036
VI	1947, 1859	2067, 2017 (2059, 2005) ^e
VII	1938, 1843	2060, 2010
VIII	1947, 1859	2063, 2005
IX	1945, 1853	2052 (m), 1998 (m), 1952 (s) (2052 (m), 1990 (m), 1945 (s)) ^e
X	1944, 1858	2048 (m), 1986 (m), 1947 (s)
XI	1945, 1851	2056 (m), 1978 (s), 1920 (m)
XII	1932, 1836	2048 (m), 1967 (s)

^a All spectra recorded on CH_2Cl_2 solutions unless otherwise stated.

^b All bands are of strong intensity. ^c All bands of strong intensity unless otherwise noted (m = medium, s = strong). ^d Insoluble. ^e Data in parentheses are for samples of the PF_6^- salt of the monocation recorded as a KBr pellet.

same as those reported previously (see Table II and Figure 2a of ref 10) for electrochemically generated solutions of I^+ and III^+ .

The dab complex (VII) is solvatochromic, being purple in CH_2Cl_2 and brown in CH_3CN ; it is the only compound studied that exhibits this property. In CH_3CN after electrolysis, the CV shows the presence of a new reduction process at -1.24 V and a small reversible oxidation wave appears at $+1.00$ V. A second scan shows that a multiplicity of secondary reactions is occurring. On the other hand, in CH_2Cl_2 the brown-yellow monocation is produced under rapid electrolysis conditions and there are only relatively minor amounts of decomposition (vide infra).

The IR spectra of the neutral Mo(II) nitrogen ligand complexes in CH_2Cl_2 , obtained by utilizing the OTTLE, exhibit two $\nu(\text{CO})$ bands at frequencies (within the ranges 1956–1933 and 1875–1838 cm^{-1}) consistent with previously reported values.^{9,19} Upon oxidation to the monocations, these bands shift by more than 100 cm^{-1} to higher frequencies (Table II); this is expected due to the decrease in the ability of the metal to back-donate electron density into the π^* orbitals of the CO ligands. Fairly rapid spectral acquisition (a few minutes) allows time-dependent spectra to be obtained and intermediate species (if any) to be observed. We observed no intermediates (see Figure 2) except in the case of the dab complex VIII. In this case, the only anomaly is the growth and then disappearance of very high frequency $\nu(\text{CO})$ bands at 2164 s and 2194 m cm^{-1} in the spectra obtained during electrolysis of VIII. In view of the fairly reactive nature of the dab monocation, these bands can be attributed to decomposition products. We believe that these observations can best be rationalized in terms of the reaction of reactive $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dab})]^+$ with trace amounts of oxygen and/or other oxidants to give very unstable Mo(IV) and/or Mo(V) species. Since the relative intensities of the bands at 2164 and 2194 cm^{-1} do not track one another, they are clearly attributable to two different carbonyl-containing species. The 2164- cm^{-1} band persists much longer than does the feature at 2194 cm^{-1} . Because of the high frequencies of these two $\nu(\text{CO})$ bands, they must be due to very high oxidation state carbonyls. Examples of high-oxidation-state carbonyl-containing complexes include $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Mo}(\text{CH}_2\text{CH}=\text{CH}_2)(\text{CO})]\text{PF}_6$ ($\nu(\text{CO}) = 2128 \text{ cm}^{-1}$),²⁰ $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{dppe})(\text{CO})](\text{PF}_6)_2$ ($\nu(\text{CO}) = 2100 \text{ cm}^{-1}$),²¹ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})\text{Br}_2(\eta^3\text{-2-R-all})$ complexes ($\nu(\text{CO}) \approx 2044 \text{ cm}^{-1}$).²² The species that are responsible for these spectral features are very unstable and decompose too quickly outside of the OTTLE cell to be isolated and identified further. These same spectral features are also seen in the spectra of

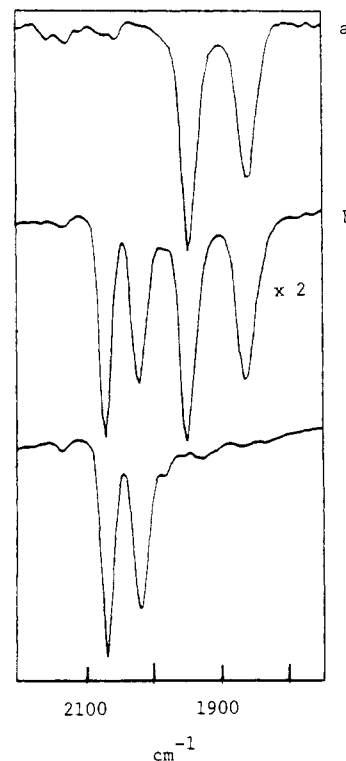


Figure 2. IR spectra obtained during the electrolysis of a 0.5 M TBAH/ CH_2Cl_2 solution of $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{phen})$: (a) $t = 0$; (b) $t = 3$ min; (c) $t = 6$ min. The intensity scale for trace b is $\times 2$ that for traces a and c.

electrolyzed solutions of the phosphine/arsine ligand complexes (see part ii).

(ii) **Phosphorus/Arsenic Donor Complexes.** In contrast to the stability of the monocations of the nitrogen donor complexes, similar complexes that contain phosphine/arsine ligands (IX–XII) are much less stable. After bulk electrolysis of CH_2Cl_2 solutions of complexes IX–XII, the cyclic voltammograms show no evidence for formation of the monocation but instead yield a different product(s) characterized by two irreversible oxidation waves. For the molybdenum complexes that contain dppe and dppm, the CV's also show an irreversible reduction process. Cyclic voltammetric data for these electrolyzed solutions, in 0.1 M TBAH/ CH_2Cl_2 at $v = 200 \text{ mV/s}$ and 25°C vs SCE, are as follows: IX, $E_{p,a}(2) = +1.85 \text{ V}$, $E_{p,a}(1) = +1.40 \text{ V}$, $E_{p,c} = -1.42 \text{ V}$; X, $E_{p,a}(2) = +1.78 \text{ V}$, $E_{p,a}(1) = +1.25 \text{ V}$, $E_{p,c} = -1.48 \text{ V}$; XI, $E_{p,a}(2) = +1.88 \text{ V}$, $E_{p,a}(1) = +1.13 \text{ V}$; XII, $E_{p,a}(2) = +1.70 \text{ V}$, $E_{p,a}(1) = +1.10 \text{ V}$. The X-band ESR spectra of these same solutions (recorded at -150°C) showed very similar features. A representative ESR spectrum is available elsewhere.¹⁸

During exhaustive bulk electrolysis of CH_2Cl_2 solutions of the dppm (IX) and dpae (XI) dicarbonyls, an orange "intermediate" was formed. Efforts to identify this species at room temperature were thwarted because it disappeared too quickly. However, at -10°C , its decomposition is sufficiently slow that it could be identified by cyclic voltammetry, following the passage of approximately one electron, as the monocationic Mo(III) complex. As the temperature was increased, decomposition occurred to yield a green solution. No such intermediate could be identified by CV during oxidation of the dppe complexes of molybdenum and tungsten (i.e. complexes X and XII).

Upon monitoring the electrolysis of the compounds IX–XII in the OTTLE at $+1.0 \text{ V}$ using FTIR spectroscopy, we observed that the two carbonyl bands of the neutral parent complexes were replaced by three carbonyl bands along with a pair of high-frequency vibrations at 2164 and 2191 cm^{-1} that were similar to those seen at intermediate stages of electrolysis of the complex $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dab})$ (vide supra). The last two bands are independent of the nature of the bidentate ligand L-L. The IR spectra of the fully electrolyzed solutions clearly demonstrate the

(19) Brisdon, B. J. *J. Organomet. Chem.* **1977**, *125*, 225.

(20) Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 262.

(21) Bao, Q.-B.; Rheingold, A. L.; Brill, T. B. *Organometallics* **1986**, *5*, 2259.

(22) Faller, J. W.; Ma, Y. *Organometallics* **1986**, *5*, 1949.

Table III. Cyclic Voltammetric and IR Spectral Data for $[(\eta^3\text{-all})\text{M}(\text{CO})_3(\text{L-L})]\text{ClO}_4$

compd	$\nu(\text{CO}), \text{cm}^{-1}$		CV ^a	
	CH ₂ Cl ₂	KBr pellet	$E_{p,a}$	$E_{p,c}$
$[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dppm})]^+$	2052 (m), 1998 (m), 1951 (s)	2048 (m), 1990 (m), 1950 (s)	+1.84	-1.40
$[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dppe})]^+$	2048 (m), 1986 (m), 1947 (s)	2044 (m), 1986 (m), 1940 (s)	+1.75	-1.45
$[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpae})]^+$	2048 (m), 1986 (m), 1947 (s)	2044 (m), 1980 (m), 1944 (s)	+1.85	
$[(\eta^3\text{-all})\text{W}(\text{CO})_3(\text{dppe})]^+$	2044 (m), 1979 (m), 1932 (s)	2040 (m), 1975 (m), 1928 (s)	+1.73	

^a Voltammograms (E in volts) recorded on solutions in 0.1 M TBAH/CH₂Cl₂ at $v = 200$ mV/s and 25 °C vs SCE.

absence of the simple oxidized monocationic species derived from IX–XII. Upon monitoring of the formation of the electrolysis products with time, no IR spectral evidence for the monocation could be found even when the spectra were recorded in less than 30 s, with the exception of the dpae complex. In this instance, a sixth $\nu(\text{CO})$ band appears at 2036 cm^{-1} that is not due either to the neutral precursor complex or to the final product. This band is assigned to the symmetric stretch of the monocation; the asymmetric stretch is apparently obscured by the 1978- cm^{-1} band of the product (Figure 3).

Since the $\nu(\text{CO})$ product bands that occur between 2060 and 1900 cm^{-1} in the FTIR spectra of electrolyzed solutions of IX–XII (Table II) are seen to be interdependent, they are in each instance due to a single species. An important difference between the spectra of the solutions formed by electrolyzing samples of IX and X and those of XI and XII is the relative intensities within the three-band patterns (i.e. m, m, s compared to m, s, m, respectively; Table II).

The identity of the chemical product formed after oxidation of IX–XII was first thought to be the reductive elimination product $[\text{M}(\text{CO})_2(\text{L-L})_2]^+$. However, neither the electrochemical properties nor the ESR spectra of these species are similar to those reported in the literature.^{23–26} A comparison of the carbonyl stretching frequencies of the main decomposition product with the spectra of possible products resulted in the conclusion that the products were metal(II) tricarbonyl complexes.

Halide ligands, X^- , in the compounds of the type $(\eta^3\text{-all})\text{-MoX}(\text{CO})_2(\text{L-L})$ are easily abstracted by using Ag(I), Na(I), or Tl(I) in the presence of a suitable donor ligand to form cationic complexes.^{4,9,15} Since cationic tricarbonyls have been synthesized under such conditions in the presence of CO(g), such compounds (viz. $[(\eta^3\text{-all})\text{M}(\text{CO})_3(\text{L-L})]^+$)¹⁶ appeared to us to be likely products of the electrochemical oxidation. Accordingly, the perchlorate salts of $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dppm})]^+$, $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dppe})]^+$, $[(\eta^3\text{-all})\text{W}(\text{CO})_3(\text{dppe})]^+$, and $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpae})]^+$ were prepared and their corresponding IR spectra and CV's were recorded (Table III and Figure S2, supplementary material). The carbonyl stretching frequencies and relative intensities in the spectra of the first two salts match almost exactly (within ± 2 cm^{-1}) the corresponding spectra of the electrolysis products of IX and X in CH₂Cl₂ (Table II). The CV's of these same two synthesized tricarbonyl cations show two irreversible processes, which have peak potentials (Table III and Figure S2) that also compare well with two of the three processes seen in the CV's following the electrolysis of IX and X (vide supra). The second oxidative wave of the electrochemically generated species (i.e. $E_{p,a}(1)$ at +1.40 and +1.25 V for IX and X, respectively) is most likely due to another decomposition product, which in this instance does not contain carbonyl ligands. Accordingly, there is little doubt that the electrolysis of IX and X results in the formation of $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ (L-L = dpmm and dppe) in good yield.

The IR spectra of the other two tricarbonyl cations $[(\eta^3\text{-all})\text{-Mo}(\text{CO})_3(\text{dpae})]\text{ClO}_4$ and $[(\eta^3\text{-all})\text{W}(\text{CO})_3(\text{dppe})]\text{ClO}_4$, however, are not the same as the spectra of the species that are formed

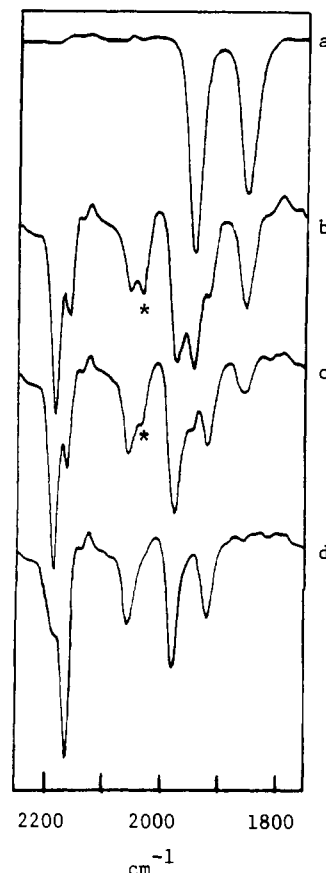


Figure 3. IR spectra obtained during the electrolysis of a 0.5 M TBAH/CH₂Cl₂ solution of $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dpae})$; (a) $t = 0$; (b) $t = 3$ min; (c) $t = 5$ min; (d) $t = 8$ min. These spectral changes show the conversion of this complex to $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpae})]^+$ via the intermediacy of the unstable cation $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dpae})]^+$ ($\nu(\text{CO})$ at 2036 cm^{-1} shown by asterisks). Note the presence of bands at 2191 and 2164 cm^{-1} , which are due to high-oxidation-state carbonyl-containing byproducts (see text).

following the electrolysis of XI and XII in the OTTLE. Since the tricarbonyl species that are formed upon electrolyzing XI and XII exhibit carbonyl stretching modes whose frequencies and relative intensities resemble those of seven-coordinate Mo(II) carbonyls of the type $\text{MX}_2(\text{CO})_3(\text{L-L})$,^{28–32} it is possible that chloride is not lost in these two cases and that the decomposition product is actually $(\eta^1\text{-all})\text{MCl}(\text{CO})_3(\text{L-L})$. Although attempts to chemically synthesize such a seven-coordinate η^1 -allyl species were unsuccessful, we favor this explanation for the following reasons. First, the IR spectral data presented in Table II for electrolyzed solutions are quite similar to those reported previously for the related seven-coordinate $(\text{CH}_2=\text{CHCH}_2\text{CH}_2)\text{MoBr}(\text{C-O})_3(\text{NCCH}_3)_2$ ³³ and $\text{Me}_2\text{NCH}_2\text{MoI}(\text{CO})_3(\text{NCCH}_3)$.³⁴ Second,

(23) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1974**, *14*, 274.

(24) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Inorg. Chem.* **1974**, *13*, 1617.

(25) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 2526.

(26) Reimann, R. H.; Singleton, E. *J. Organomet. Chem.* **1971**, *32*, C44.

(27) Anker, M. W.; Colton, R.; Rix, C. J.; Tomkins, I. B. *Aust. J. Chem.* **1969**, *22*, 1341.

(28) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1970**, *23*, 441.

(29) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 2543.

(30) Colton, R.; Rix, C. J. *Aust. J. Chem.* **1969**, *22*, 2535.

(31) Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *19*, 1519.

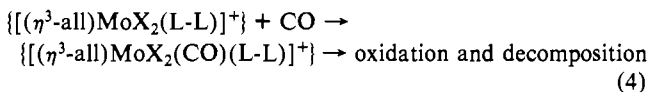
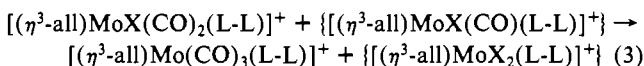
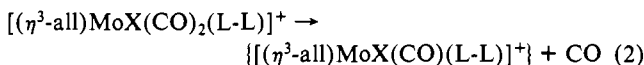
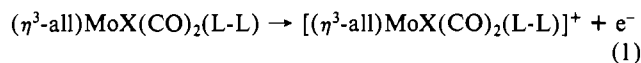
(32) Anker, M. W.; Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1968**, *21*, 1159.

(33) Mércour, J. Y.; Charrier, C.; Benaim, J.; Roustan, J. L.; Commereuc, D. *J. Organomet. Chem.* **1972**, *39*, 321.

the addition of Cl^- (in the form of benzyltriethylammonium chloride) to electrochemically and chemically generated solutions of the cationic molybdenum tricarbonyls $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ that contain the dpmm and dppe ligands resulted in the formation of an equilibrium between the cationic tricarbonyl species and the neutral precursor dicarbonyl complexes $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{L-L})$. A similar equilibrium, which was confirmed by IR spectroscopy (with the OTTLE) and cyclic voltammetry, was established upon treating the chemically prepared tricarbonyl cation $[(\eta^3\text{-all})\text{W}(\text{CO})_3(\text{dppe})]^+$ with Cl^- . However, the electrochemically generated tricarbonyl complex of tungsten, which we believe is $(\eta^3\text{-all})\text{WCl}(\text{CO})_3(\text{dppe})$, was unaffected by Cl^- , indicating that this species and presumably the dpae analogue XI are structurally different from the other systems.

In an effort to elucidate the mechanism for the formation of the molybdenum tricarbonyl cations $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ (for L-L = dpmm or dppe) from the electrochemically generated monocations $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{L-L})]^+$, the effect of an excess of $\text{CO}(\text{g})$ upon the redox chemistry was studied. The bulk electrolysis (at +0.75 V) of solutions that had been saturated with $\text{CO}(\text{g})$ produced the cation $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{L-L})]^+$ with $n_{\text{app}} \approx 1$ without any perceptible decomposition. Decomposition of the tricarbonyl is then initiated by the removal of $\text{CO}(\text{g})$. IR spectroscopy of these quickly decomposing solutions ($t_{1/2} \approx 1$ min) showed that the tricarbonyl $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ was the only carbonyl-containing product.

The preceding observations can be incorporated into a plausible mechanism (eq 1-4). In these reactions, braces denote a very



unstable species. Since the monocation produced by oxidation

(34) Wong, C. F.; Wilkinson, G. J. *Chem. Soc., Dalton Trans.* 1975, 1100.

of the neutral species (eq 1) is stabilized in the presence of added $\text{CO}(\text{g})$, the first chemical step is probably the loss of a carbonyl ligand (eq 2). There is no evidence that the 17-electron cation $[(\eta^3\text{-all})\text{MoX}(\text{CO})_2(\text{L-L})]^+$ reacts with CO to form the tricarbonyl $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^{2+}$. Note that the relative instability of this later dication has been demonstrated (vide supra) by the irreversibility of the oxidation of $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^+$ to $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{L-L})]^{2+}$ (see Figure S2). Consequently, this dication would not be a stable chemical product formed by $[(\eta^3\text{-all})\text{MoX}(\text{CO})_2(\text{L-L})]^+$ in the presence of $\text{CO}(\text{g})$. Subsequent reaction of the highly reactive 15-electron monocarbonyl cation $[(\eta^3\text{-all})\text{MoX}(\text{CO})(\text{L-L})]^+$ with the 17-electron dicarbonyl monocation seems to be a feasible means of producing the observed monocationic tricarbonyl (eq 3). This reaction, which formally represents a disproportionation (i.e. $2\text{Mo}(\text{III}) \rightarrow \text{Mo}(\text{II}) + \text{Mo}(\text{IV})$), is written as giving the 14-electron $\text{Mo}(\text{IV})$ complex as a second product. This is an attractive possibility in view of the observed formation of transients having C-O stretching modes at very high frequencies, 2191 and 2164 cm^{-1} . Such a $\text{Mo}(\text{IV})$ complex would most likely scavenge any free CO in the system to form a 16-electron monocarbonyl complex that contains halide (eq 4). The ESR activity of the electrolyzed solution and the >1 coulometric electron count (Table I) can then be attributed to the subsequent oxidation and decomposition of this highly unstable moiety.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE85-06702 to R.A.W. and Grant No. CHE85-13732 to M.J.W.) for generous research support. The FTIR spectrometer was acquired through a DOD University Instrumentation Award (to M.J.W.). We appreciate the experimental assistance of Dennis S. Corrigan in recording the FTIR spectra and Dr. K. A. Conner for some very helpful preliminary experiments.

Registry No. I, 12245-57-7; II, 110174-39-5; III, 110222-34-9; IV, 47462-49-7; V, 12091-83-7; VI, 12245-84-0; VII, 57811-37-7; VIII, 60214-54-2; IX, 62662-28-6; X, 33135-95-4; XI, 66615-65-4; XII, 62960-06-9; $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{bpy})]\text{PF}_6$, 110174-41-9; $[(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{phen})]\text{PF}_6$, 110174-43-1; $[(\eta^3\text{-all})\text{Mo}(\text{O}_2\text{CCF}_3)(\text{CO})_2(\text{bpy})]\text{PF}_6$, 110174-45-3; $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpmm})]^+$, 66518-78-3; $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dppe})]^+$, 66518-74-9; $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpae})]^+$, 110174-46-4; $[(\eta^3\text{-all})\text{W}(\text{CO})_3(\text{dppe})]^+$, 66518-80-7.

Supplementary Material Available: Figures S1 and S2, showing the cyclic voltammograms of $(\eta^3\text{-all})\text{MoCl}(\text{CO})_2(\text{dpmm})$ and $[(\eta^3\text{-all})\text{Mo}(\text{CO})_3(\text{dpmm})]^+\text{ClO}_4^-$ (2 pages). Ordering information is given on any current masthead page.

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

Reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{I}_2]_2$ (M = Mo, W) Dimers by PMe_3 : Synthesis and Properties of the Novel Complexes $\text{M}(\text{NO})(\text{PMe}_3)_4\text{I}^1$

Nancy J. Christensen, Allen D. Hunter, Peter Legzdins,* and Luis Sánchez²

Received April 1, 1987

The diiodo dimers $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{I}_2]_2$ (M = Mo, W) react with 10 equiv of PMe_3 to produce the new electron-rich nitrosyl complexes $\text{M}(\text{NO})(\text{PMe}_3)_4\text{I}$, the other product being $[(\text{C}_5\text{H}_5)\text{PMe}_3]\text{I}$. It has been shown that the formation of the tetrakis(phosphine) complexes proceeds sequentially via the isolable intermediate species $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{I}_2(\text{PMe}_3)$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})\text{I}(\text{PMe}_3)_2]\text{I}$. Treatment of the diiodo dimers with 4 equiv of PMe_3 in the presence of a reducing agent such as sodium amalgam affords excellent yields of the related complexes $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})(\text{PMe}_3)_2$ (M = Mo, W), which also contain electron-rich transition-metal centers. The analytical and spectroscopic properties of all new complexes prepared are presented.

Introduction

Because of its relatively small cone angle and strong Lewis basicity, trimethylphosphine (PMe_3) often exhibits distinctive

behavior during its reactions with organo transition-metal complexes.³ Particularly interesting in this regard are the reactions of PMe_3 with cyclopentadienyl-containing compounds. Previous work by Casey and co-workers⁴ has established the occurrence

- (1) Organometallic Nitrosyl Chemistry. 31. Part 30: Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* 1986, 108, 3843.
(2) Present address: Departamento de Química Inorgánica, Facultad de Química, Universidad de Sevilla, Sevilla, Spain.

- (3) Tolman, C. A. *Chem. Rev.* 1977, 77, 313.

- (4) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* 1987, 87, 307 and references cited therein.