atom techniques which conventionally operate at 77 K.

The intense visible absorptions of these odd-electron lanthanoid complexes resemble the open-shell group IB (11) metal complexes (metal-to-ligand charge-transfer transitions) more closely than those of the group VIII (8–10) metals. UV–vis absorption spectroscopy of the reaction of Eu with ethylene diluted in argon gave evidence for products of different ligand stoichiometry. These results were confirmed by dopant gas dilution matrix-isolation infrared spectroscopic studies which gave evidence for π-complex formation, a highly coordinatively unsaturated monoethylene europium complex, and a species having higher ethylene coordination.

Molecular orbital calculations indicate that these molecules are weakly bonded by europium f orbital donation to the olefin π^* system, with forward donation from the occupied ethylene π orbital providing little enhancement of overall complex stability.

Experimental Methods

Materials. Research grade rare gases (Matheson) were used throughout these studies. Europium powder was obtained from Aesar.

Manipulations and Methods. Europium powder was transferred under argon in a Vacuum Atmospheres drybox to a boron nitride lined tantalum Knudsen cell. The cell was then mounted onto the water-cooled resistance electrodes of a plexiglass flanged furnace assembly and the entire unit sealed under argon in a plastic bag. Transfer of the furnace unit to the cryostat of the matrix-isolation unit was accomplished under a vigorous argon purge. A customized metal vapor cryogenic unit (Torromis, available from Torrovap Industries, Toronto, Canada) was employed in this work.

Metal and substrate vapors were cocondensed onto a sodium chloride (UV–vis) or cesium iodide (IR) window maintained at 12 K by an Air Products Displex CSW 202 variable-temperature He gas refrigerator. A quartz crystal microbalance strategically positioned in the furnace provided quantitative measure of the Eu atom deposition rate. The flow of gas was determined from measurements of the pressure drop per unit time in a reservoir of known volume. Matrix sample preparations typically required 1–2 h for UV–vis studies and 5–8 h for IR spectroscopic analyses. UV–vis spectra were obtained with a Cary 17 spectrometer. IR spectra were obtained by using a Nicolet 5DX-FTIR.

Acknowledgment. We thank Mr. V. Lamberti for technical assistance in modifying the matrix-isolation and spectroscopic equipment and for carrying out some of the experiments on which this work is based.

Note Added in Proof. The synthesis of the first authentic Ln(0) species, the crystallographically characterized bis(η-1,3,5-tri-*tert*-butylbenzene) sandwich complexes of Y and Gd has recently been reported. (Brennan, J. G.; Cloke, F. G. N.; Sameh, A. A.; Zaikin, A. *J. Chem. Soc., Chem. Commun.* **1987**, 1668.)

Registry No. Eu(C_2H_4), 111559-70-7; C_2H_4, 74-85-1; Eu, 7440-53-1.

Electrochemical Oxidative Induced Isomerization of Dicarbene Metal Carbonyl Complexes

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The one-electron oxidation of *trans*-(carbene)$_2$M(CO)$_4$ (M = Cr, Mo, W) complexes results in their rapid isomerization to the corresponding cis cations. Remarkably, the cis cations have an oxidation potential approximately 200 mV higher than the trans complexes. This apparent paradox is explicable by the large difference in thermodynamic stabilities of the cis and trans neutral complexes. Rates of isomerization as well as energies of activation were determined. A novel photoelectric cell was developed utilizing the dicarbene complexes.

Introduction

Electron-transfer chain catalyzed isomerizations of organometallic complexes represent an ever growing area of study. These studies not only are of theoretical interest but also can be highly useful synthetically.[1–15] Busch's original report is a classic example of how ETC-catalyzed reactions can be used synthetically.[11] In this paper, we would like to report some unusual observations regarding the electrochemical oxidation of some dicarbene carbonyl

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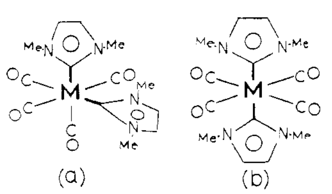


Figure 1. (a) *cis*- and (b) *trans*-(Imid)$_2$M(CO)$_4$ (Me = CH$_3$).

chromium, molybdenum, and tungsten complexes.[3] Several years ago, Fisher's pioneering work generated the first carbene metal complexes.[16-18] Recently, the preparation of *cis*- and *trans*-dicarbene tetracarbonyl metal complexes was reported by Öfele et al.[19,20] It has been shown that the cis complexes undergo photoisomerization, forming the thermodynamically less stable *trans*-dicarbene complexes which are reconverted thermally to the original cis isomers.[21,22] We have examined the electrochemical oxidation of a series of these complexes. An unusual isomerization of the trans cation to the cis cation was observed. Also, a novel photoelectric cell was designed employing these complexes.

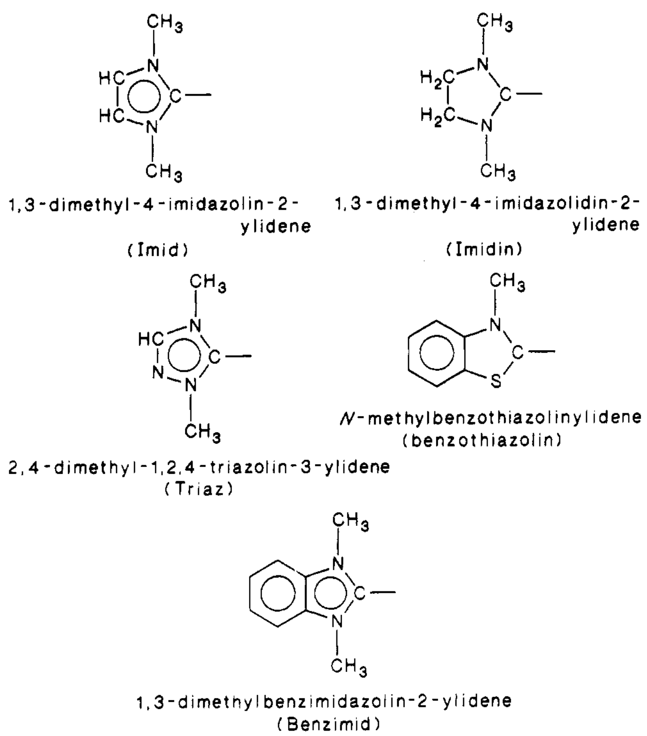
Experimental Section

All manipulations of air-sensitive materials were conducted in a VAC argon drybox or under argon using a Schlenk apparatus connected to a double manifold providing vacuum and dry argon. THF was freshly distilled from Na/K alloy under argon. ^{1}H NMR and ^{13}C NMR spectra were obtained on either a Varian EM-390 or a Varian XL-100 NMR spectrometer and referenced to either Me$_4$Si or the deuteriated solvent, as appropriate. Infrared spectra were obtained on a Perkin-Elmer 283 IR spectrophotometer. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are corrected. GLC was performed on a Hewlett-Packard 5730A gas chromatograph interfaced with a Perkin-Elmer LC-100 integrator. Elemental analyses were performed by Galbraith Labs, Knoxville, TN. High-resolution mass spectra were obtained from the Midwest Regional Center for Mass Spectrometry, University of Nebraska—Lincoln.

All electrochemical experiments were performed with either a homemade potentiostat/galvanostat, coulometer (541 Koslow Scientific Company), Hewlett-Packard Model 7004B X-Y recorder, and Tektronic type R564B storage oscilloscope with tektronic C-12 polaroid camera or a PAR Model 173 potentiostat/galvanostat equipped with IR compensation in conjunction with a PAR Model 175 universal programmer and Model 179 digital coulometer. The electrochemical cell was of a standard three-electrode configuration. A platinum disk polished with SnO$_2$ powder, a Metrohm E410 hanging mercury drop electrode (HMDE), or a Sargent-Welch dropping mercury electrode (DME) served as the working electrode. A saturated calomel electrode or Ag/AgCl-saturated NaCl(aq) electrode was used as the reference electrode. Platinum foil was used as the working electrode for the bulk electrolysis. The counter electrode compartment was separated from the working electrode by a buffer compartment with a medium-porosity-fritted glass disk and an agar salt bridge.

Propylene carbonate (PC) was generally vacuum distilled once, discarding the first fraction, and then stored over 4A molecular sieves. No particular changes or advantage were noted when using doubly distilled PC. Methylene chloride (MC) was purified by vacuum distillation twice from phosphorus pentoxide. Acetonitrile (AN), dimethyl sulfoxide (DMSO), and acetone (AC) were purified according to published procedures. Polarographic grade tetraethylammonium perchlorate (TEAP), tetrabutylammonium perchlorate (TBAP), and lithium perchlorate (LiClO$_4$) were purchased from Eastman and used without any further purification except for drying under vacuum at 70 °C for 1 h prior to use. The electrochemical measurements were made under positive argon pressure.

Chart I



Synthesis of Complexes. Ligands used for the present studies with their abbreviations in parentheses include 2,4-dimethyl-1,2,4-triazolin-3-ylidene (Triaz), 1,3-dimethyl-4-imidazolin-2-ylidene (Imid), 1,3-dimethylbenzimidazolin-2-ylidene (Benzimid), 1,3-dimethylimidazolidin-2-ylidene (Imidin), and *N*-methylbenzothiazolinylidene (benzothiazolin). Their structures are given in Chart I.

Cis and trans complexes of these ligands (except benzothiazolin) with Cr(0), Mo(0), and W(0) were reported earlier[19-25] and were synthesized accordingly. These complexes were characterized by melting point, IR, and NMR. They were stored in the freezer to prevent oxidation or isomerization. Although these compounds were reasonably stable in the solid state, they were found to be partially oxidized (10%) after storage for several months. The decomposition products were easily removed by filtration from THF.

Synthesis of *trans*-Tetracarbonylbis(*N*-methylbenzothiazolinylidene)molybdenum(0). In a 50-mL two-necked round-bottomed flask equipped with a water condenser, argon inlet, magnetic stirring bar, and a rubber septum were placed molybdenum hexacarbonyl (1.92 g, 7.27 mmol) and bis(*N*-methylbenzothiazolinylidene) (2.0 g, 7.27 mmol). The flask was evacuated and filled with argon three times. Freshly distilled argon saturated methylcyclohexane (20 mL) was syringed in. The resulting mixture was refluxed for 6 h. Upon cooling, a brown product separated out. It was filtered and recrystallized from THF: yield 90%; mp >275 °C; ^{1}H NMR (CDCl$_3$) δ 7.3–6.5 (m, 4 H, aromatic protons), 3.22 (s, 3 H, NCH$_3$); IR (CHCl$_3$) 1970 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_2O_4S_2Mo$: C, 47.43; H, 2.76; N, 5.53. Found: C, 47.57; H, 2.90; N, 5.74.

***trans*-Tetracarbonylbis(*N*-methylbenzothiazolinylidene)tungsten(0).** This preparation was similar to the molyb-

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Table I. Reversible Half-Wave Potentials[a] and Isomerization Rates[b,d]

compound	$E_{1/2}$ (V vs. SCE) cis	$E_{1/2}$ (V vs. SCE) trans	$\Delta E_{1/2}{}^{r}$ (cis–trans)	k_1 (s^{-1}) 22 °C	k_1 (s^{-1}) t, °C	$E_a{}^c$ (kcal/mol)
$(Triaz)_2Cr(CO)_4$[e]	0.17 (± 0.005)	–0.11 (± 0.02)	0.28	0.34 (± 0.2)	0.015 (± 0.02) (0)	21 (± 1.0)
$(Triaz)_2Mo(CO)_4$	0.528 (± 0.005)	0.36 ± 0.02)	0.17	2.0 (± 0.2)	0.2 (± 0.02) (–11)	10.7 (± 1.0)
$(Benzimid)_2Mo(CO)_4$	0.477 (± 0.005)	0.24 (± 0.02)	0.24	7 (± 2)	0.6 (± 0.2) (–12)	11 (± 1.0)
$(Imid)_2Mo(CO)_4$	0.335 (± 0.005)	0.11 (± 0.02)	0.23	14 (± 3)	1.4 (± 0.3) (–16)	9 (± 1.0)
$(Imid)_2W(CO)_4$	0.337 ± 0.005)	0.14 (± 0.03)	0.20	400 (± 200)	90 (± 20) (–2)	10 (± 2.0)
$(Imidin)_2Cr(CO)_4$	0.106 (± 0.005)					
$(Imidin)_2Mo(CO)_4$	0.343 (± 0.005)	0.17	0.18	39 (± 10)	3.1 (± 0.30) (–16)	10 (± 1.0)
$(Imidin)_2W(CO)_4$	0.365 (± 0.005)					

[a] $E_{1/2}$ = reversible half-wave potential for $R \xrightarrow{-e^-} R^+$ vs SCE in the system of 0.3 M TBAP in methylene chloride solution. The values are approximate for the trans compounds due to kinetic complication. [b] k_1 = rate constant of trans to cis isomerization of cations. [c] E_a = activation energy (approximate value). [d] Error is estimated in parentheses. [e] $E_{1/2}$ vs NCE.[36]

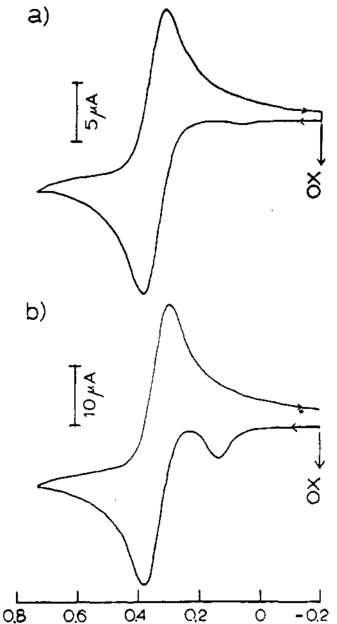

Figure 2. Cyclic voltammogram of *trans*-$(Imid)_2W(CO)_4$. The solution contained 5.2 mM *trans*-$(Imid)_2W(CO)_4$ and 0.25 M TBAP in methylene chloride. The scan rates are (a) 0.2 V/s at 22 °C and (b) 1.0 V/s at –2 °C.

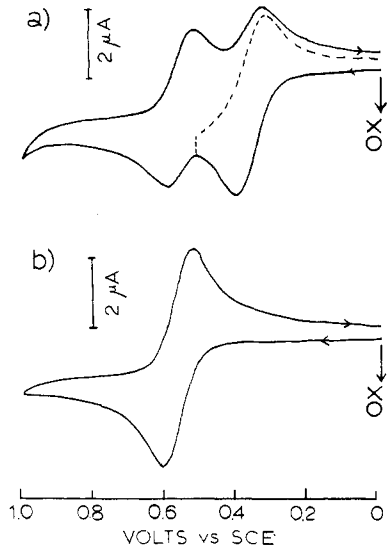

Figure 3. Cyclic voltammogram of *trans*-$(Triaz)_2Mo(CO)_4$. The solution contained 1.7 mM *trans*-$(Triaz)_2Mo(CO)_4$ and 0.25 M TBAP in methylene chloride. The runs were made with the scan rate 0.2 V/s at –10 °C: (a) before and (b) after bulk electrolysis at 0.40 V vs SCE.

denum complex preparation. Tungsten hexacarbonyl (1.6 g, 4.70 mmol) and bis(*N*-methylbenzothiazolinylidene) (1.0 g, 3.64 mmol) were refluxed in methylcyclohexane (15 mL) for 4 h. The solution was cooled, and a greenish brown product separated out. This was recrystallized from THF: yield 90–95%; mp >275 °C; ^1H NMR ($CDCl_3$) δ 7.26–6.56 (m, 4 H, aromatic protons), 3.23 (s, 3 H, NCH_3); IR ($CHCl_3$) 1970 cm^{-1}. Anal. Calcd for $C_{20}H_{14}N_2O_4S_2W$: C, 40.40; H, 2.35; N, 4.71. Found: C, 40.39; H, 2.36, N, 4.73.

Results and Discussion

The redox properties of the dicarbene complexes were determined in several solvents including AN, DMF, DMSO, AC, and MC. The solvent that proved to be most inert toward the neutral complexes as well as the cations was MC. Except for a few experiments, the majority of the results reported here are in MC.

The cis compounds examined in this study exhibited only a single redox couple in the potential range +1.0 to –2.7 V vs SCE using a Pt working electrode. For all the complexes, this single redox couple was a reversible oxidative wave in the region +0.3 to +0.5 V. The anodic to cathodic peak separation was relatively constant with sweep rate and was in the range of 60–70 mV. The ratio of anodic to cathodic current heights was essentially unity at sweep rates of 0.01–1.0 V/s at ambient temperatures, demonstrating a high degree of chemical reversibility. Coulometry on several of the complexes at –5 °C confirmed that the oxidation wave was, in fact, a one-electron oxidation yielding a stable cation. This result is substantiated by a recent report that these complexes can be oxidized by ferrocenium salts to yield paramagnetic cation complexes that are isolable as PF_6 salts.[26] The reversible half-wave potentials are reported in Table I.

The redox properties of the trans complexes were then examined at room temperature. Most remarkable, they demonstrated only a single redox couple of absolutely identical characteristics to that observed for the corresponding cis complexes. In some cases, a small irreversible wave was observed at about 0.2V more negative potential than the main oxidative wave. The magnitude of this small wave changed dramatically depending on the particular complex, sweep rate, and temperature of the electrochemical cell. In the case of *trans*-$(Imid)_2W(CO)_4$ (Figure 2a), this wave is hardly distinguishable at normal sweep rates at room temperature, but it is well-recognized at higher sweep rates at low temperatures (Figure 2b). In the case of *trans*-$(Triaz)_2Mo(CO)_4$, the magnitude of this first wave was about half that of the main wave even at room temperature; however, there was no accompanying cathodic

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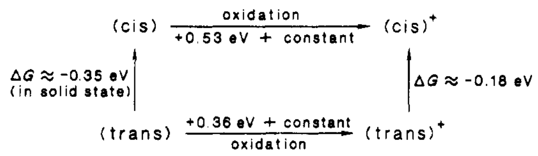
Scheme I



wave. At low temperatures (−11 °C), this trans complex showed two well-defined reversible waves (Figure 3a).

Coulometry was carried out on *trans*-(Triaz)$_2$Mo(CO)$_4$ at −7 °C at a potential slightly anodic of the small first wave. The current passed during the bulk electrolysis was very small, being at most 10% of what was expected of a one-electron oxidation, and the current reversed direction at the late stages. Also, the electrolysis was completed within a few minutes. A cyclic voltammogram of this solution showed only the wave corresponding to that observed for the cis complex (Figure 3b). The current height was that expected for complete trans to cis conversion. The color of the solution changed from orange (trans complex) to colorless or the same as the cis complex. Also the IR band due to (C=O) of the trans complex at 1850 cm^{-1} vanished after bulk electrolysis, and three new bands at 2000, 1870, and 1830 cm^{-1} appeared which matched those of *cis*-(Triaz)$_2$Mo(CO)$_4$. Bulk electrolysis was carried out at the second wave, and the current passed corresponded to a one-electron oxidation. The other trans complexes showed similar behavior. IR spectra indicated that the trans complexes had been converted to the cis complexes upon bulk electrolysis at the first wave even though little or no current flow was observed at room temperature. Finally, isolation and characterization definitely established that the trans complexes had isomerized to the cis complexes.

From these observations, it is apparent that the trans complexes are isomerized to the cis complexes upon oxidation at the first wave. All of the electrochemical data can be understood if we make the following assumptions: (a) in the oxidation of the trans complexes the first wave corresponds to the generation of the trans cation and the second wave that is common to both cis and trans complexes corresponds to the oxidation of the cis cation and (b) the trans cation is rapidly isomerized to the cis cation.

The first assumption is straightforward and follows from the bulk electrolysis and IR data. The second assumption at first appears unreasonable as it would seem from the oxidation potentials that the trans cations are more stable than the cis cations by about 0.2 eV. However, Öfele and Herberhold[21,22] have reported that in the solid state the neutral cis complex is about 0.35 eV more stable than the corresponding trans complex. If this difference holds for the neutral complexes in solution, the $\Delta G°$ for the isomerization of the trans cation to the cis cation would be approximately $\Delta G° = -0.35\ \text{eV} + (+0.52 - 0.36)\ \text{eV} = -0.18$ eV. As this isomerization is occurring in solution and the solvation energy of the cis cation is expected to be much larger than that of the trans cation, the free energy change is probably much more negative. A schematic diagram of the free energy difference is shown in Scheme I.

All of the experimental results can now be readily understood. The sequence of events occurring at the first wave in the oxidation of the trans complex is summarized in eq 1. The trans complex is oxidized to the trans cation

$$\text{(trans)} \xrightarrow{-e^-} \text{(trans)}^+ \xrightarrow{\text{rapid}} \text{(cis)}^+ \xrightarrow{+e^-} \text{(cis)} \qquad (1)$$

that rapidly isomerizes to the cis cation. Since the potential is much more negative than the reduction potential of the cis cation, it is immediately reduced to neutral cis. Thus the magnitude of the first wave is determined by the rate of isomerization of the trans cation to the cis cation. If this rate is extremely high, no net current flow will be observed as the oxidation current will about equal the reduction current. It is also likely that homogeneous electron exchange between cis cation and neutral trans complex is contributing to the isomerization.

The reversible half-wave potentials are summarized in Table I. Also the approximate isomerization rate constants are found in Table I. This was estimated from the half-life, $t_{1/2}$. The procedure[27] involved the determination of the sweep rate at which the cathodic wave height becomes half of that observed in the absence of the isomerization using sweep rates from 0.01 to 50 V/s.[28] The isomerization rates were determined at several temperatures. The activation energies for the isomerizations were then determined from Arrhenius plots. The energy of activation for the isomerization process for the Mo and W complexes was found to be approximately 10 kcal/mol. This is much less than the energy of activation for the thermal trans–cis isomerization of the neutral compounds which is about 20 kcal/mol.[21,22]

McCleverty et al. has reported on the oxidative electrochemistry of ligand-substituted metal carbonyl complexes of group VI metals.[29,30] They observed that as the π-accepting ability of the ligand was reduced, the complexes were easier to oxidize (i.e., the oxidation potential became more cathodic). This result was consistent with molecular orbital calculations, IR spectral shifts of CO absorption, and charge-transfer spectra of π-complexes. Our observations are consistent with these conclusions. For example, in the Mo series the order of ease of oxidation is Imid > Benzimid > Triaz while the order of the π-accepting abilities of these ligands is just the opposite. The lower oxidation potentials of the trans complexes relative to the corresponding cis complexes is also consistent with this logic. The back-donation to the carbene ligands is expected to be reduced in the trans complexes relative to the cis complexes because of the shared metal d orbitals in the former but not in the latter case.

A detailed analysis of the relative rates of isomerization of the various complexes is not possible because the details of the mechanism are not known. A nondisassociative twist mechanism has been proposed for the isomerization of the neutral complexes.[22] It is likely that the isomerization of the cations is also a nondisassociative mechanism. If, for example, the mechanism did involve the dissassociation of a CO, it would seem that the vacant site would be rapidly captured by a solvent molecule such as AN with destruction of the original complex. As the cations have substantial lifetimes, it is most unlikely that a disassociative process is involved. Assuming a twist mechanism, the rates of isomerization of the trans cations can be correlated with the size of the central metal atom. The larger the metal atom, the smaller the steric repulsions in the transition state.

(Imidin)$_2$M(CO)$_4$ Complexes. All of the *cis*- and *trans*-dicarbene complexes discussed so far are characterized by having a six-electron monocyclic π-system. Accordingly, the carbene ligands are usually indicated as

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Table II. $E_{1/2}$ of the Anodic Wave[a] of *cis*-(Imidin)$_2$M(CO)$_4$ on DME

M	MC[c]	AN[b]	AC[b]	DMSO[b]
Mo	0.274	0.265	0.365	0.310
W	0.241	0.220	0.321	0.285

[a] All compounds were approximately 1 mM concentration with 0.25 TBAP. All measurements were carried out at 23 ± 2 °C. [b] Reference electrode is AgCl/Ag, saturated NaCl(aq). [c] Reference electrode is SCE.

having aromatic character. In order to determine the effect of the aromatic π-system on the unusual electrochemical behavior of these complexes, a series of cis and trans complexes were prepared in which the 4,5-bond was saturated. The electrochemical properties of the *cis*- and *trans*-(Imidin)$_2$M(CO)$_4$ (M = Cr, Mo, W) were determined in MC at a Pt working electrode. As is apparent from Table I, the redox properties of (Imidin)$_2$M(CO)$_4$ complexes are essentially identical with those of the corresponding (Imid)$_2$M(CO)$_4$ complexes. For example, *cis*-(Imidin)$_2$Mo(CO)$_4$ oxidizes at +0.343 V while *cis*-(imid)$_2$Mo(CO)$_4$ oxidizes at +0.335 V. The trans isomers are also very similar. The rate of isomerization from the trans cation to the cis cation is essentially identical when experimental error is taken into account. Similar results were observed for the Cr and W isomers.

These results suggest that the π-molecular orbitals are not weighed heavily in the HOMO nor do they strongly affect the isomerization. Recently, Hoffman and Öfele have reported a molecular orbital scheme for the *cis*-(Imid)$_2$M(CO)$_4$ complex.[26] In that scheme, the HOMO is composed of metal d orbitals and the ligand's σ orbitals with no mixing of the π orbitals. Our experimental results are totally consistent with the MO scheme.

There was, however, one very important difference that we did observe regarding the electrochemical characteristics. The use of a mercury working electrode instead of Pt leads to some very different results in the case of some of the *cis*-(Imidin)M(CO)$_4$ complexes.

We examined cis-(Imidin)$_2$M(CO)$_4$ (M = Cr, Mo, W) in a variety of solvents using a DME as the working electrode. The *cis*-(Imidin)$_2$Cr(CO)$_4$ complex yielded identical electrochemical results on a DME to those obtained with a platinum electrode. In marked contrast, the *cis*-(Imidin)$_2$Mo(CO)$_4$ and *cis*-(Imidin)W(CO)$_4$ complexes showed strong absorption as well as possible reaction with the mercury electrode. The observed $E_{1/2}$ values, Table II, were different from those on Pt. The anodic to cathodic peak separations were also highly sweep rate dependent. Coulometry in MC, AN, and AC indicated a one-electron process while in DMSO it was a two-electron process. Wave heights were consistent with these observations. Bulk electrolysis at a mercury electrode indicated the destruction of the original complexes. However, GC analysis of the solution did not indicate any free ligand. All the electrochemical data are consistent with the formation of (Imidin)$_2$Hg^{2+} complexes at the electrode surface. Similar (carbene)$_2$Hg^{2+} complexes are well-known.[31,32] However, all attempts to isolate the (Imidin)$_2$Hg^{2+} complexes failed. All further electrochemical studies on these complexes were carried out on a Pt working electrode to avoid this complication.

(Benzothiazolin)$_2$M(CO)$_4$ Complexes. In our attempts to design dicarbene complexes that had larger potential differences between the cis and trans isomers, we prepared the *trans*-(Benzothiazolin)$_2$M(CO)$_4$ (M = Mo, W) complexes. We examined their redox properties in a variety of solvents (MC, AN, DMSO) and on both Pt and mercury electrodes. For these complexes, identical electrochemical results were obtained on both Pt and mercury with no indications of any complex decomposition at the electrode surface. In marked contrast to all the other trans cations, no isomerization of the trans cations to cis cations could be detected. Also now for the first time, a second oxidative couple appeared very close to the first wave, in which the cation was oxidized to the dication.

Table III. Polarographic Half-Wave Potentials[b,c] of *trans*-(Benzothiazolin)$_2$M(CO)$_4$

M	origin of wave	MC	AN	DMSO
MO	[0] [+]	−0.155[a]	−0.173[a]	
	[+] [++]	+0.004[d]	−0.033[a]	
	[0] [++]			−0.104[e]
W	[0] [+]	−0.134[a]	−0.173[a]	
	[+] [++]	−0.050[c]	−0.033[a]	
	[0] [++]			−0.098[e]

[a] Reversible electrode processes. [b] All compounds were approximately 1 mM concentration with 0.25 TBAP. All measurements were carried out at 23 ± 2 °C. Potentials in volts. [c] Reference electrode is AgCl/Ag, saturated NaCl (aq). [d] Insoluble oxidation product. [e] Electrode reaction slightly irreversible (quasi-reversible).

The complexes were of limited solubility in MC. More importantly, serious adsorption effects complicated the electrochemical determinations in this solvent and limited its use.

Use of AN and DMSO avoided these problems. In AN, both the Mo and W trans complexes gave two separate, well-defined waves (Table III). Both waves were highly electrochemically and chemically reversible. Diffusion current heights as well as coulometry indicated an overall two-electron oxidation.

In DMSO, the two oxidation waves were nearly merged into a single two-electron wave. The fact that DMSO is a much stronger donor solvent probably accounts for the near merging of the second wave with the first wave.[33] It has been demonstrated in earlier work that a stronger donor solvent such as DMSO promotes a greater cathodic shift of the oxidation potential for a wave involving cation to dication formation than for a wave involving the formation of a cation.[34,35]

The marked difference in redox properties of the sulfur-containing complexes is most likely explained by the carbene ligand itself. All three complexes are much easier to oxidize than any of the other complexes mentioned. Also, they all have oxidation potentials that are very similar regardless of the metal. These facts, coupled with the know facile oxidation (i.e. very cathodic) of many sulfur-containing compounds, suggest that in this case the HOMO is primarily ligand in nature. Thus, the first wave represents the formation of a cation primarily localized in one benzothiaolin ring, and the second wave represents the oxidation of the second ligand. This oxidation would, accordingly, have little effect on the bond orders and bond lengths about the central metal atom. Thus, it is not expected to accelerate any isomerization to the cis isomers and would be relatively independent of the metal.

A Novel Photoelectric Cell. The oxidatively induced isomerization of a cation of lower redox potential to an

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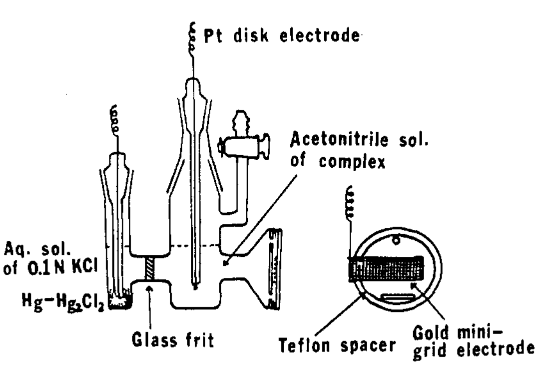

Figure 4. Thin-layer cell for photoelectric cell.

isomer with a higher redox potential represents an unusual situation. In the case of the complexes listed in Table I, the cis complexes have redox couples approximately 200 mV higher than the corresponding trans complexes. This fact, coupled with the fact that the neutral cis complexes can be photochemically converted into the thermodynamically less stable trans isomers, provides a unique combination of properties that can be utilized in the construction of a novel alternating current photoelectric cell.

It can be seen from Table I that the cis cations of the molybdenum and tungsten complexes have rather limited lifetimes and would appear to be of little value in any photoelectric cell; however, the chromium complexes are much more stable. Therefore, the principal complexes used in this study were the *cis*- and *trans*-(Triaz)$_2$Cr(CO)$_4$. The cyclic voltammogram of *trans*-(Triaz)$_2$Cr(CO)$_4$ in acetonitrile with a platinum disk electrode shows a wave at +0.17 V vs 0.1 NCE[36] and a small irreversible wave at −0.11 V. The wave at +0.17 V was reversible on the basis of peak-potential separation and peak-current ratio. However, the peak-current ratio of the wave at −0.11 V changed depending on the sweep rate and temperature. Bulk electrolysis of the trans complex at a potential slightly anodic of the first wave gave the cyclic voltammogram corresponding to the cis complex (+0.17 V). These observations are identical with the molybdenum and tungsten complexes and indicate that the trans cation is readily isomerizing to the cis cation. Cyclic voltametric studies indicated that the trans cation was more stable than the trans cations of either the Mo or W complexes. The rate constant for isomerization of the trans cation to the cis cation was determined by the cathodic–anodic peak current ratios and were 0.34 ($t_{1/2}$ = 2 s at 20 °C) and 0.015 s^{-1} ($t_{1/2}$ = 50 s at 0 °C). These rate constants are much smaller than those for the corresponding Mo and W complexes. Again, it is the large thermodynamic stability of the neutral cis over the neutral trans complex that makes the isomerization of the trans cation to the cis cation thermodynamically favorable.

The photoelectric cell (Figure 4) is composed of a thin-layer cell with a gold minigrid[37] electrode (10 × 14 mm^2) and a 0.10 mm thick Teflon tape spacer. The dicarbene complex was placed in this compartment. The counter electrode was a 0.1 NCE as its redox potential lies between those of (trans)/(trans)$^+$ and (cis)/(cis)$^+$.

The basic sequence of events upon closing this circuit is as follows: trans complex in the thin layer cell is oxidized to the cation along with reduction of Hg^{2+} at the counter electrode. The trans cation then isomerizes to the cis

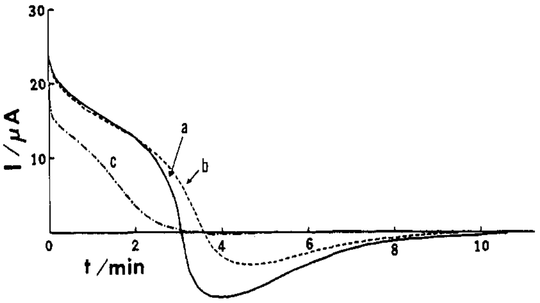

Figure 5. Current–time curve through 100-Ω resistor (15 mM *trans*-(Triaz)$_2$Cr(CO)$_4$ in 0.2 M TBAP acetonitrile): (a) first cycle, sample not irradiated; (b) after one current cycle followed by irradiation for 20 min with light below 360 nm; (c) after seven complete cycles.

cation which upon diffusing back to the elecrode is reduced to the neutral cis complex with oxidation of Hg to Hg^{2+} at the counter electrode. The circuit is now opened while the neutral cis is photolyzed to the neutral trans complex. The light source[38] is removed, and the above electrochemical sequence is again initiated by closing the circuit. Thus an alternating current is expected from operation of this cell.

The open circuit output voltage of a 15 mM *trans*-(Triaz)$_2$Cr(CO)$_4$ in 0.2 M TBAP/acetonitrile solution vs 0.1 NCE at 0 °C was 350–400 mV. This large output voltage is probably due to the small concentration of trans cation. Figure 5 shows the closed circuit current (passed through a 100-Ω resistor) at 0 °C. Irradiation was carried out with a mercury lamp with a filter to remove all light above 360 nm.[39,40] The photolysis times were 20 min. Up to six cycles could be obtained at 0 °C and three cycles at 20 °C. For each cycle, the ratio of I_c/I_a decreased and finally no reverse current could be observed. The I_a of the first cycle represented 22% (at 0 °C) and 8% (at 20 °C) of the total amount of theoretical current based on the initial trans complex in the thin-layer cell. The corresponding cathodic currents (I_c) on the first cycle were 13% (at 0 °C) and 4% (at 20 °C) of the initial concentration of trans complex.[41] These relatively small efficiencies are probably arising from homogeneous electron-exchange reactions in solution.

$$\text{trans} + (\text{cis})^+ \rightarrow (\text{trans})^+ + \text{cis}$$

$$(\text{trans})^+ \rightarrow (\text{cis})^+$$

The chemical binding of the complex to an electrode surface would eliminate the solution homogeneous electron-exchange short circuiting of the system and greatly increase the efficiency of the cell. No attempt was made to determine the quantum yield of the photoisomerization, and hence no overall efficiency for conversion of light energy to electrical energy could be made.

Conclusions

The electrochemically induced isomerization of a species of higher redox potential to a species of lower redox potential is fairly common. However, the reverse situation is extremely rare. In this paper, we reported a series of

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[36] Hg/Hg$_2$Cl$_2$/0.1 KCl aqueous EMF of 0.1 NCE is +97 (20 °C) and 79 mV (0 °C) vs SCE: Dobos, D. *Electrochemical Data*; Elsevier: Amsterdam, 1975; p 264.

[37] The 100 wires/inch gold minigrid was purchased from Buckbee Mears, St. Paul, MN.

[38] Hanovia, Type 679A36 450W; the lamp is enclosed in a water-cooled quartz jacket.

[39] The absorption spectrum of the cis complex in acetonitrile consists of two broad maxima at ~350 and 280 nm.

[40] A nickel–cobalt sulfate filter that transmits light in the region of 270–350 nm was used. Bowen, E. J. *J. Chem. Soc.* **1935**, 76.

[41] The volume of the cell was calibrated by electrochemical oxidation of a standard acetonitrile solution of ferrocene.

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trans-(carbene)$_2$M(CO)$_4$ complexes (M = Cr, Mo, W) which upon oxidation rapidly isomerized to the corresponding cis cations which have a higher oxidation potential of approximately 200 mV. The approximate rates of isomerization and activation energies were determined and are consistent with a nondisassociative twist mechanism. Utilizing the facts that the trans cations isomerize to cis cations with a higher redox couple and that the neutral cis complexes can be photochemically converted into the neutral trans cations, a simple AC photoelectric cell was designed. It was demonstrated that the carbene ligands do not need to contain an aromatic six-electron π-system to undergo this type of oxidatively induced isomerization.

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Registry No. *trans*-(benzothiazolin)$_2$Mo(CO)$_4$, 112021-83-7; *trans*-(benzothiazolin)$_2$W(CO)$_4$, 112021-84-8; *cis*-(Triaz)$_2$Cr(CO)$_4$, 61825-97-6; *cis*-(Triaz)$_2$Mo(CO)$_4$, 60971-03-1; *cis*-(Benazmid)$_2$Mo(CO)$_4$, 61046-06-8; *cis*-(Imid)$_2$Mo(CO)$_4$, 52082-57-2; *cis*-(Imid)$_2$W(CO)$_4$, 52194-73-7; *cis*-(Imidin)$_2$Cr(CO)$_4$, 41654-74-4; *cis*-(Imidin)$_2$Mo(CO)$_4$, 64161-93-9; *cis*-(Imidin)$_2$W(CO)$_4$, 64514-96-1; *trans*-(Triaz)$_2$Cr(CO)$_4$, 61729-86-0; *trans*-(Triaz)$_2$Mo(CO)$_4$, 61009-21-0; *trans*-(Benzimid)$_2$Mo(CO)$_4$, 60971-04-2; *trans*-(Imid)$_2$Mo(CO)$_4$, 52194-74-8; *trans*-(Imid)$_2$W(CO)$_4$, 52082-58-3; *trans*-(Imidin)$_2$Mo(CO)$_4$, 64161-94-0; Mo(CO)$_6$, 13939-06-5; W(CO)$_6$, 14040-11-0; bis(*N*-methylbenzothiazolinylidene), 2786-70-1.

Catalyst Design. The Activation of a Trinuclear Metal Cluster Complex by Metal Atom Substitution

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The trinuclear cluster complex Mo$_2$Ru(CO)$_7$(C$_5$H$_5$)$_2$(μ_3-S) (**1**) has been shown to produce the oligomerization of HC$_2$Ph. The reaction of **1** with HC$_2$Ph at 98 °C has yielded the products Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ_3-η^6-HCC(Ph)C(H)C(Ph)C(H)C(Ph)](μ_3-S) (**2**) in 15% yield and Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ-η^3-PhCC(H)CPh][μ_3-η^3-HCC(Ph)CH](μ_3-S) (**3**) in 11% yield. **2** and **3** were characterized by crystallographic methods. For **2**: space group $P2_1/c$, a = 10.899 (2) Å, b = 23.563 (5) Å, c = 14.562 (3) Å, β = 91.97 (2)°, Z = 4. The structure was solved by direct methods and was refined (3060 reflections) to the final value of the residuals R = 0.045 and R_w = 0.045. Compound **2** consists of a sulfur-bridged Mo$_2$Ru cluster that contains 1,3,5-triphenyldimetallahexatrienyl ligand bridging one face of the cluster. The hexatrienyl ligand was formed by the head-to-tail coupling of three HC$_2$Ph molecules. For **3**: space group $C2/c$, a = 35.86 (1) Å, b = 12.454 (6) Å, c = 14.622 (3) Å, β = 98.60 (2)°, Z = 8. The structure was solved by direct methods and was refined (1867 reflections) to the final values of the residuals R = 0.054 and R_w = 0.051. Compound **3** consists of a sulfur-bridged Mo$_2$Ru cluster that contains a triply bridging 2-phenyldimetallaallyl ligand and an edge-bridging 1,3-diphenyldimetallaallyl ligand. **3** was formed from **2** by the splitting of the hexatrienyl ligand into two three carbon groupings. Compound **3** was obtained from **2** in 57% yield by heating to 125 °C, but this also yielded Mo$_2$Ru(CO)$_2$(C$_5$H$_5$)$_2$[μ-η^3-HCCPhCPh][μ_3-η^3-HCCPhCH](μ_3-S) (**4**), an isomer of **3** in 38% yield. **4** was characterized by crystallographic methods: space group $P\bar{1}$, a = 13.545 (2) Å, b = 15.869 (3) Å, c = 9.746 (2) Å, α = 90.37 (2)°, β = 104.11 (1)°, γ = 82.22 (1)°, Z = 2. The structure was solved by the heavy-atom method and refined (2717 reflections) to the final values of the residuals R = 0.044 and R_w = 0.042. **4** differs from **3** only in the structure of the edge-bridging dimetallaallyl group that has phenyl substituents in the 1- and 2-positions whereas **3** has the phenyl substituents in the 1- and 3-positions. **4** was obtained directly from **3**, 24% yield, by heating to 125 °C for 3 h. The compound Mo$_2$Ru(CO)$_5$(C$_5$H$_5$)$_2$[μ-η^4-PhCC(H)CC(H)Ph](μ_3-S) (**5**) was obtained (11% yield) from the reaction of **1** with HC$_2$Ph in the presence of Me$_3$NO. The structure of **5** was determined crystallographically: space group $P\bar{1}$, a = 12.906 (3) Å, b = 13.916 (4) Å, c = 9.708 (4) Å, α = 91.54 (3)°, β = 100.82 (2)°, γ = 95.48 (2)°, Z = 2. The structure was solved by the heavy-atom method and was refined (2522 reflections) to the final values of the residuals R = 0.050 and R_w = 0.054. **5** consists of an open Mo$_2$Ru cluster bridged by a sulfido ligand and a Ph(H)CCC(H)CPh group that is π-bonded to one metal atom and σ-bonded a second metal atom. This ligand appears to have been formed by a head-to-head coupling of two HC$_2$Ph molecules and was accompanied by a hydrogen atom shift. **5** does not appear to be an intermediate in the formation of **2**, **3**, or **4**. The reactivity of **1** is compared with that of Ru$_3$(CO)$_9$(μ_3-HC$_2$Ph)(μ_3-S) and Mo$_2$(CO)$_4$(C$_5$H$_5$)$_2$.

Introduction

The ability to vary the ligands has been one of the most important methods of modifying and controlling the reactivity and catalytic properties of metal complexes.[1-3] However, in polynuclear metal complexes, one has an additional variable: variation of the relative identities of the metal atoms, themselves. It is known that certain multimetallic heterogeneous catalysts exhibit catalytic behavior that exceeds that of their homonuclear components.[4]

Recently, there has been considerable interest in the synthesis and study of heteronuclear metal cluster com-

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