(13) We recognize that **6** is the only *formal* d^0 transition metal carbonyl complex thus far reported. It is unfortunate that due to experimental difficulties we have not yet been able to obtain its infrared spectrum.

(14) **9** is isolated at room temperature from toluene/pentane as pale yellow microcrystals. Calculated for $C_{21}H_{32}OZr$: C, 64.39; H, 8.24; Zr, 23.29. Found: C, 64.09; H, 8.40; Zr, 23.30.

(15) While our physical characterization (^{1}H and ^{13}C NMR, ir) of **9** is completely in accord with this structure, we are also investigating its structure by x-ray diffraction methods.

(16) The ten line AA′XX′ pattern centered at δ 6.55 was analyzed as described by Emsley, Feeney, and Sutcliffe, "High Resolution Magnetic Resonance Spectroscopy", Vol. 1, Pergamon Press, Oxford, 1965, p 396. $^1J_{^{13}C-H}$ = 176.5 Hz, $^1J_{^{13}C-^{13}C}$ = 99 Hz, $^2J_{^{13}C-H}$ = 7.5 Hz, $^3J_{H-H}$ = 9 Hz. $\{^1H\}$ ^{13}C NMR, s, 137.4 δ (Me_4Si). Non-$\{^1H\}$ ^{13}C NMR spectrum shows the same AA′XX′ pattern.

(17) Calculated for $C_{21}H_{31}OIZr$: C, 48.73; H, 6.04; I, 24.52; Zr, 17.62. Found: C, 49.03; H, 6.09; I, 24.20; Zr, 17.61. Ir (Nujol mull) ν(C–O) 1195 (vs); $\nu(^{13}C-O)$ 1175 (vs). NMR (benzene-d_6) $[C_5(CH_3)_5]$, s, δ 1.94 (30 H); (–OCH═CHO–) s, δ 6.83 (1H) ^{1}H NMR for $\{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(O^{13}CH{=}^{13}CHO)$ (chloroform-d_1): s, δ 2.00; ten line AA′XX′ pattern centered at δ 6.38 with $^1J_{^{13}C-H}$ = 180.3 Hz, $^1J_{^{13}C-^{13}C}$ = 100.3 Hz, $^2J_{^{13}C-H}$ = 6.7 Hz, $^3J_{H-H}$ = 10.4 Hz.

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Electrochemical Oxidation of Dicarbene Metal Carbonyl Complexes. Isomerization via an Electrochemical Reaction with No Net Current Flow[1]

Sir:

Fischer's pioneering work on carbene metal complexes has developed considerable interest in this new class of metal complexes.[2-4] Recently, the preparation of *cis*-dicarbenetetracarbonylmetal complexes has been reported by Öfele et al.[5,6] It has further been shown, that these compounds undergo photoisomerization forming the thermodynamically less stable corresponding trans-dicarbene complexes which are reconverted thermally to the original cis isomers.[7,8]

In this manuscript, we would like to report some unusual observations regarding the electrochemical oxidation of some dicarbene molybdenum and tungsten complexes. The ligands studied included 2,4-dimethyl-1,2,4-triazolin-3-ylidene (Triaz), 1,3-dimethyl-4-imidazolin-2-ylidene (Imid), and 1,3-dimethylbenzimidazolin-2-ylidene (Benzimid) (Figure 1). Both the corresponding cis and trans isomers were examined. The electrochemical oxidations were carried out in degassed methylene chloride with tetrabutylammonium perchlorate (TBAP) as electrolyte. The working electrode was a platinum disk which was polished before each use.

Cyclic voltammetry of the cis compounds yielded only a single electrochemical wave from +2.0 to −2.7 V vs. SCE.[9] This single wave was an oxidative wave in the region of +0.3 to +0.5 V for all the cis compounds. The wave is reversible with about a 60-mV separation of the anodic and cathodic peaks. Also, the ratio of the anodic and cathodic currents are unity at sweep rates of 0.01-1.0 V/s. Coulometry of this wave at −5 °C showed that this was a one-electron oxidation. Similar results were obtained for the other cis compounds.

Remarkably, the trans complexes yielded essentially the same cyclic voltammograms as the cis complexes showing only a single reversible wave at identically the same potential. This wave was accompanied by a small irreversible wave at about 0.2 V more negative potential than the main wave. The magnitude of this small wave changed remarkably depending on the particular complex, sweep rate, and temperature of the electrochemical cell. In the case of *trans*-(Imid)$_2$W(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)$_2$Mo(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 wave. At low temperatures (−11 °C), this trans complex showed two well-defined reversible waves (Figure 3a).

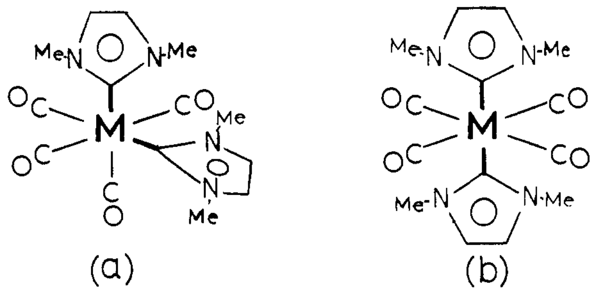

Figure 1. (a) *cis*- and (b) *trans*-(Imid)$_2$M(CO)$_4$ (-Me:-CH$_3$).

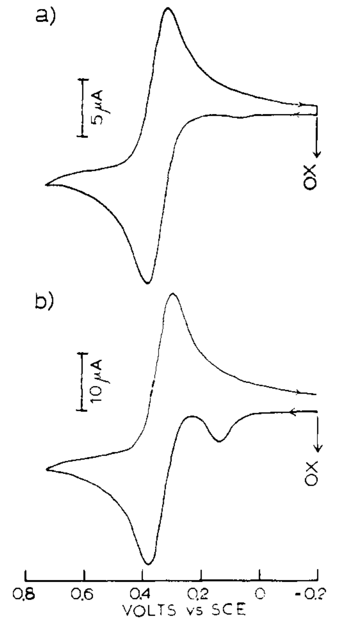

Figure 2. Cyclic voltammogram of *trans*-(Imid)$_2$W(CO)$_4$. The solution contained 5.2 mM *trans*-(Imid)$_2$W(CO)$_4$ and 0.25 M TBAP in methylene chloride. The scan rates are (a) 0.2 V/s at 22 °C and (b) 1.0 V/s at −2 °C.

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.

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. The ir spectrum of the solution after bulk electrolysis was identical with that of the cis complex. Bulk electrolysis was now carried out at a potential corresponding to the first wave of the neutral cis complex 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.

From these observations, it is apparent that the trans com-

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

Compounds	$E_{1/2}{}^r$ (V vs. SCE) Cis	Trans	$\Delta E_{1/2}{}^r$ (cis–trans)	k_1 (s^{-1}) (22 °C)	(t °C)	($E_a{}^c$ (kcal/mol)
(Triaz)$_2$Mo(CO)$_4$	0.528	0.36	0.17	2.0	0.2 (±0.02)	5.5
	(±0.005)	(±0.02)		(±0.2)	(−11 °C)	(±1.0)
(Benzimid)$_2$Mo(CO)$_4$	0.477	0.24	0.24	7	0.6 (±0.2)	5.1
	(±0.005)	((±0.02)		(±2)	(−12 °C)	(±1.0)
(Imid)$_2$Mo(CO)$_4$	0.335	0.11	0.23	14	1.4 (±0.3)	5.1
	(±0.005)	(±0.02)		(±3)	(−16 °C)	(±1.0)
(Imid)$_2$W(CO)$_4$	0.337	0.14	0.20	400	90 (±20)	5.1
	(±0.005)	(±0.03)		(±200)	(−2 °C)	(±2.0)

[a] $E_{1/2}$: reversible half-wave potential for R-e$^-$ → R$^+$ vs. SCE in the system of 0.3 M TBAP of methylene chloride solution. The values are approximate for the trans compounds due to kinetic complications. [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.

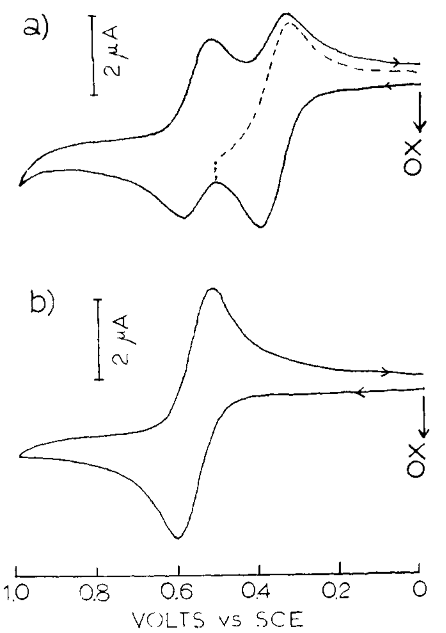

Figure 3. Cyclic voltammogram of *trans*-(Triaz)$_2$Mo(CO)$_4$. The solution contained 1.7 mM *trans*-(Triaz)$_2$Mo(CO)$_4$ and 0.25 M TBAP in methylene chloride. The runs were made with the scan rate 0.2 V/s at −10 °C: (a) before and (b) after bulk electrolysis at 0.40 V vs. SCE.

plexes 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 which is common to both cis and trans complexes corresponds to the oxidation of the cis complex to 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[5] 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 $\Delta G° \cong -0.35$ eV + (+0.52 − 0.36)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.

Scheme I. Approximate Free Energy Diagram for (Triaz)$_2$Mo(CO)$_4$ Complex

$$\begin{tikzcd}
(\text{cis}) \arrow[r, "\text{oxidation}", "+0.53\text{ eV} + \text{constant}"'] & (\text{cis})^+ \\
(\text{trans}) \arrow[u, "{\Delta G \simeq -0.35\text{ eV (in solid state)}}"] \arrow[r, "+0.36\text{ eV} + \text{constant}", "\text{oxidation}"'] & (\text{trans})^+ \arrow[u, "\Delta G \simeq -0.18\text{ eV}"']
\end{tikzcd}$$

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 are summarized below. The

$$(\text{trans}) \xrightarrow{-e^-} (\text{trans})^+ \xrightarrow{\text{rapid}} (\text{cis})^+ \xrightarrow[+e^-]{} (\text{cis})$$

trans complex is oxidized to the trans cation which 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 for 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[10] involves the determination of the sweep rate at which the cathodic wave height becomes half of that in the absence of the isomerization using the sweep rates from 0.01 to 50 V/s.[11] The energy of activation for the isomerization process was found to be approximately 5 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.[8]

We are continuing our studies on these and other dicarbene complexes. The fate of the cis cations along with the mechanism of the isomerization (a twist mechanism or a dissociative mechanism) will be reported in the near future. One potentially exciting possibility is use of these complexes in the development of a photoelectric cell. Thus the fact that the trans cation is isomerized into the cis cation which is a species of higher potential coupled with the fact that the cis isomer can be photochemically converted into the trans isomer allows several possibilities for design of photoelectric cells. We will report on some of these designs in the near future.

Acknowledgment. Financial support of this investigation by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) This is the fourth communication in this series; studies on transition metal complexes with cyclic carbene ligands. For last paper in series, see ref 5.

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Polymer Supported Reagents. Chromic Acid on Anion Exchange Resins. A Simple and Practical Oxidation of Alcohols to Aldehydes and Ketones

Sir:

Although many useful procedures for oxidation of alcohols to the corresponding carbonyl compounds have been reported,[1] the general problem cannot be considered definitely settled. The chief drawbacks of these procedures are the relative difficulty in the preparation of the reagents and in the working-up of the reaction mixture.

It has been found recently that reagents supported on insoluble polymers are particularly convenient for solving many problems in organic synthesis.[2] The polymeric support provides a particular reaction environment capable of enhancing the reactivity of many reagents, and moreover, turns out to be very profitable in the working-up, which becomes reduced to a mere filtration. Thus, anion exchange resins are, for example, useful in C-alkylation of phenols,[3a] O-alkylation of carboxylate anions,[3b] and alkyl or aralkyl fluorides preparation.[3c] A polymeric thioanisole has been reported[4] to be an effective coreactant for the sulfide-based Corey oxidation of alcohols.[5]

Although this oxidation technique has been demonstrated to be useful in dealing with highly sensitive compounds, specifically for certain prostaglandin intermediates,[4] the whole procedure seems to be somewhat laborious and requires ad hoc prepared polymers.

We have now found that it is possible to obtain in a simple way a polymer supported reagent very useful for the oxidation of alcohols utilizing, without modification, commercial anion exchange resins. To prepare the reagent, 35 g of the chloride form of Amberlyst A-26, a macroreticular anion exchange resin containing quaternary ammonium groups,[6] was added under stirring into a solution of 15 g of chromium trioxide in 100 ml of water.[7] Chloride ions were readily displaced and a CrO_4H^- form of the resin was quantitatively obtained in 30 min. The resin was successively rinsed with water, acetone, and ether and finally dried in vacuo at 50 °C for 5 h.

The capacity of the resin was determined by stirring overnight 0.5 g of the resin with 10 ml of 2 N aqueous potassium hydroxide, filtering off and titrating iodometrically the obtained chromate solution. The determined average capacity of the dried resin was 3.8 mmol CrO_3/g of resin. The resin so obtained did not noticeably lose activity neither on storing in air at room temperature for several weeks nor on refluxing for 5 h in benzene or hexane.

Our polymeric reagent is remarkably effective in oxidizing primary and secondary alcohols to aldehydes and ketones in high yields (Table I). The reaction is simply performed by a

Table I. Oxidation of Alcohols to Aldehydes and Ketones[a]

Alcohol	Ratio mmol substrate/g resin[j]	Reaction time, h	Yield, %
1-Octanol	1/3.5	3	93,[b,d] 94[b,e]
	1/3.5	9	89[e,k]
	1/1.2	9	97[b,e]
1-Dodecanol	1/3.5	3	83,[b,d] 87[b,e]
	1/1.2	9	94[b,e]
1-Tetradecanol	1/3.5	3	93[b,d]
Benzyl alcohol	1/3.5	1	98,[b,g] 96[b,e]
	1/0.75	2	98[b,e]
Cinnamyl alcohol	1/3.5	1	95,[b,g] 96[b,f]
	1/0.75	2	92[b,g]
3-Methyl-2-buten-1-ol	1/3.5	1	91[b,d]
3-Methyl-3-buten-1-ol	1/3.5	3	93[b,d,h]
2-Hendecanol	1/3.5	3	73[b,d]
Cyclohexanol	1/3.5	3	77[b,d]
Geraniol	1/3.5	1	90,[b,d,i] 92[b,e,i]
	1/0.75	2	90[b,e,i]
9-Fluorenol	1/0.75	1	97[c,e]
Menthol	1/3.5	3	86,[b,d] 93[b,e]
	1/1.2	9	91[b,e]
Diphenylcarbinol	1/3.5	1	77[c,e]
2-(Hydroxymethyl)naphthalene	1/3.5	1	90[c,e]
4-Benzensulfonyl-3-methyl-2-buten-1-ol	1/0.75	1	98[c,f]

[a] The reactions were carried out with 2 mmol of alcohol in 15 ml of refluxing solvent. [b] Yield determined by GLC analysis. Column ⅛ in. × 6 ft 20% DEGS. Column temperature, program from 50 to 200 °C at 10 °C/min; injection port, 280 °C; detector, 280 °C; carrier gas, N_2, 1.0 Kg/cm^2. [c] Yield determined on pure isolated products. [d] In hexane. [e] In benzene. [f] In $CHCl_3$. [g] In THF. [h] A mixture of 3-methyl-2-buten-1-al (48%) and 3-methyl-3-buten-1-al (52%) was obtained. [i] *Z–E* isomerization occurs and one obtains a mixture of geranial and neral. [j] The determined average capacity of the dried resin was 3.8 mmol CrO_3/g resin. [k] Yield refering to pure distilled product in a run of 100 mmol of alcohol in 250 ml of refluxing solvent.