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Preliminary communication

THE ELECTROCHEMICAL REDUCTION OF ARYLMETHOXYCARBENE COMPLEXES OF CHROMIUM, MOLYBDENUM AND TUNGSTEN

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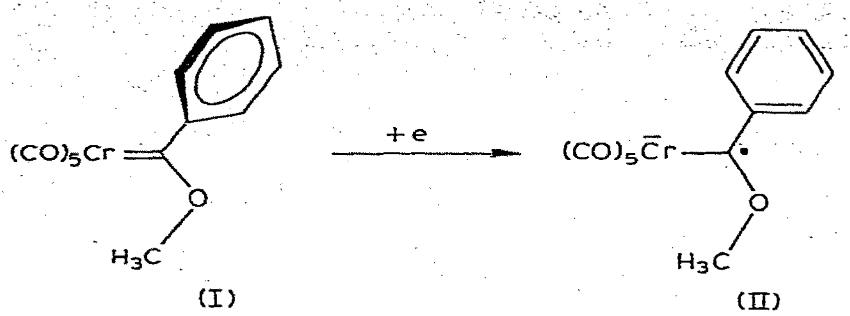
Summary

The reduction of a series of (arylmethoxycarbene)pentacarbonyltunsten(0) compounds was studied by cyclic voltammetry and a dependence of $E_{1/2}$ of the quasi-reversible voltammogram on the conformation of the aryl ring of the carbene complex was observed.

Transition metal carbene complexes have been extensively studied in recent years primarily due to their importance in catalysis [1] and their use in organic synthesis [2]. Carbene complexes of Cr, Mo, and W are polarized $^{\delta-}M{=}C^{\delta+}$ as suggested by ^{13}C NMR studies [3] and their reactions with nucleophiles [4]. MO calculations showing that the LUMO is localized on the carbene ligand provide a rationalization for attack of nucleophiles at the carbene carbon atom [5]. Recent work has shown that transition metal carbene complexes readily undergo reduction by one electron reducing agents to give radical anions stable below $-50°$ [6]. ESR experiments indicate that the radical anion, II, generated by addition of an electron to $(CO)_5CrC(OCH_3)C_6H_5$ (I), is a carbon centered radical with the odd electron localized on the carbene ligand. The metal apparently has only a small effect on the electron density distribution as the ESR spectrum of II and that of the α-methoxybenzyl radical show similar ESR splittings.

An interesting aspect of the reduction process is the change in the conformation of the phenyl ring upon reduction. The phenyl ring of the carbene complex I lies in a plane perpendicular to the Cr—C(carbene)—O plane as shown by X-ray crystallography [7]. However the radical anion II shows an unsymmetrical phenyl ring on the ESR time scale [6]. This implies a change in geometry upon reduction where the phenyl ring is brought into conjugation with the *p*-orbital of the carbene carbon atom. Such a scheme receives theoretical support from MO calculations where the orientation of the phenyl ring is chosen either to be coplanar or perpendicular to the Cr—C(carbene)—O plane (Fig. 1) [8]. The HOMO's for the two cases are nearly equal in energy



(perpendicular 0.03 eV more stable than planar) while the LUMO for the planar case is 2.53 eV more stable than the LUMO for the perpendicular case. The small energy difference between the HOMO's implies a low barrier to rotation at the phenyl ring in I. The large energy difference in the LUMO's of I implies that the rotation of the phenyl ring becomes frozen in the planar conformation when I is reduced to give II. We have attempted to test this scheme by preparing model compounds in which the phenyl ring is sterically constrained and observing the effects on their reduction potentials by cyclic voltammetry.

The cyclic voltammogram of I (Pt working electrode) at a scan rate of 1 V/sec shows a one electron reduction peak at −1.55 V with a small return peak at −1.13 V. A return peak of theoretical height is not observed unless faster scan rates ($\geq$ 20 V/sec) are used indicating that a following chemical reaction is occurring [9]. Since the separation between the peaks (ΔE_p) increases with increasing scan rate, the system appears to be quasi-reversible ($\Delta E_p > 422$ mV at 1 V/s compared with 58 mV expected for reversible single electron transfer) at scan rates fast enough (1—100 V/sec) to observe a return peak [9,10]. Since $(CO)_5WC(OCH_3)C_6H_5$ (V) shows a full return peak at slower scan rates ($\geq$5 V/sec) and smaller ΔE_p's (163 mV at 1 V/sec, Pt working electrode) tungsten carbene complexes were chosen for further study.

For this study model compounds were needed in which the phenyl ring is constrained to either the planar or perpendicular conformation. Models show

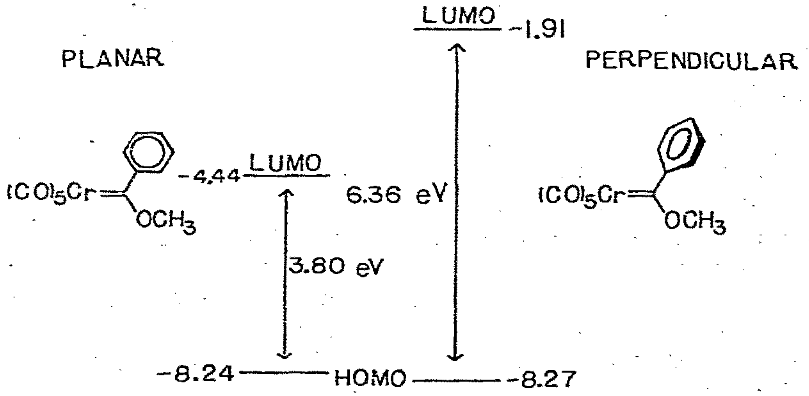


Fig.1.

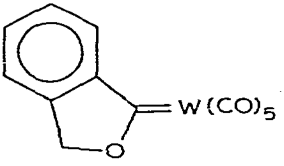
TABLE 1

CYCLIC VOLTAMMOGRAMS OF Cr, Mo AND W CARBENE COMPLEXES[a,b]

	$E_{1/2}$(Pt)[c] (V)	ΔE_p(Pt)[d] (mV)	$E_{1/2}$(Au)[c] (V)	ΔE_p(Au)[d] (mV)
$(CO)_5Cr{=}C(OCH_3)C_6H_5$ (I)	—1.34	422	—1.34	173
$(CO)_5Cr{=}C(OCH_3)(C_6H_4\text{-}p\text{-}CH_3)$ (III)	—1.37	444	—1.37	169
$(CO)_5W{=}C(\overline{O)(C_6H_4\text{-}o\text{-}C}H_2)$ (IV)	—1.31	84	—1.31	68
$(CO)_5W{=}C(OCH_3)C_6H_5$ (V)	—1.25	163	—1.25	84
$(CO)_5W{=}C(OCH_3)(C_6H_4\text{-}p\text{-}CH_3)$ (VI)	—1.30	166	—1.29	77
$(CO)_5W{=}C(OCH_3)(C_6H_4\text{-}o\text{-}CH_3)$ (VII)	—1.48	320	—1.47	123
$(CO)_5W{=}C(OCH_3)(C_5H_4\text{-}o\text{-}CH_2OCH_3)$ (VIII)	—1.45	419	—1.44	149
$(CO)_5W{=}C(OCH_3)[C_6H_2\text{-}2,4,6\text{-}(CH_3)_3]$ (IX)	—1.60	559	—1.61	166
$(CO)_5Mo{=}C(OCH_3)(C_6H_4\text{-}p\text{-}CH_3)$ (X)	—1.35	217	—1.34	98

[a] All CV's were run with 1—1.5 × 10^{-3} *M* carbene complex in CH_3CN with 0.1 *M* tetrabutylammonium perchlorate supporting electrolyte at 19 ± 2°C using either a gold or platinum working electrode. Electrochemical instrumentation was based on a PAR 173 potentiostat and PAR 175 programmer. Positive feedback iR compensation was employed. [b] I, III, V—VII, IX and X were prepared according to standard procedures by the addition of the appropriate ArLi reagent to $M(CO)_6$ (M = Cr, Mo and W) in ether to give the acyl anion followed by alkylation with either CH_3OSO_2F or $(CH_3)_3OBF_4$. Addition of $LiC_6H_4\text{-}o\text{-}CH_2OLi$ to $W(CO)_6$ in ether to give the acyl anion followed by (a) aqueous acid workup gave IV or (b) alkylation with CH_3OSO_2F gave VIII. [c] $E_{1/2}$ vs. SCE. $E_{1/2}$ was taken as $(E_p^{ox} + E_p^{red})/2$ for at least 2 scans at each of 5 scan rates (1, 5, 20, 50, and 100 V/sec). The standard deviation of $E_{1/2}$ varied from 2 to 13 mV for different compounds. [d] Average separation between reduction and reoxidation peaks at a scan rate of 1 V/sec for at least 2 runs. ΔE_p shows large variation depending on electrode condition, necessitating the use of a freshly polished electrode before each scan.

that the phenyl ring of the cyclic carbene complex IV (Table 1) is rigidly constrained to a planar conformation by the five-membered ring. Models also



(IV)

show that placing *ortho* alkyl substituents on the phenyl ring (VII—IX) should increase the preference for the perpendicular conformation by making the planar conformation sterically crowded*. The cyclic voltammograms of these compounds indicate that the $E_{1/2}$'s show a dependence on the constraints placed on the conformation of the phenyl ring. The compounds with *ortho* substituents and a sterically crowded planar conformation (VII—IX) have more negative $E_{1/2}$'s than those compounds with an uncrowded planar conformation (IV—VI). The change in $E_{1/2}$ when adding alkyl substituents clearly cannot be explained by inductive substituent effects alone as can be seen by comparing the *para* methyl compound VI ($E_{1/2} = -1.30$ V) and the *ortho* methyl compound VII ($E_{1/2} - 1.48$ V) which should have similar inductive substituent effects [11]. The $E_{1/2}$ of the more severely crowded 2,4,6-trimethyl-

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*It is unclear from models whether the major steric interaction is due to interaction of the *ortho* substituent with the metal carbonyls or with the methoxy attached to the carbene carbon atom.

phenyl carbene complex IX appears at even a more negative potential, −1.60 We suggest that the reduction of the arylmethoxy carbene complexes is accompanied by a change in the conformation of the aryl ring from a perpendicular to a coplanar geometry relative to the M—C(carbene)—O plane.

Another interesting feature of these reductions is that the ΔE_p's tend to increase as the $E_{1/2}$'s become more negative. For the tungsten carbene complexes, the cyclic carbene complex IV in which the phenyl ring is constrained to a planar conformation has the smallest ΔE_p (84 mV, 1 V/sec scan rate, Pt working electrode) while the sterically crowded 2,4,6-trimethylphenyl carben complex IX has the largest ΔE_p (559 mV, 1 V/sec scan rate, Pt working electrode). The increase in ΔE_p as the planar conformation of the phenyl ring becomes more crowded indicates a corresponding decrease in the heterogeneous electron transfer rate constant. The ΔE_p's also depend upon the working electrode, Pt giving larger ΔE_p's than Au. The data presented suggests the possibility of an internal reorganization in the carbene complex (change in the conformation of the phenyl ring) giving rise to a slow electron transfer process*. These transition metal carbene complexes appear to be good models for quasi-reversible electron transfer at solid electrodes which is currently being investigated.

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*Considerable controversy has arisen in recent years over claims of slow electron transfer being due to conformational changes [12].