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(17) Q was calculated from the expression, $Q = (2.52 \times 10^{-3})d^3 \exp[-(Z_1 Z_2 e^2/dD_S kT)]$[5,18] using $Z_1 = 1$, $Z_2 = 2$, and $d = 11.4$ Å.
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(20) Reference 5, chapter 4.
(21) On sabbatical leave at the University of Sydney.

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Stoichiometric Hydrogen Reduction of Carbon Monoxide to Methanol Promoted by Derivatives of Bis(pentamethylcyclopentadienyl)zirconium

Sir:

The lack of a homogeneous analogue of methanol synthesis, methanation, or Fischer-Trospch synthesis of hydrocarbons from CO and H_2 is a conspicuous difference between heterogeneous and homogeneous catalysis. Recently it has been suggested[1] that, since no well-established precedent exists either for the formation of a metal-formyl complex from a metal carbonyl hydride via migratory insertion[2] or for the conversion of a metal-formyl species to CH_3OH, metal clusters may be required to achieve the H_2 reduction of CO. Indeed, $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ were found to catalyze the dihydrogen reduction of carbon monoxide to methane at 140 °C and ~2 atm, although rates were rather low.

We recently observed reduction of CO in moderate yields when $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ is treated with HCl.[3] Further studies revealed that mononuclear carbonyl and hydride complexes of bis(pentamethylcyclopentadienyl)zirconium are capable of promoting the stoichiometric H_2 reduction of CO to methoxide under very mild conditions. Herein we report the results of those studies.

Treatment of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ (**1**)[3-5] with carbon monoxide in toluene at 25 °C leads to the absorption of CO (3.95 mol/mol of **1**), the evolution of N_2 (2.84 mol/mol of **1**), and the purple-brown crystalline complex $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ (**2**).[6] **2** reacts with H_2 (~1.5 atm) in toluene to yield $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$ (**3**) when photolyzed (366 nm) at room temperature or when heated to 110 °C. H_2 (2.10 mol/mol of **2**) is absorbed and CO (0.984 mol/mol of **2**) is evolved during the reaction. (equation 1).

$$(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2 + 2H_2 \xrightarrow[\text{or } 110\ ^\circ\text{C}]{h\nu} (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + CO \quad (1)$$

3 is isolated nearly quantitatively as white crystals upon removal of toluene but may be further purified by sublimation at 130 °C (10^{-3} Torr). Analytical, molecular weight, infrared, and NMR data[7] for **3** are in accord with a monomeric pseudotetrahedral structure analogous to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$. Hydrolysis of **3** with aqueous HCl leads to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$ and to H_2 (0.74 mol/mol of **3**), and CH_3OH[8] (0.78 mol/mol of **3**), slightly lower yields than those expected according to equation 2:

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + 2HCl \rightarrow (\eta^5\text{-}c_5Me_5)_2ZrCl_2 + H_2 + CH_3OH \quad (2)$$

Generation of the reactive, coordinatively unsaturated species $(\eta^5\text{-}C_5Me_5)_2Zr(CO)$ in the thermal or photolytic reaction of **2** with H_2 is supported by experiments with $\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2$ (**4**).[3] Treatment of **4** with H_2 (~1 atm) at room temperature leads predominantly[9] to **3** with the absorption of H_2 (3.53 mol/mol of **4**) and evolution of N_2 (1.00 mol/mol of **4**), eq 3.

$$\{(\eta^5\text{-}C_5Me_5)_2Zr(CO)\}_2N_2 + 4H_2 \rightarrow 2(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) + N_2 \quad (3)$$

It occurred to us that a plausible step in the reaction sequence would involve oxidative addition of H_2 to $(\eta^5\text{-}C_5Me_5)_2Zr(CO)$ generating the intermediate $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$, and furthermore that this complex might be prepared by an alternate route. Treatment of **1** with H_2 in toluene at room temperature affords $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ (**5**) quantitatively according to eq 4.

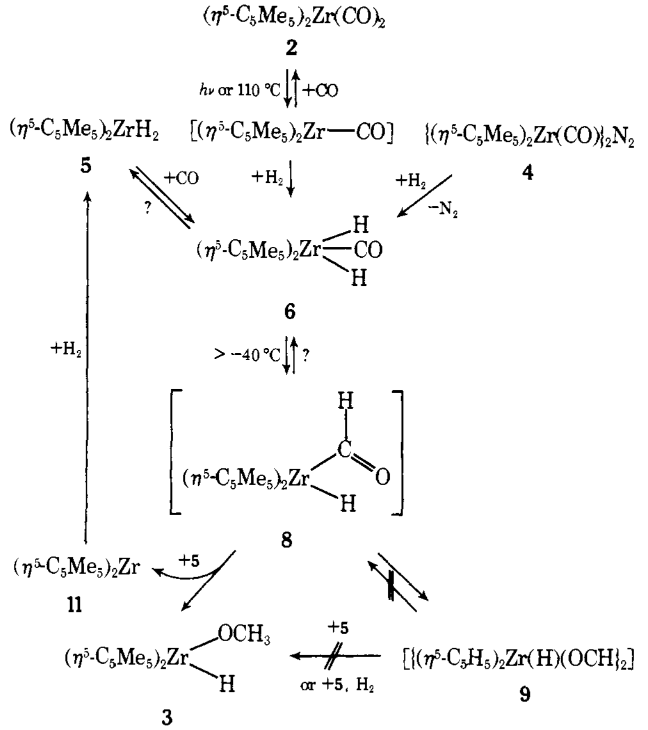
$$\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2 + 2H_2 \rightarrow 2(\eta^5\text{-}C_5Me_5)_2ZrH_2 + 3N_2 \quad (4)$$

In contrast to polymeric $\{(\eta^5\text{-}C_5H_5)_2ZrH_2\}_x$,[10,11] **5** is very soluble in hydrocarbons and ethers. Analytical, molecular weight, infrared, and NMR data[12] are indicative of a monomeric structure completely analogous to $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$.

5 absorbs CO (0.97 mol/mol of **5**) in toluene at −80 °C to generate the carbonyl hydride $(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO)$ (**6**).[13] Although **6** is not sufficiently stable for its isolation (see below), it has been partially characterized in solution at low temperature. Thus **6** reacts with HCl at −80 °C to yield $(\eta^5\text{-}C_5Me_5)_2ZrCl_2$, H_2 (1.78 mol/mol of **6**), and CO (0.85 mol/mol of **6**), equation 5.

$$(\eta^5\text{-}C_5Me_5)_2Zr(H)_2(CO) + 2HCl \rightarrow (\eta^5\text{-}C_5Me_5)_2ZrCl_2 + 2H_2 + CO \quad (5)$$

Scheme I



Its NMR spectrum at −64 °C (toluene-d_8) consists of a singlet at δ 1.84 due to the methyl hydrogens of the two equivalent (η^5-C_5Me_5) rings and a singlet at δ 1.07 attributable to the two equivalent hydride ligands. The spectrum of **6**-(^{13}CO) exhibits the same singlet at δ 1.84 but the hydride resonance is now the expected doublet ($^2J_{^1H-^{13}C}$ = 25.1 Hz). The unstable complex (η^5-$C_5Me_5)_2Zr(H)_2(PF_3)$ (**7**), prepared similarly, exhibits a ^1H NMR spectrum at −50 °C (toluene-d_8) consisting of a singlet at δ 1.77 due to the methyl hydrogens of the (η^5-C_5Me_5) rings and a doublet of quartets centered at δ 0.55 attributable to the two equivalent hydride ligands ($^2J_{^1H-^{31}P}$ = 108 Hz; $^3J_{^1H-^{19}F}$ = 21.5 Hz). Based on these data the structures of **6** and **7** appear to be similar to (η^5-$C_5H_5)_2TaH_3$ with CO and PF_3 occupying the central equatorial positions mutually cis to both hydride ligands.

When solutions of **6** are warmed above ca. −50 °C, the appearance of a new set of ^1H NMR signals consisting of a (η^5-C_5Me_5) resonance at δ 1.94 (30 H), a singlet at δ 5.73 (1 H), and a singlet at δ 6.55 (1 H) accompanies the disappearance of the spectrum for **6**. Independent experiments indicate that no H_2 or CO evolution is associated with the conversion of **6** to this new compound (**9**), so that both must have the same empirical formula.[14] While our initial interpretation of these NMR data was that **9** was the formyl hydride species **8**, further experiments indicated that it is rather the unusual enedioxy bridged dimer tentatively assigned the structure shown below.[15] This structure is supported by its infrared spectrum

$$(\eta^5\text{-}C_5Me_5)_2\underset{\displaystyle H}{Zr}OCH{=}CHO\underset{\displaystyle H}{Zr}(\eta^5\text{-}C_5Me_5)_2$$

9

(Nujol mull) which exhibits bands attributable to ν(Zr–H) at 1580 cm^{-1} (ν(Zr–D) at 1130 cm^{-1}) and ν(C–O) at 1205 cm^{-1} (ν(^{13}C–O) at 1180 cm^{-1}), and by ^1H and ^{13}C NMR data for $\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(O^{13}C(H){=}^{13}C(H)O)$, prepared from **5** and ^{13}CO: a singlet at δ 1.94 (30 H) due to the (η^5-C_5Me_5) ring hydrogens, a singlet at δ 5.73 (1 H) assigned to the Zr–H resonance, and an AA′XX′ pattern[16] centered at δ 6.55 attributable to the hydrogens of the ($H^{13}C{=}^{13}CH$) moiety. Furthermore **9** reacts smoothly with methyl iodide to yield methane and the orange crystalline complex $\{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(OCH{=}CHO)$ (**10**) (eq 6).

$$\{(\eta^5\text{-}C_5Me_5)_2ZrH\}_2(OCH{=}CHO) + 2CH_3I \rightarrow \{(\eta^5\text{-}C_5Me_5)_2ZrI\}_2(OCH{=}CHO) + 2CH_4 \quad (6)$$

On the basis of infrared and NMR data[17] **10** appears to have a structure analogous to **9**.

9 could not be reduced to **3** with H_2 with or without added **5**. If **6** is warmed to room temperature under an H_2 atmosphere, again only **9** is obtained. A mixture of **6** (1 mol) and **5** (1.29 mol) does, however, yield **3** (0.92 mol) along with a trace of **9** (0.08 mol) when warmed (−80 to 25 °C) under H_2; **5** is recovered nearly quantitatively. Furthermore we find that slow diffusion of CO into an N_2-blanketed solution of **5** at 25 °C also gives **3** and a transient dark red complex (believed to be **1** or **4**) which is eventually converted to **2** by excess CO. These observations indicate that **3** is formed from **6** only in the presence of **5** and that dimerization to **9** occurs in its absence. We therefore suggest that **6** rearranges to the reactive formyl hydride complex **8**, which is subsequently reduced to **3** by **5** (releasing (η-^{5}-$C_5Me_5)_2Zr$ (**11**)) in competition with its dimerization to **9** (Scheme I). This mechanism bears similarity to some of the steps proposed by Treichel and Shubkin[18] for the reduction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(PPh_3)]^+$ to (η^5-$C_5H_5)Mo(CO)_2(PPh_3)CH_3$ with borohydride. In both cases it appears that attack of a metal hydride on a metal-formyl intermediate is required for further reduction. The hydridic character of the hydrogen ligands for **5** (cf. BH_4^-) stands in contradistinction to group 6–8 transition metal hydrides which behave chemically more like protonated metal complex anions. This hydridic character may be the determining factor in the rearrangement of **6** to **8** and in the subsequent reduction of **8** to **3**.

Whether this mechanism is operative in the H_2 reduction of **2** to **3** is still open to some question since we have no direct evidence for the presence of **5** in this system. It may be, however, that under the reaction conditions (~1.5 atm of H_2, 110 °C or hν), sufficient **5** is formed to catalyze the reduction to **3**. We are presently investigating further the mechanism and scope of this reaction type.

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(7) Calculated for $C_{21}H_{34}OZr$: C, 64.06; H, 8.71; Zr, 23.17. Found: C, 64.14; H, 8.90; Zr, 23.12. Molecular weight determined cryoscopically for 85.7 mg of **3** per g of C_6H_6: 402 ± 30 (calcd 394). NMR (benzene-d_6) [η^5-$C_5(CH_3)_5$] s, δ 1.96 (30 H); $-OCH_3$ s, δ 3.87 (3 H); Zr*H* s, δ 5.70 (1 H). Ir (Nujol mull) ν(Zr–H) 1590, ν(Zr–D) ~1130, ν(C–O) 1140.
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(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. {^{1}H} ^{13}C NMR, s, 137.4 δ (Me_4Si). Non-{^{1}H} ^{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); ν(^{13}C–O) 1175 (vs). NMR (benzene-d_6) [$C_5(CH_3)_5$], s, δ 1.94 (30 H); (-OC*H*═C*H*O–) s, δ 6.83 (1H) ^{1}H NMR for {(η^5-$C_5Me_5)_2ZrI\}_2(O^{13}CH═^{13}CHO)$ (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).

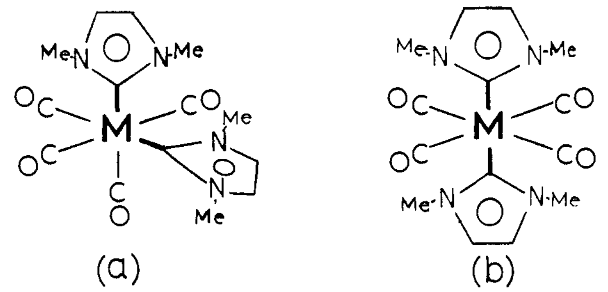

Figure 1. (a) *cis*- and (b) *trans*-(Imid)$_2$M(CO)$_4$ (-Me:-CH_3).

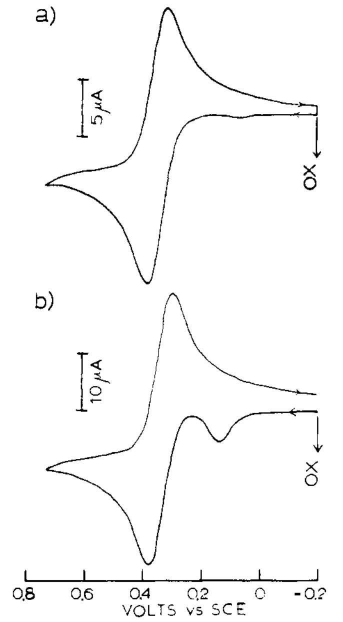

Figure 2. Cyclic voltammogram of *trans*-(Imid)$_2$W(CO)$_4$. The solution contained 5.2 mM *trans*-(Imid)$_2$W(CO)$_4$ and 0.25 M TBAP in methylene chloride. The scan rates are (a) 0.2 V/s at 22 °C and (b) 1.0 V/s at −2 °C.

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-