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Supplementary Material Available: Experimental description of $\mathbf{1}^{\cdot+}$ generation for solution ESR and UV-vis studies and Th reduction, description of $\mathbf{1}^{\cdot+}$ decomposition with gas-evolution measurement, cyclic voltammogram of **1**, UV-vis spectrum of $\mathbf{1}^{\cdot+}$, and solid-state ESR spectra of $\mathbf{1}^{\cdot+}$ in CH_2Cl_2 (6 pages). Ordering information is given on any current masthead page.

Carbonyl Coupling on the $TiO_2(001)$ Surface

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The formation of carbon-carbon bonds is the basis for a number of important catalytic processes, including olefin polymerization, carbonylation, hydroformylation, alkylation, and Fischer-Tropsch synthesis. While surface science studies of reactions on single-crystal surfaces under ultrahigh vacuum conditions have yielded significant information on catalytic oxidation and hydrogenation reactions, there are few examples of carbon-carbon bond formation on surfaces at these pressures. We have previously observed two such reactions which occur on single-crystal surfaces of TiO_2. Coupling of a pair of adsorbed carboxylates, $C_nH_{2n\pm1}COO$, to a higher ketone, $(C_nH_{2n\pm1})_2C{=}O$, requires surface Ti(IV) cations with a pair of coordination vacancies.[1-3] Aldol condensation of acetaldehyde to crotonaldehyde and crotyl alcohol also takes place on Ti(IV) sites on a fully oxidized surface, but only a single coordination vacancy per surface cation is required.[4] We report here an additional class of C-C formation reactions involving the carbonyl group: carbonyl metathesis to form higher olefins via

$$2RCHO \rightarrow RCH{=}CHR$$

This reaction requires prior partial reduction of the TiO_2 surface.

Carbonyl coupling to olefins can be carried out with a number of metals.[5] This synthesis with titanium reagents utilizes a slurry of solid $TiCl_3$ in the presence of a strong reducing agent such as $LiAlH_4$, Li, K, or Zn-Cu.[6] The salient features of this reaction are as follows: (1) The active reagent consists of multiple reduced Ti sites at the solid surface; the oxidation state of these reduced sites is assumed to be Ti(0).[6,7] (2) The mechanism involves reductive dimerization to form a C-C bond followed by rate-determining, sequential deoxygenation of the 1,2-diolate intermediate.[6] In contrast, we find no evidence for the presence of Ti(0) on our TiO_2 surfaces under conditions where carbonyl coupling to olefins is appreciable.

The apparatus and the procedures in our studies of TiO_2 single-crystal surfaces have been previously described.[1,8] X-ray photoelectron spectroscopy (XPS) demonstrated that the disordered, argon ion bombarded (001) surface contained titanium(II), -(III), and -(IV),[1,8] but there was no evidence for the characteristic $2p_{3/2}$ line of Ti(0) at 454.5 eV, consistent with other reports for sputtered TiO_2[9] and the equilibrium between titanium and its oxides.[10] Annealing the surface at higher temperatures oxidizes the surface by diffusion from the bulk[1] as evidenced by (1) an increase of the surface O/Ti ratio by Auger electron spectroscopy (AES); (2) attenuation of the Ti(II) and Ti(III) peaks in XPS (these were not detectable after annealing above 750 K); and (3) reconstruction of the surface to a (011)-faceted structure above 750 K.[11]

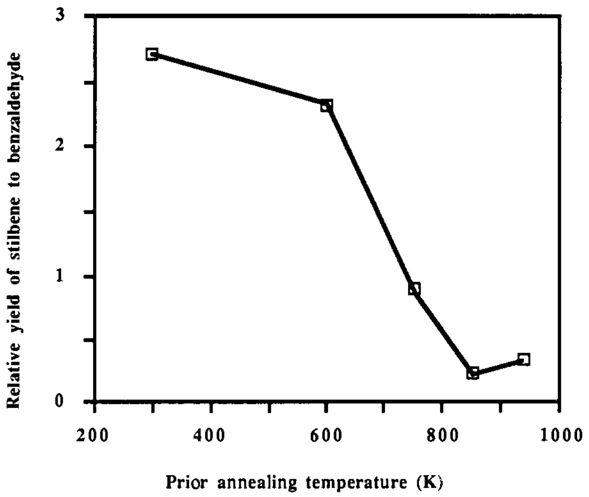

Figure 1. Ratio of stilbene to benzaldehyde desorbed following benzaldehyde adsorption at 300 K on sputtered $TiO_2(001)$ surfaces previously annealed at 300-930 K.

We report here the following examples of olefin formation by coupling of aliphatic, α,β-unsaturated, and aromatic aldehydes on the sputtered and low-temperature (below ca. 750-800 K) annealed surfaces:

$$2CH_3CHO \rightarrow CH_3CH{=}CHCH_3$$

$$2CH_2{=}CHCHO \rightarrow CH_2{=}CHCH{=}CHCH{=}CH_2$$

$$2PhCHO \rightarrow PhCH{=}CHPh$$

The ratio of stilbene to benzaldehyde observed in temperature-programmed desorption (TPD) experiments is illustrated in Figure 1. The TiO_2 surface was exposed at 300 K to benzaldehyde from a dosing needle at a background pressure of 1.5×10^{-8} Torr for 100 s. After evacuation, the temperature of the TiO_2 sample was ramped at a rate of 1.2 K/s. Products were detected with an onboard UTI 100C quadrupole mass spectrometer multiplexed with an IBM PC. All masses between 2 and 260 amu were examined in experiments in which 8, 20, 50, or 100 masses were monitored concurrently. Stilbene was identified by the prominent signal for m/e = 180 as well as its fragmentation to m/e = 179, 178, 165, 152, 115, and 102. Quantitative determination of the relative sensitivities[12] from the corresponding fragmentation patterns indicated that the yield of stilbene at 440 K from the sputtered surface was ca. 2.7 times that of the benzaldehyde which desorbed at 385 K.

Annealing the surface at temperatures to 930 K prior to aldehyde adsorption produced a monotonic decrease in the yield of olefins. The stilbene yield from the surface annealed at 850 K was less than 10% of that from a freshly bombarded surface. Since annealing the surface progressively decreases the concentration of Ti(II) and Ti(III) species at the surface to the limits of XPS detection by 750-850 K, the parallel decrease of the stilbene yield from benzaldehyde suggests that the active sites for this reaction are Ti(III) and possibly Ti(II) cations at the surface. The participation of multiple surface cations and the facile rearrangement of lattice oxygen may circumvent the need for a single metallic site, e.g., Ti(0), which can effect a four-electron reduction.

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Additional studies by angle-resolved XPS are continuing in order to determine quantitative surface concentrations of surface titanium species and to probe the identity of organic adsorbates in these reactions. Our studies to date demonstrate that (1) carbon-carbon bond formation reactions with synthetic utility can occur even under UHV conditions; (2) surface science approaches can identify active sites for novel heterogeneous syntheses; and (3) carbonyl coupling to olefins on oxophilic metals under reducing conditions occurs at mild temperatures and may be important in selective hydrocarbon synthesis with oxide-promoted metal catalysts.

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Reductive Activation of the η^5-Methylcyclopentadienyl Ligand in $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ and Evidence for a Ring-Slipped Intermediate Containing an η^3-Methylcyclopentadienyl Ligand

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We recently reported that the η^6-arene ligands in complexes such as $[Cr(\eta^6\text{-}C_6H_6)(CO)_3]$ (**1**) and $[Mn(\eta^6\text{-}C_6H_6)(CO)_3]^+$ (**2⁺**) can be activated toward electrophiles by two-electron naphthalenide reduction, and we have proposed that the highly reduced intermediates contain η^4-arene ligands.[1-3] Cymantrene, $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ (**3**), is isoelectronic with **1** and **2⁺**, and it occurred to us that it might also be possible to induce a hapticity change in the η^5-methylcyclopentadienyl ligand in **3**, and that this might similarly result in activation of the aromatic ligand toward electrophiles. We now report (Scheme I) that **3** undergoes a reduction to give a complex formulated as $[Mn(\eta^3\text{-}C_5H_3)(CO)_3]^{2-}$ ($\mathbf{4}^{2-}$), and that $\mathbf{4}^{2-}$ can be protonated to give a cyclopentadiene complex $[Mn(\eta^4\text{-}C_5H_5CH_3)(CO)_3]^-$ ($\mathbf{5}^-$) which undergoes facile naphthalene substitution.

Reduction of $[Mn(\eta^5\text{-}C_5H_4Me)(CO)_3]$ (**3**) (0.30 g, 1.38 mmol) was best carried out with the alkalide [K(18-C-6)]K, freshly prepared as reported by Dye.[4] Dropwise addition of 13.8 mL of a 0.2 M solution of [K(18-C-6)]K in tetrahydrofuran (THF) to a solution of **3** in 30 mL of THF at 0 °C resulted in color changes from yellow through orange to purple, just before the alkalide blue began to persist. The loss of CO stretching absorptions at 2021 (s) and 1929 (vs) cm^{-1} (Figure 1a) showed that **3** had been consumed and had been replaced by a species with a single broad, very strong absorption at 1630 cm^{-1} (Figure 1b).[5] This is a very low carbonyl stretching absorption, and the shift of ca. 250 cm^{-1} is consistent with the formation of a dianionic complex. The spectrum is not, however, at all like that of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2]^{2-}$ (the only previously reported dianion in this system[7]).

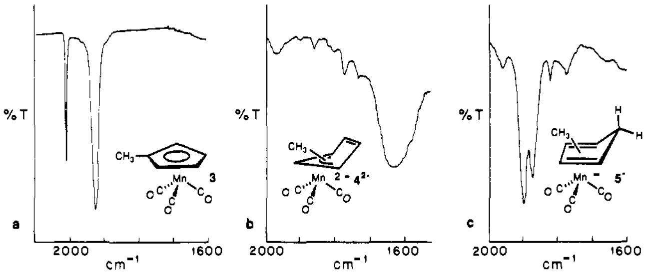
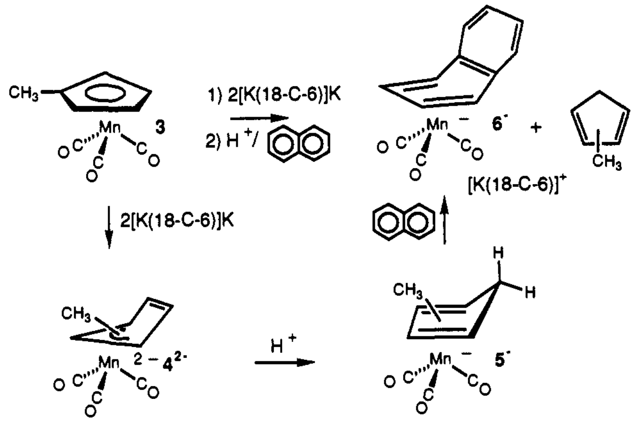


Figure 1. IR spectra in C≡O stretching region of a solution of $[Mn(\eta^5\text{-}C_5H_4CH_3)(CO)_3]$ (**3**) at various stages of the reduction/protonation sequence: (a) before reduction; (b) following dropwise addition of 2 equiv of [K(18-C-6)]K at 0 °C; (c) following further addition of 3 equiv of triflic acid at 0 °C.

Scheme I



The reduction product would appear to have retained three carbonyl ligands and the cyclopentadienyl ligand, as indicated by I_2 (2.5 equiv of I_2) oxidation of a solution of the dianion in THF at room temperature to give **3** in 70% yield (absorption-mode IR), and we propose that the reduction gives the ring-slipped dianion $[Mn(\eta^3\text{-}C_5H_4CH_3)(CO)_3]^{2-}$ ($\mathbf{4}^{2-}$).

As in the case of $[Cr(\eta^4\text{-}C_6H_6)(CO)_3]^{2-}$,[1,2] the product of two-electron reduction of **1**, the aromatic ligand in $\mathbf{4}^{2-}$ is activated toward electrophiles. This has been demonstrated by the reaction of $[K(18\text{-}C\text{-}6)]_2\cdot\mathbf{4}$ [freshly prepared from 0.31 g (1.42 mmol) of **3**] with 3.0 equiv of triflic acid in THF at 0 °C. The broad, strong carbonyl stretching absorption of $\mathbf{4}^{2-}$ at 1630 cm^{-1} is slowly replaced by a two-band pattern at 1898 (vs) and 1874 (s) cm^{-1} (Figure 1c), indicating formation of a complex with a considerably less electron rich transition-metal center which we propose to be the cyclopentadiene complex $[Mn(\eta^4\text{-}C_5H_5CH_3)(CO)_3]^-$ ($\mathbf{5}^-$). Attempts to isolate this material as a $[K(18\text{-}C\text{-}6)]^+$, $[Ph_3PNPPh_3]^+$, or $[NEt_4]^+$ salt have been unsuccessful to date, but we have been able to prepare a stable derivative by carrying out the protonation in the presence of 10 equiv of naphthalene. This gave an orange crystalline compound, isolated by precipitation from THF by addition of ether and recrystallization from THF/ether. The product was shown (IR, ^1H NMR, ^{13}C NMR) to be the η^4-naphthalene complex $[K(18\text{-}C\text{-}6)][Mn(\eta^4\text{-}C_{10}H_8)(CO)_3]$ ($[K(18\text{-}C\text{-}6)]\cdot\mathbf{6}$, 0.47 g, 60%) (Scheme I), which we have previously prepared as a $[PPN]^+$ salt by another route.[3]

X-ray diffraction studies have established that $[PPN]\cdot\mathbf{6}$ contains an η^4-naphthalene ligand,[3] and $\mathbf{6}^-$ could reasonably be formed by substitution of naphthalene for the methylcyclopentadiene ligand in $\mathbf{5}^-$. Such a reaction would be analogous to the facile substitution which we have reported of η^4-naphthalene for the η^4-benzene in $[Cr(\eta^4\text{-}C_6H_6)(CO)_2]^{2-}$.[8] The diene substitution is unprecedented and involves replacement of an unstrained diene with a highly

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(5) This band does not have a Lorentzian envelope and is probably a composite of a number of absorptions. This would be a typical consequence of the existence of the anion in THF as a mixture of several ion pairs with distinct IR spectra, as often observed in solutions of carbonylmetalates.[6] If the complex is $[Mn(\eta^3\text{-}C_5H_5)(CO)_3]^{2-}$, as proposed below, we would expect more than one carbonyl absorption in its IR spectrum. The details of the IR spectrum of the tricarbonyl may, however, be masked by such ion-pairing effects.

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