supported, and the unusual concept that an apparently reversible process is observed when nonequilibrium conditions apply must be invoked. The observed single wave Nernstian response for oxidation of the mixture of isomers must therefore be a consequence of the rapid isomerization of the oxidized cis<sup>+</sup> species. Alternatively, or in addition, a rapid cross redox reaction represented by the equation

$$\operatorname{cis}^+ + \operatorname{trans} \stackrel{K_3}{\longleftarrow} \operatorname{trans}^+ + \operatorname{cis}$$
 (11)

would lead to the same observation where  $K_3 = K_2/K_1$ . Spectroscopic evidence indicates that both these reactions are fast.

The voltammetric results are deceptively simple because oxidation and reduction of both equilibrium and nonequilibrium mixtures of *cis*- and *trans*-Cr(CO)<sub>4</sub>(P{OMe}<sub>3</sub>)<sub>2</sub> occurs at the oxidation potential for the trans<sup>+</sup>/trans<sup>0</sup> couple. However, the cis<sup>+</sup>/cis<sup>0</sup> couple, unperturbed by chemical reactions, really occurs at a considerably more positive potentials than the trans<sup>+</sup>/trans<sup>0</sup> couple. If chemical reactions following the charge-transfer step are fast as in eq 12, the cis oxidation process would be shifted

cis - Cr(CO)<sub>4</sub>(P{OMe}<sub>3</sub>)<sub>2</sub>  $\rightleftharpoons$  cis - [Cr(CO)<sub>4</sub>(P{OMe}<sub>3</sub>)<sub>2</sub>]<sup>+</sup> + e<sup>-</sup>

$$trans - [Cr(CO)_4 (P|OMe|_3)_2]^+$$
(12)

toward the potential for the trans oxidation process. However, the limit of the shift in potential of the cis<sup>0</sup> oxidation process (which generates trans<sup>+</sup>) cannot be shifted beyond that for the trans<sup>0</sup> oxidation. This limit applies because the trans<sup>+</sup> isomer cannot exist at less positive potentials than the  $E^{\circ}$  value for the trans<sup>+</sup>/trans<sup>0</sup> couple. At such potentials trans<sup>+</sup> is reduced to trans<sup>0</sup> at the diffusion-controlled rate. The cross redox reaction similarly constrains the position of the chemically perturbed cis<sup>0</sup> oxidation. Since only one response is observed under all conditions, it can be concluded that this limit has been reached and that redox responses are always observed at the trans<sup>+</sup>/trans<sup>0</sup> redox potential, irrespective of whether equilibrium or nonequilibrium mixtures of the cis and trans isomers are present in the bulk solution. This study emphasizes that deceptively simple reversible electrochemical responses can be observed that involve substantial structural changes of an isomeric kind or large changes in bond lengths.<sup>25</sup>

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**Registry No.** TBAP, 1923-70-2; TEAP, 2567-83-1; *cis*-[Cr-(CO)<sub>4</sub>(P{OMe}\_3)<sub>2</sub>]<sup>+</sup>, 115888-45-4; *trans*-[Cr(CO)<sub>4</sub>(P{OMe}\_3)<sub>2</sub>]<sup>+</sup>, 100165-44-4; *cis*-Cr(CO)<sub>4</sub>(P{OMe}\_3)<sub>2</sub>, 16027-43-3; *trans*-Cr(CO)<sub>4</sub>(P{OMe}\_3)<sub>2</sub>, 21370-42-3; Pt, 7440-06-4; P, 7723-14-0; NOPFe, 16921-91-8; AgClO<sub>4</sub>, 7783-93-9; [NH(C<sub>6</sub>H<sub>4</sub>Br)<sub>3</sub>]SbCl<sub>6</sub>, 40927-19-3; LiAlH<sub>4</sub>, 16853-85-3; dichloromethane, 75-09-2; acetonitrile, 75-05-8.

# Communications

### Stoichiometric Hydroformylation of Coordinated Acetone

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Summary: The bridging acetone in Cp<sub>2</sub>Zr[( $\mu$ -OC)Mo-(CO)<sub>2</sub>Cp][( $\mu$ - $\eta^2$ , $\eta^1$ -CMe<sub>2</sub>O)Zr(Me)Cp<sub>2</sub>] (1) undergoes CO insertion into its Zr–C bond, with the oxygen of the new  $\eta^2$ -acyl ligand displacing the acetone oxygen from one Zr. Acidification of the  $\eta^2$ -acyl complex **2** gives  $\alpha$ -hydroxy-isobutyraldehyde, the product of the formal hydroformylation of the coordinated acetone.

While the hydroformylation of formaldehyde has been effected stoichiometrically with  $HCo(CO)_4^1$  and has been catalyzed by a number of other reagents,<sup>2</sup> the hydro-

formylation of higher aldehydes and ketones has not been reported.<sup>3</sup> The difficulty of inserting carbon monoxide into bonds between metals and oxygen-bearing carbons<sup>4</sup> makes such reactions uncommon. One approach to them involves the aldehyde and ketone complexes (I) of the early transition metals—complexes which are better described as metallaoxiranes (II) with metal-carbon  $\sigma$  bonds.<sup>5</sup> Most



such complexes have proven unreactive toward carbon monoxide, but we have been able to carbonylate the Zr-C

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<sup>(3)</sup> The cobalt-catalyzed addition of CO and  $R_3Si-H$  to aldehydes has been reported: Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. Angew. Chem., Int. Ed. Engl. 1979, 18, 3393. The cobalt-catalyzed addition of CO and  $R_3Si-H$  to cyclobutanone has also been reported: Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. J. Am. Chem. Soc. 1984, 106, 430.

<sup>(4)</sup> Examples of such insertions, and discussions of the general problem, can be found in: (a) Berke, H.; Huttner, G.; Weiler, G.; Zeolnai, L. J. Organomet. Chem. 1981, 219, 353. (b) Selover, J. C.; Vaughn, G. D.; Strouse, C. E.; Gladysz, J. A. J. Am. Chem. Soc. 1986, 108, 1462 and references therein. (c) Tso, C. C.; Cutler, A. R.; Kullnig, R. K. J. Am. Chem. Soc. 1987, 109, 5844 and references therein.

bond of an acetone complex of zirconium and thus to effect the stoichiometric hydroformylation of its acetone ligand.

We have already reported<sup>6</sup> the preparation of acetone complexes 1 by the addition of  $Cp_2ZrMe_2$  to  $\eta^2$ -Ac complexes of zirconium (eq 1).<sup>7</sup> In the structure of 1b<sup>6</sup> the

$$Cp_{2}Zr \xrightarrow{+} O \xrightarrow{-} O \xrightarrow{-} Mo(CO)_{2}(\eta^{5} - C_{5}H_{5}) + Cp_{2}ZrMe_{2} \xrightarrow{25 \circ C} toluene 1a, b (1)$$

$$C \xrightarrow{+} O \xrightarrow{-} O \xrightarrow{-}$$

acetone oxygen is much closer to the right-hand zirconium than to the left-hand one, implying that the compound is better described by limiting structure IV than by limiting structure III. As the Zr–C bond in limiting structure IV



should differ little from the Zr–C bonds in normal Cp<sub>2</sub>Zr alkyl complexes, it is not surprising that in toluene solution 1 smoothly (1 atm, 0 °C, 4 h) takes up 1 equiv of CO to form 2 (eq 2).<sup>8</sup>



The exact structure of 2 has been established by X-ray crystallography. As had been the case with 1, repeated attempts to grow crystals of the all-cyclopentadienyl complex 2a gave only microcrystalline powders; the derivative 2b with a single methyl substituent on all the cyclopentadienyl ligands of Zr (but not on that of Mo) formed crystals suitable for study by X-ray diffraction.<sup>9</sup> The



Figure 1. Molecular structure of 2b. Selected bond lengths (Å) and angles (deg): Zr1-O5, 1.933 (6); O5-C34, 1.40 (1); C33-O4, 1.24 (1); Zr2-C33, 2.182 (7); Zr2-O4, 2.256 (6); Zr2-O3, 2.205 (7); Zr2-O3-C3, 142.4 (6); Zr2-C33-O4, 77.1 (4); C33-C34-C35, 107.3 (7); C35-C34-C36, 112.1 (8); C35-C34-O5, 110.5 (7); Zr2-O4-C33, 70.5 (4); Zr1-O5-C34, 168.9 (5). Carbon atoms of  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> and  $\eta^5$ -C<sub>5</sub>H<sub>4</sub>Me rings are drawn as spheres, with arbitrary radii.

molecular structure is shown in Figure 1.

As the structure makes clear, the incoming CO has inserted into the Zr–C bond of the original acetone ligand on Zr2. The oxygen of the resulting  $\eta^2$ -acyl ligand has displaced the oxygen of the acetone ligand from Zr2; the latter oxygen now forms an alkoxide ligand on Zr1. The presence of this alkoxide ligand in 2, and the alkoxide character of the Zr1–O bond in 1, explain why the methyl ligand on Zr1 never takes up CO in reaction 2:  $\pi$ -donor ligands such as alkoxide are known to decrease the equilibrium constant for CO uptake and  $\eta^2$ -acetyl ligand formation by adjacent methyl ligands.<sup>10</sup>

One would expect acidification of 2 to remove the bridging ligand as  $\alpha$ -hydroxyisobutyraldehyde (3). Treatment of 2a in toluene with 5 equiv of CF<sub>3</sub>COOH at -30 °C gave two products observable by <sup>1</sup>H NMR. One was the expected 3 (reaction 3), as confirmed by comparison of its <sup>1</sup>H NMR spectrum in toluene- $d_8^{11}$  with that of an authentic sample prepared by literature methods.<sup>12</sup> The other protonolysis product had four methyl peaks of equal intensity<sup>13</sup> and was identified as the 2,5-dihydroxy-1,4-dioxane derivative, 4, arising from acid-catalyzed dimerization of 3 (reaction 4).<sup>14,15</sup>

<sup>(6)</sup> Martin, B. D.; Matchett, S. A.; Norton, J. R.; Anderson, O. P. J. Am. Chem. Soc. 1985, 107, 7952.

<sup>(7)</sup> Although we originally<sup>6</sup> assumed that reaction 1 occurred by nucleophilic attack at the  $\eta^2$ -acyl carbon, recent work on the reaction of organoaluminum reagents with  $\eta^2$ -acyl zirconium complexes suggests that such reactions may instead proceed by transmetalation and Lewis acid induced reductive coupling: Waymouth, R. M.; Clauser, K. R.; Grubbs, R. H. J. Am. Chem. Soc. 1986, 108, 6385.

<sup>(8)</sup> The <sup>1</sup>H NMR ( $C_6D_6$ ) of **2a**:  $\delta$  5.76 (s, 10 H,  $Cp_2Zr$ ), 5.74 (s, 10 H,  $Cp_2Zr$ ), 5.39 (s, 5 H, CpMo), 1.01 (s, 6 H, acetone Me), 0.25 (s, 3 H, ZrMe). Of **2b**:  $\delta$  6.4–5.4 (ring H), 5.38 (s, 5 H, CpMo), 1.96 (s, 6 H, MeCp), 0.21 (s, 3 H, ZrMe).

<sup>(9)</sup> **2b** crystallizes in the orthorhombic space group  $Pbc2_1$  (nonstandard version of  $Pca2_1$  (No.29)): a = 8.663 (2) Å, b = 19.900 (4) Å, c = 20.157 (5) (137 K), Z = 4. Reflections with  $4^{\circ} < 20 < 50^{\circ}$  were recorded, 3619 were considered observed  $(I > 2.5\sigma(I))$ . The structure was solved by interpretation of the Patterson map (for Mo and Zr atom positions); carbon and oxygen atoms were found in subsequent difference Fourier maps. One methylcyclopentadienyl ring (C27-C31) exhibited disorder, and its site occupancy factors were refined; the atoms of the disordered ring were given isotropic thermal parameters. The hydrogen atoms of the nondisordered rings were included in idealized positions (C-H = 0.96 Å). The methyls were modeled as rigid groups, with hydrogen atoms at idealized tetrahedral positions. The thermal parameters of all hydrogen atoms were fixed at 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which they were attached. No absorption correction was performed. After the final refinement cycle R = 0.042,  $R_w = 0.041$ , and GOF = 1.29.

<sup>(10) (</sup>a) Fachinetti, G.; Fochi, G.; Floriani, C. J. Chem. Soc., Dalton Trans. 1977, 1946. (b) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. J. Organomet. Chem. 1980, 201, 389.

<sup>(11)</sup> The <sup>1</sup>H NMR (toluene- $d_8$ , -30 °C) of 3:  $\delta$  8.79 (s, CHO), 0.84 (s, Me<sub>2</sub>C). IR data, and <sup>13</sup>C NMR data in CDCl<sub>3</sub>, have recently been reported for 3 (Nagashima, E.; Suzuki, K.; Ishikawa, M.; Sekiya, M. *Heterocycles* 1985, 23, 1873), along with a <sup>1</sup>H NMR aldehyde chemical shift in CDCl<sub>3</sub> ( $\delta$  9.22) somewhat different from the one which we have observed in the same solvent ( $\delta$  9.52).

<sup>(12)</sup> Dworzak, R.; Pierri, J. Monatsh. Chem. 1929, 52, 141. Takeda, A.; Tsuboi, S.; Sakai, T. Bull Chem. Soc. Jpn. 1974, 47, 2440.

<sup>(13)</sup> The <sup>1</sup>H NMR (toluene- $d_8$ ) of 4:  $\delta$  4.73 (CH), 4.6 (CH), 1.19 (Me), 1.07 (Me), 0.98 (Me), 0.91 (Me).



The formation of 3 by the acidification of 2 completes the stoichiometric hydroformylation of the coordinated acetone in 1. In contrast to the ketone ligands in mononuclear Zr complexes,<sup>5</sup> the acetone ligand in 1 is surprisingly unreactive toward potential insertion reagents other than CO: ethylene, butadiene, and cyclopentadiene do not react with 1 in toluene solution at room temperature; diphenylacetylene and 1 do not react in toluene at room temperature and decompose at 70 °C. Also in contrast to the ketone ligands in mononuclear Zr complexes,<sup>16</sup> the acetone ligand in 1 does not react with MeI. The addition of PMe<sub>3</sub> to 1a (toluene, 50 °C) leads to formation of an oxo-bridged dimer with a vinyl ligand on one zirconium (5),<sup>17</sup> presumably by substitution on Mo.<sup>18</sup> deprotonation of the acetone by the resulting strongly basic molybdenum anion, and C-O bond cleavage of the enolate thereby formed (eq 5). The same product is formed when 1a is



treated with  $K[(\eta^5-C_5H_5)Mo(CO)_2(PMe_3)]$  performed from KH and  $(\eta^5-C_5H_5)Mo(CO)_2(PMe_3)H$ . As the carbonyl of

1 is derived from CO, reaction 5 finishes a stoichiometric cleavage of the CO triple bond. The structure of 5 has been confirmed by observing the formation of propene upon its acidification with CF<sub>3</sub>COOH.

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Supplementary Material Available: Atomic coordinates and isotropic thermal parameters (Table S-2), bond lengths (Table S-3), bond angles (Table S-4), anisotropic thermal parameters (Table S-5), and hydrogen coordinates and thermal parameters (Table S-6) for 2b (8 pages); observed and calculated structure factors for 2b (Table S-1, 18 pages). Ordering information is given on any current masthead page.

# Metal Vapor Synthesis of Bis(arene)manganese **Cations Utilizing in Situ Oxidation**

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Summary: The cocondensation of Mn atoms, I2, and arenes at -196 °C provides a general route to homoleptic 18-electron ( $\eta^6$ -arene)<sub>2</sub>Mn<sup>+</sup> sandwich complexes. The reaction presumably involves in situ oxidation of unstable 19-electron  $(\eta^6$ -arene)<sub>2</sub>Mn species.

Metal vapor synthesis has proven to be a valuable synthetic technique in the organometallic chemistry of many transition metals.<sup>1</sup> Manganese appears to be an exception as there are few references to manganese atom chemistry<sup>2</sup> and low yields are generally found in reactions which lead to organomanganese products.<sup>2,3</sup> Among the postulates presented for the source of the low yields is the tendency for manganese atoms to react with themselves rather than with organic ligands, possibly because of the stability of the half-filled 3d shell in the Mn ground state.<sup>2</sup> A more compelling explanation may be the instability of the Mn(0)odd-electron intermediates which would typically be formed in reactions of Mn atoms with organic ligands. This communication describes the trapping of such intermediates by cocondensation of an oxidant with arenes and manganese atoms; a series of new bis(arene)manganese cations is obtained.

A bell-jar metal reactor<sup>4</sup> was designed which incorporated a resistively heated furnace and a dual ligand inlet system. Cocondensation of manganese metal, toluene, and elemental iodine yielded  $(\eta^6-C_6H_5CH_3)_2Mn^+PF_6^-(1a)$  on

<sup>(14)</sup> To our surprise, the axial-equatorial isomer shown for 4 (the only isomer with four inequivalent methyl groups) appears to be the most stable dimer of 3; heating a solution of 4 only regenerates 3. Apparently the geometry of 4 is a compromise between the diaxial hydroxyls expected on electronic grounds (the anomeric effect<sup>15</sup>) and the diequatorial hy-

on electronic grounds (the anomeric effect<sup>10</sup>) and the diequatorial hydroxyls expected on steric grounds. (15) Deslongchamps, P. Stereoelectronic Effects in Organic Chemistry; Pergamon: New York, 1983; p 5. (16) Erker, G.; Rosenfeldt, F. Tetrahedron 1982, 38, 1285. (17) The <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) of 5:  $\delta$  6.02 (d of q, <sup>2</sup>J<sub>HH</sub> = 4.2 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 1 H vinyl), 5.81 (s, 10 H, Cp<sub>2</sub>Zr), 5.77 (s, 10 H, Cp<sub>2</sub>Zr), 5.26 (d of q, <sup>2</sup>J<sub>HH</sub> = 4.2 Hz, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 1 H, vinyl), 2.09 (t, <sup>4</sup>J<sub>HH</sub> = 1.2 Hz, 3 H, ZrCMe=CH<sub>2</sub>), 0.27 (s, 3 H, ZrMe). IR (KBr): 1434.5 (C=C), 1011, 884, 800, 733.5 (Zr=O-Zr) cm<sup>-1</sup>. Anal. (C<sub>24</sub>H<sub>26</sub>OZr<sub>2</sub>) C, H. (18) Lewis acid cations are known to labilize [CnMo(CO)<sub>2</sub>]<sup>-</sup>: Der-

<sup>(18)</sup> Lewis acid cations are known to labilize [CpMo(CO)<sub>3</sub>]: Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. J. Am. Chem. Soc. 1982, 104, 1521.

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