by 18 kcal/mol,[18] so too is the FeHFe interaction the favored one. The observation that in clusters bridging hydrides are the rule, terminal hydrides the exceptions, is consistent with these energetics.[19]

It is educational to compare the cycle in Scheme I with a similar cycle for the FeCO interaction (Scheme II). This comparison emphasizes the weakness of the FeCO interaction compared to FeHFe, the difference in the energies for CO and H necessary to create an unsaturated Fe center and a terminal bond, and the difference in the energies for CO and H in creating a terminal interaction from a bridging one.

The M-H bond strength is one factor important in determining the thermodynamics of several interconversions involving metals and hydrocarbon fragments.[7] The numerical value of E(FeHFe) reported here has several implications in this regard. For example, E(FeC) and E(FeH) (terminal) suggest that β-hydrogen elimination (eq 3) on

$$FeCH_2CH_3 \rightarrow FeH + C_2H_4 \qquad (3)$$

a mononuclear metal center is an endothermic reaction,[20] albeit with a favorable entropy change. In a polynuclear system, the hydride has the possibility of ending up bridging, which will favor the elimination reaction by about another 10–11 kcal/mol (Scheme I). Thus, hydride "eliminations" from carbon resulting in MHM hydrides are possible in the absence of a favorable mole change. One example is provided by an internal rearrangement in a triosmium system,[21] where MC(O) and CH bonds are converted into MHM and C=C(O) bonds in a unimolecular process.

The additional stability of a bridging hydride over a terminal hydride suggests the possibility of a real difference between the chemistry of mono- and polynuclear metal hydride systems. Further exploration of this and related systems is in progress.

Acknowledgment. Helpful discussions with Dr. C. E. Housecroft as well as the support of the National Science Foundation under Grant No. CHE 81-09503 are gratefully acknowledged. The NMR facility used was obtained with the aid of the National Institutes of Health (Grant No. GM 25845-0251).

Registry No. I, 69440-00-2; II, 88610-52-0.

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(20) With E(FeC) = 30 kcal/mol, E(FeH) = 55 kcal/mol, E(CH) = 98 kcal/mol, and $E(C{=}C) - E(C{-}C)$ = 62 kcal/mol, ΔH = 11 kcal/mol.

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Oxidative Carbonylation of Alcohols: Dialkyl Oxalates from (Dialkoxycarbonyl)rhodium Complexes

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Summary: The oxidative carbonylation of alcohols to generate dialkyl oxalates has, for the first time, been accomplished with rhodium-based complexes.

The employment of synthesis gas (mixtures of CO and H_2) as a reactant for the generation of organic products that contain new carbon–carbon bonds encompasses such diverse reactions as olefin hydroformylation,[1] Fischer–Tropsch catalysis,[2] alcohol and carboxylic acid homologation,[3,4] and, of particular interest to us, ethylene glycol synthesis.[5] The direct production of ethylene glycol from synthesis gas has required both high pressures and elevated temperatures. Another attractive, less vigorous route to this diol makes sequential rather than concomitant use of the gases CO and H_2. First, CO and an alcohol are oxidatively coupled to generate a dialkyl oxalate, which is subsequently reduced by H_2 to produce ethylene glycol and the starting alcohol (eq 1). The oxalate-producing step

$$2ROH + 2CO + {}^1/_2O_2 \xrightarrow[-H_2O]{\text{"Pd"}} [CO_2R]_2 \xrightarrow{H_2} HOCH_2CH_2OH + 2ROH \qquad (1)$$

has thus far been accomplished only with palladium-based catalysts.[6,7] The key palladium carbonylation intermediate appears to be a dicarboalkoxy complex 1 which releases oxalate to the system by reductive coupling of the two alkoxycarboxylato ligands (eq 2).[8] We now report the

$$L_2PdX_2 + 2CO + 2ROH \xrightarrow[-2HX]{\text{room temp}} \underset{\mathbf{1}}{L_2Pd(COOR)_2} \rightarrow [CO_2R]_2 + L_2Pd \qquad (2)$$

$$X = OAc;\ L = Ph_3P$$

synthesis of a new class of rhodium dicarboalkoxy complexes which upon gentle prodding produce dialkyl oxalates.

Treatment of a methanol suspension of $[Me_5CpRhCl_2]_2$ (**2**) with bubbling CO and an excess of triethylamine at room temperature (eq 3) produced, after 3 h, a deep red-orange solution. Evaporation of the solvent in vacuo gave a solid which was extracted with diethyl ether. Addition of hexane to this ether solution followed by cooling to −40 °C overnight gave the yellow crystalline solid **3a** (40%).[9] The ^1H NMR ($CDCl_3$–Me_4Si) of **3a** contained two singlets at 3.6 and 1.9 ppm in a ratio of 2:5, which suggested the product contained two methoxy groups per Me_5Cp ligand. The IR spectrum (Nujol) of **3a** showed three absorption bands between 2200 and 1600 cm^{-1}: 2056, 1668, and 1645 cm^{-1}. The bands between 1700 and 1600 cm^{-1} are characteristic of carboalkoxy ligands;[12] however, bridging carbonyls and carboxylates also absorb in this region. The

$$\underset{\mathbf{2}}{[Me_5CpRhCl_2]_2} + Et_3N + CO\ (1\ atm) \xrightarrow{ROH} Me_5CpRh(CO)(COOR)_2 + 2Et_3N{\cdot}HCl \qquad (3)$$

$$\mathbf{3a},\ R = CH_3$$
$$\mathbf{3b},\ R = CH_2CH_3$$

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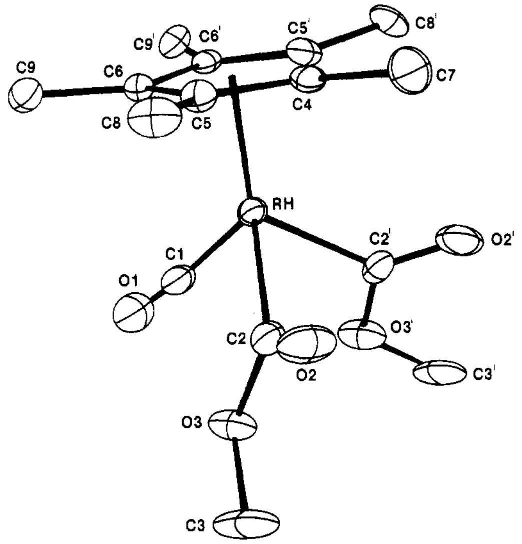

Figure 1. Molecular structure of $Me_5CpRh(CO)(CO_2Me)_2$. Dimensions: Rh–C(1) 1.879 (9), Rh–C(2) 2.041 (5), Rh–X 1.897(X = centroid of Cp), C(1)–O(1) 1.136 (10), C(2)–O(2) 1.185 (6), C(2)–O(3) 1.349 (7), O(3)–C(3) 1.418 (7) Å.

^{13}C NMR spectrum[13] confirmed the presence of the methoxy group(s) but more importantly allowed us to discard possible structures which contained bridging carbonyls since the low-field absorptions at 188.1 and 185.2 ppm were split only into doublets by $^{103}Rh-^{13}C$ coupling.

Although the spectral data were consistent with a mononuclear rhodium dicarboalkoxy complex, multinuclear Me_5Cp complexes of the cobalt triad containing such bridging groups as oxo,[14] aryloxy,[15] and carboxalato[16] are not uncommon. In fact, alcohol solvents such as were used in the preparation of **3a** have been known to serve as precursors to carboxylate ligands;[14] therefore, a structure determination of **3a** was undertaken.

Small single crystals were obtained from a pentane solution of **3a** cooled overnight at −40 °C, and the structure of **3a** was determined from X-ray diffraction data.[17] A perspective of the molecular structure is shown in Figure 1 with a skeletal view presented in Figure 2. The planar Me_5Cp ligand is symmetrically coordinated to the rhodium atom.[21] The most intriguing feature of the molecule is the presence of two carbomethoxy groups unidentately bound to the rhodium. The Rh–COO moieties are essentially planar,[23] with the planes of the COO groups intersecting at an angle of 79.5°. The sp^2 hybridized carbons are separated by 2.65 Å. The metal–ester bond length of 2.041 (5) Å is similar to other rhodium–acyl bond distances,[24] and the ester carbon–oxygen bonds of 1.185 (6) and 1.349 (7) Å are normal. Although the M—C═O angle of 126.1° deviates from an ideal sp^2 hybridization on the carbon, this apparent distortion is not unexpected. A recent comparison of the structures of $Ir(CO)(COOCH_3)(bpy)I_2$, $Pt(COOCH_3)_2(Ph_3P)_2$, and a methoxycarbonyl derivative of a dimethano[14]annulene with respective M—C═O angles of 126.6 (16), 125.9 (5), and 126.3 (1)° demonstrated that the angular pattern around the carbon atom of an ester remains relatively unperturbed in quite diverse environments.[25]

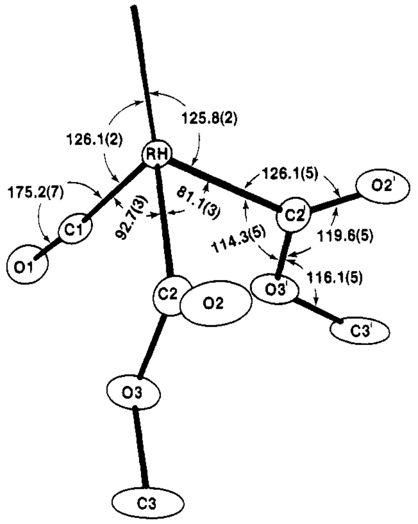

Figure 2. Schematic with important bond angles of $Me_5CpRh(CO)(CO_2Me)_2$.

In the solid state both **3a** and **3b**[26] displayed only slight sensitivity to air or water and, if protected from light, were stable indefinitely under N_2. To induce coupling of the alkoxycarbonyl ligands to produce a dialkyl oxalate, **3b** was dissolved in CH_2Cl_2 under N_2[27] and at room temperature a solution of I_2 in CH_2Cl_2 was added dropwise (final mole ratio of $Rh:I_2 = 1:1$) (eq 4). After stirring for 0.5 h, the reaction was quenched with aqueous bisulfite, and upon

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(13) $^{13}C\{^1H\}$ NMR ($CDCl_3$) for **3a**: δ 9.3 (s, $C_5(CH_3)_5$, 52.6 (s, CH_3O), 104.8 (d, $J(^{103}Rh-^{13}C) = 3$ Hz, $C_5(CH_3)_5$), 185.2 (d, $J(^{103}Rh-^{13}C) = 55$ Hz, RhCOO), 188.1 (d, $J(^{103}Rh-^{13}C) = 79$ Hz, RhCO).

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(17) A yellow crystal with dimensions 0.2 × 0.2 × 0.3 mm was sealed in a glass capillary. All data with $2\theta \leq 50°$ were examined on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a variable-speed $\omega-2\theta$ scan. Of the 1278 unique reflections measured, 843 were considered observed $[|F_o|^2 \geq 1.5\sigma(F_o^2)]$.[18,19] Three check reflections, monitored throughout data collection, displayed no significant loss of intensity with time. ψ scans indicated that absorption effects were negligible, so corrections were not applied $[\mu(\text{Mo K}\alpha) = 10.25\ \text{cm}^{-1}]$. The structure was solved by a combination of Patterson, Fourier, and least-squares refinement techniques.[20] Most of the hydrogens were located on a difference Fourier map calculated after the refinement of all non-hydrogen atoms. The remaining hydrogens were entered at the theoretically calculated positions. The compound crystallizes in the orthorhombic space group *Pnma* (D_{2h}^{16}, No. 62) with $a = 10.499$ (1) Å, $b = 14.323$ (2) Å, $c = 11.064$ (2) Å, $V = 1664$ (1) Å^3, $Z = 4$, and $\rho_{\text{calcd}} = 1.53\ \text{g/cm}^3$. The four molecules in the unit cell are centered on the mirror planes at $y = \pm 0.25$. The final crystallographic residual was $R = 0.037$ and the weighted residual $R_w = 0.042$. All the non-hydrogen atoms were varied anisotropically; the hydrogen atoms were not varied. A final difference Fourier synthesis displayed a maximum intensity of 0.404 e/Å^3.

(18) $|F_o|^2 = I/Lp$ and $\sigma(F_o^2) = \sigma(I)/LP$ where $I = S(C - RB)$ and $\sigma(I) = [S^2(C + R^2B) + (KI)^2]^{1/2}$ with S = scan rate; C = total integrated peak count; $R = 2.0$, the ratio of scan time to background time; B = background count; $K = 0.05$, a factor introduced to weight down intense reflections; Lp = the Lorentz and polarization corrections.

(19) $w = \sigma(F_o)^{-2}$; $\sigma(F_o) = \sigma(F_o^2)/2|F_o|$.

(20) All crystallographic calculations were performed by using the Enraf-Nonius structure determination package on a PDP 11/60 computer.

(21) The distance from the rhodium to the plane of the ring of pentamethylcyclopentadienyl ligand is 1.89 Å, which falls considerably outside the range (1.745–1.815 Å[22]) of previously determined mononuclear Rh(III) complexes.

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(23) The metal atom is only 0.1 Å out of the plane defined by the COO group.

(24) (a) Bennett, M. A.; Jeffrey, J. C.; Robertson, G. B. *Inorg. Chem.* **1981**, *20*, 330–335 and references cited therein. (b) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *J. Organomet. Chem.* **1982**, *236*, C49–C52. (c) Schaverien, C. J.; Green, M.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1982**, 912–914.

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(26) **3b**: ^1H NMR ($CDCl_3-Me_4Si$) δ 1.15(t, $J = 7$ Hz, 6 H, CH_3CH_2), 1.87(s, 15 H, $C_5(CH_3)_5$), 4.10 (q, 4 H, CH_2CH_3); IR (Nujol) 2050, 1662, 1642 cm^{-1}.

(27) GLPC analysis of the solution of **3b** prior to the addition of I_2 showed no diethyl oxalate was present.

$$3\mathbf{b} \xrightarrow[CH_2Cl_2]{I_2} \underset{30\text{–}40\%}{[CO_2C_2H_5]_2} + \underset{40\%}{C_{10}H_{15}\cdot CO_2C_2H_5} + \underset{\text{trace}}{H_5C_2OC(=O)OC_2H_5} \qquad (4)$$

subjecting the product mixture to GLPC/mass spectral analysis, diethyl oxalate[28] was observed in a 30–40% yield. The other organic products which contained "CO" were diethyl carbonate (trace) and a compound with the formula $C_{10}H_{15}\cdot CO_2C_2H_5$ (4) (~40%).[29] Upon changing the reaction solvent from CH_2Cl_2 to diethyl ether, only 4 was produced. The mechanism of this iodine promoted carbon–carbon bond forming reaction is under current investigation and will be reported at a later date.

The carbon–carbon bond-forming step in oxalate synthesis from CO and alcohol has now been demonstrated for the metals rhodium and palladium to involve a dicarboalkoxy mononuclear intermediate. Current studies are under way to further elucidate the chemistry of these and other cobalt triad complexes which contain two alkoxycarbonyl ligands.

Acknowledgment. We wish to thank R. L. Pruett, S. L. Soled, and J. S. Merola for helpful discussions. We also thank C. S. Hsu for assistance in obtaining the GLPC/mass spectra and R. V. Kastrup for the ^{13}C NMR spectra.

Registry No. 2, 12354-85-7; **3a**, 88825-23-4; **3b**, 88841-56-9; 4, 35211-68-8; $[CO_2C_2H_5]_2$, 95-92-1.

Supplementary Material Available: Tables of interatomic distances and angles, fractional coordinates, F_o/F_c, and thermal parameters for $Me_5CpRh(CO)(CO_2Me)$ (9 pages). Ordering information is given on any current masthead page.

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[28] The obtained diethyl oxalate spectrum was consistent with published spectra: "EPA/NIH Mass Spectral Data Base"; Heller, S. R.; Mime, G. W. A., Eds.; National Bureau of Standards: Washington, DC, 1978; Vol. 1, p 410.

[29] The base peak in the mass spectrum of 4 at 135 corresponded to $M^+ - CO_2C_2H_5$, which strongly suggests this compound is ethyl pentamethylcyclopentadiene carboxylate.

Synthesis of 2,2′,5,5′-Tetramethylbibismole. A Thermochromic Dibismuthine

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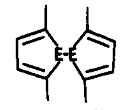
Summary: The reaction of 1,1-dibutyl-2,5-dimethylstannole with iodine gave 2(*Z*),5(*Z*)-diiodohexa-2,4-diene, which on treatment with butyllithium followed by phenylbismuth diiodide afforded 1-phenyl-2,5-dimethylbismole. The bismole was converted to the thermochromic 2,2′,5,5′-tetramethylbibismole by reaction of sodium in liquid ammonia followed by treatment with 1,2-dichloroethane.

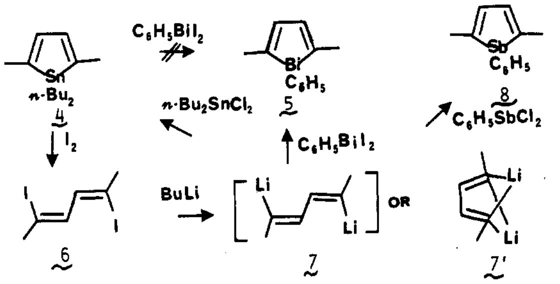
The thermochromic distibine 2,2′,5,5′-tetramethylbistibole (1) forms intensely colored blue crystals which melt to a pale yellow oil and form yellow solutions in organic solvents.[1] The crystal structure of 1 shows that the antimony atoms are aligned in linear chains with very short Sb–Sb··Sb–Sb separations. A molecular orbital treatment by Hoffmann et al. suggests that the solid-phase color is due to intermolecular interaction involving the Sb–Sb σ-bonds.[2]



1, E = Sb
2, E = As
3, E = Bi

In order to explore the generality of this effect, we have investigated a variety of dipnicogen compounds including the arsenic and antimony analogues of 1.[3-5] The synthesis of the nonthermochromic 2,2′,5,5′-tetramethylbiarsole (2) was recently reported.[6] We now wish to report a synthesis of the thermochromic 2,2′,5,5′-tetramethylbibismole (3) that involves several intermediates of theoretical interest.

The attempted exchange reaction between 1,1-dibutyl-2,5-dimethylstannole (4)[7] and phenylbismuth diiodide gave only an intractable black material. This failure may be due to the known great sensitivity of vinylbismuth compounds to acidic conditions.[8] Alternatively, treating stannole 4 with iodine in carbon disulfide afforded 2(Z),5(Z)-diiodohexa-2,4-diene (6): mp 36–39 °C; ^1H NMR ($CDCl_3$) δ 2.60 (s, 6 H), 6.20 (s, 2 H).[9] Metalation of 6 with butyllithium gave a solution of 7, a 1,4-dilithiobutadiene. This reagent may be used to prepare a variety of five-membered ring heterocycles.[10] Thus treating 7 with dibutyltin dichloride affords 4, while reaction with phenylantimony dichloride gave the known 1-phenyl-2,5-dimethylstibole (8).[7] On theoretical grounds it has been suggested that 1,4-dilithiobutadienes have bridged structures.[11] Whether 7 has bridged structure 7′ is currently under investigation.



The reaction of 7 with a suspension of phenylbismuth diiodide in diethyl ether gave 28% of the desired 1-phenyl-2,5-dimethylbismole (5): ^1H NMR (CD_2Cl_2) δ 2.35

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