The concentrations of the spin adduct of SDS radical (Figure 2B) were determined by comparing the double integration of the first-derivative ESR spectra of the spin adduct with that of tetramethylpiperidine-1-oxyl (TEMPO) in SDS micellar solution. The maximal concentration of the spin adduct was 2.4×10^{-5} M (Figure 2B), which corresponds to 9.2% of the initial concentration of naphthoquinone. As shown in the reaction scheme, (1) escaping of the SDS radical from the triplet radical pair $(NQH\cdot\cdot R)^3$ is competing with the product (nonradical species) formation via singlet radical pair $(NQH\cdot\cdot R)^1$. (2) SDS radical is an alkyl radical and very reactive. Therefore, before being trapped by PBN, some part of the radical may react with other components, such as naphthosemiquinone, other SDS radical, etc. Besides, (3) the UV light was irradiated through the grid of the ESR cavity wall: i.e., only 50% of the reactant solution was irradiated. Taking into account these yield-determining factors, (1)-(3), the yield of the spin adduct (about 9% of the initial NQ) is quite large, thus the trapped SDS radical is not due to a side reaction which does not appear in the reaction scheme. Because the spin trapping process may not likely have dependence on magnetic field strength, we conclude that the yield of SDS radical itself have a dependence on the magnetic field strength qualitatively in the same manner as Figure 2B.

A slight increase in the yield of the spin adduct from 0.14 to 0.5 T was noticed. Sakaguchi and Hayashi[4] also observed a steady increase in the UV absorption of naphthosemiquinone up to 1.4 T, and they interpreted this phenomenon with the spin relaxation effect.

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Selective Hydroformylation of Ethylene on Rh-Zn/SiO_2. An Apparent Example of Site Isolation of Rh and Lewis Acid Promoted CO Insertion

M. Ichikawa,* A. J. Lang, D. F. Shriver,* and W. M. H. Sachtler*

Ipatieff Laboratory and Department of Chemistry Northwestern University, Evanston, Illinois 60201

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The hydrogenation of CO over supported metal catalysts to form simple hydrocarbons and oxygen-containing products appears to proceed by the elementary steps outlined in Scheme I.[1] The step requiring the largest ensemble of contiguous surface metal atoms is the dissociation of adsorbed CO (1).[2] Oxygenates appear to result from migratory insertion between a surface alkyl and surface CO (3).[3] The generation of hydrocarbons by H addition or β-H elimination of surface alkyl groups (5) competes with the migratory CO insertion process (3).[3]

High yields of oxygen-containing products are achieved with supported rhodium, which has been promoted by cations of certain electropositive metals. The mode of action of these promoters on the elementary steps in CO hydrogenation is a topic of considerable interest and debate.[3,4] It has been proposed that (a) the electropositive promoter ion stabilizes a catalytically active oxidation state of rhodium,[4a,5] (b) the promoter blocks sites that

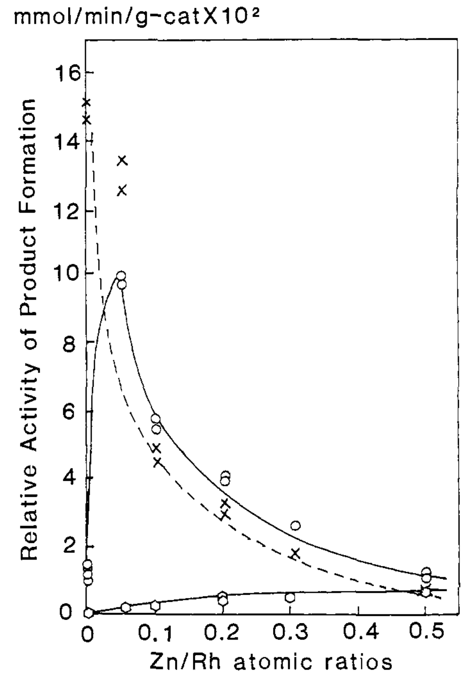
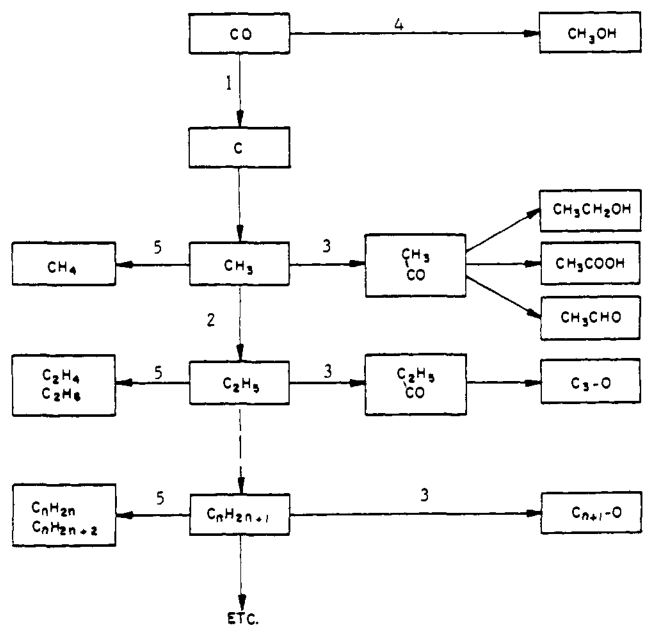


Figure 1. Rates of product formation (mmol/min/g of catalyst) C_2H_5CHO (O), C_3H_7OH (O), and C_2H_6 (×), by changing Zn contents (Zn/Rh atomic ratios) in SiO_2-supported Rh-Zn catalysts. Catalyst; 4.0 wt % Rh loading, 0.4-0.5 g. Reaction conditions: C_2H_4:CO:H_2 = 10:10:10 mL/min, 180 ± 2 °C, 1 atm, SV = 1200 L/L/h.

Scheme I



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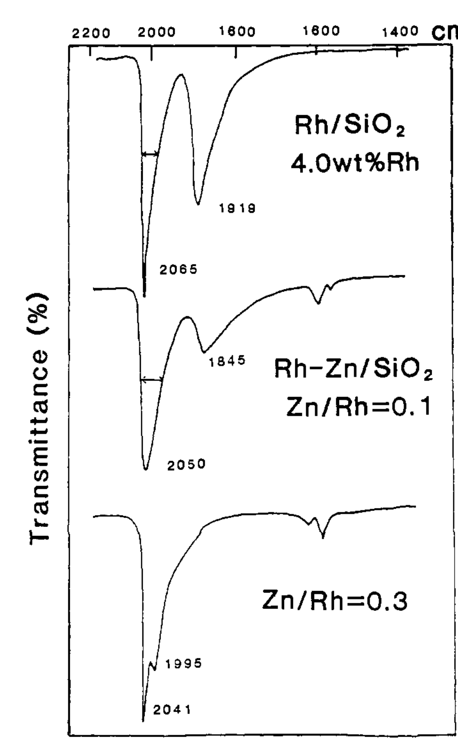
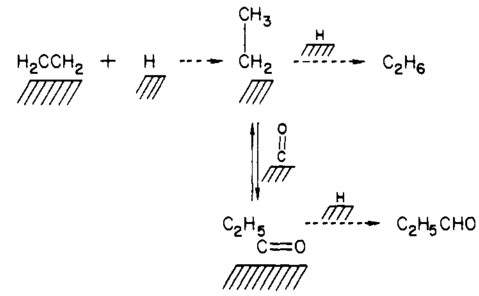


Figure 2. IR spectra of CO chemisorbed on Rh–Zn/SiO_2 as a function of Zn content (Zn/Rh atomic ratios: 0, 0.1, 0.3) 4.0 wt % loading Rh, CO 1 atm for 2 min at 25 °C, replaced CO with argon at 1 atm.

favor CO dissociation,[2] or (C) the promoter might accelerate the CO insertion step by direct interaction with the oxygen of the adsorbed CO.

These interpretations are not mutually exclusive. The catalytic evidence shows[3,4] that two types of promoters must be discerned on rhodium: (a) Highly oxophilic elements such as Mn, Ti, or Zr that are present as (sub-) oxides and form an incomplete overlayer on the metal; they interact with the O atom of CO, coadsorbed on the same metal, thus weakening the C–O bond, favoring CO dissociation and, hence, the formation of CH_4 or alkyl groups.[1a,15] (b) The second group includes Zn, Mg, and Fe, they suppress CH_4 formation but promote CH_3OH formation, evidently by impeding CO dissociation and accelerating migratory insertion of adsorbed CO. In order to investigate the insertion into Rh–alkyl bonds without the complexities of syngas conversion, we have chosen to study the influence of Zn ions on the Rh-catalyzed hydroformylation. Further information on the nature of the catalytic surface was obtained from an infrared spectroscopic study of the effect of the Zn ions on the nature of adsorbed CO.

Scheme II



As shown in Figure 1, the addition of Zn to Rh/SiO_2 increases the hydroformylation activity up to 50 times over that of the unpromoted catalyst.[6,7] Moreover, the selectivity toward hydroformylation, expressed by the ratio C_2H_5CHO/C_2H_6, is improved by a factor of 15 by the addition of Zn at Zn/Rh = 0.05–0.3. Apparent activation energies for hydroformylation were found to be 71 ± 8 kJ/mol for Rh/SiO_2 and 59 ± 8 kJ/mol for Zn/Rh/SiO_2. For the hydrogenation of ethylene, the measured activation energy was 121 kJ/mol for Rh/SiO_2 and 134–167 kJ/mol for Zn–Rh/SiO_2, in which Zn/Rh = 0.05–0.2. These measurements were performed in the temperature range 150–200 °C. The addition of Zn also completely suppresses the formation of methane. The latter result suggests that Zn blocks sites for CO dissociation and increases selectivity toward hydroformylation. At the Zn/Rh ratio of 0.3 also CO insertion into surface ethyl groups is favored over the hydrogenation of surface ethyl groups to ethane (Scheme II).

The nature of the surface carbon monoxide was studied by infrared spectroscopy. Samples were prepared by adsorbing carbon monoxide on a series of catalysts with 4 wt % Rh/SiO_2 and increasing quantities of Zn. Infrared spectra for these samples are shown in Figure 1.[8] Two strong bands at 2065 (HF band) and 1918 (LF band) cm^{-1} for CO on Rh/SiO_2 are reasonably assigned to the linearly bonded (terminal) carbonyl and bridging carbonyl, respectively. In the absence of added Zn the two bands are of comparable intensity, but with increasing Zn content the LF band attributed to bridging CO decreases significantly and the HF band broadens and splits into a doublet (2041 and 1995 cm^{-1}) at high Zn content. In the presence of Zn, weak but distinct bands also are observed at 1620 and 1580 cm^{-1}. The dramatic change in the ratio of intensities of bridging and linear CO is similar to earlier observations with Fe-promoted Rh/SiO_2[11] and qualitatively different from the IR evidence obtained with oxophilic promoters on Rh.[4c] Clearly, a specific effect of the promoting cation is revealed. The observation is strikingly similar to that in our earlier work with Pd and PdAg alloys[10] and strongly suggests that an analogous interpretation is valid: the multicenter or "Freundlich" sites on the Rh surface are blocked by the Zn ions, forcing the adsorbing CO molecules into the "on top" or "linear" positions. Electroneutrality requires, of course, that anions also are occupying surface sites on Rh; but the striking difference between the two groups of cations would justify our interpretation

(6) Catalysts were prepared by a conventional coimpregnation method. SiO_2 gel (Carb-o-sil 300; 60–80 mesh granule Davison Grade no. 62, surface area = 260–280 m^2/g) was impregnated with $RhCl_3 \cdot 3H_2O$ (Johnson Mathey, Inc.), and $ZnCl_2$ (Mallinckrodt, Inc.), from methanol solutions. After removal of solvent, the impregnated catalysts were reduced by flowing H_2 (1 atm, 35–40 mL/min) at a temperature rising from 200 to 400 °C and held at 400 °C for 6 h, oxidized, and again reduced in H_2 at 400 °C.

(7) Hydroformylation of ethylene was carried out with a flow mode Pyrex-glass reactor (i.d. = 6 mm and 200 mm long tubing) into which the catalyst, 0.4–0.5 g, was charged. A mixture gas of C_2H_4, CO, and H_2 (1:1:1 volume ratios) was introduced at 30 mL/min and 150–200 °C. The gases, C_2H_4, H_2, and CO, had a purity higher than 99.9 vol % and were pretreated with Mn/MnO and MS-5A to eliminate oxygen, moisture, and possible carbonyls such as $Fe(CO)_5$ and $Ni(CO)_4$. The oxygenated products such as C_2H_5CHO and C_3H_7OH were collected in a water trap and analyzed by FID GLC using a Porapak P column (4 m, He carrier) at 165 °C. The effluent gas was also analyzed for C_1–C_5 hydrocarbons by a FID GC, with a "pona" 50 m, 0.2-mm diameter capillary column which was temperature-programmed from 0 to 70 °C.

(8) For IR observation, the samples were dried and pressed into wafers, which were reduced in a H_2 flow. After cooling to room temperature, H_2 was replaced by argon and the sample was passivated by air oxidation. The catalyst was again reduced in the IR cell with an H_2 flow at 400 °C for 2 h, and then H_2 was replaced by ultrapure argon. The IR spectra were recorded of a Nicolet 60SX single-beam Fourier transform infrared spectrometer at a resolution of 1 cm^{-1}. Generally, 20–100 interferograms were coadded to improve signal-to-noise ratios. CO was introduced at 20 °C and 1 atm to the catalyst disk, and then the cell was purged with argon. The background spectra were obtained on a catalyst wafer which had been reduced with H_2 but not exposed to CO.

(9) Sites that the adsorbed moiety would occupy if it were an atom of the same element as the adsorbent, i.e., if the metal crystal grew in its own vapor, are called "Freundlich sites".

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that the blocking of Freundlich sites by zinc ions is dominantly responsible for the dramatic reversion of relative band intensities; i.e., CO is forced into the linear mode.

Weaker bands in the vicinity of 1600 cm^{-1} may arise from CO that is C coordinated to Rh and O coordinated to Zn similar to the case of the Mn-promoted Rh.[13,1a] These carbonyl groups may account for an apparent increase in CO insertion rate in the presence of Zn, because carbonyl interaction with electron acceptors is implicated in dramatic increases in the rate of CO insertion in organometallic compounds.[14]

In summary, Zn atoms or ions on Rh apparently occupy Freundlich sites which block CO dissociation. The Zn also appears to increase the rate of CO insertion as indicated by an increase in selectivity for C_2H_5CHO formation.

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Comparisons of the Heterobimetallic and Heterotrimetallic Anions $HFeW(CO)_9^-$ and $Ph_3PAuFeW(CO)_9^-$

Larry W. Arndt, Marcetta Y. Darensbourg,*
John P. Fackler, Jr., Richard J. Lusk, David O. Marler, and Kay A. Youngdahl

Department of Chemistry, Texas A&M University
College Station, Texas 77843

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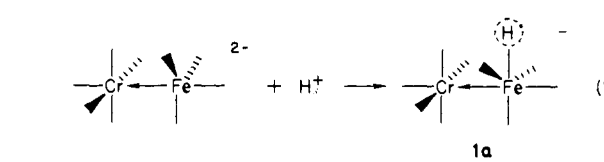
Recently we reported, without benefit of a neutron diffraction study and location of the hydride position, the molecular structure of $PPN^+HFeW(CO)_9^-$, a mixed-metal adduct formed when $HW(CO)_5^-$ reacted with $Fe(CO)_5$ or when $HFe(CO)_4^-$ was added to $THF{\cdot}W(CO)_5$.[1] Because of the ^1H chemical shift (−11.8 ppm), the observation of W–H coupling (J_{WH} = 15.0 Hz), and the occurrence of hydride bridge bonding in both parents $(\mu_2\text{-H})(\mu_2\text{-CO})_2Fe_2(CO)_6^-$ and $(\mu_2\text{-H})W_2(CO)_{10}^-$,[2,3] we referred to this new heterobimetallic hydride as a "bridging" or "semibridging" hydride, possessing considerable Fe–H terminal character. Subsequent theoretical[4] and experimental[5,6] work is convincing of the dominant metal-based, rather than hydride-based, nucleophilicity in anionic iron hydrides, and the possibility that the hydride ligand in $HFeW(CO)_9^-$ had *no* bridge bonding contributing to the ground state returned to confront us. Most convincing was the lack of change in bond length upon protonation of the $FeCr(CO)_9^{2-}$ dianion to yield $HFeCr(CO)_9^-$ (**1a**) (eq 1; (H) represents unlocated hydride, expected position).[6]



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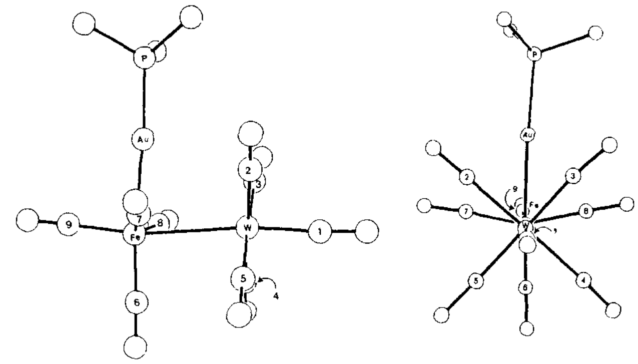

Figure 1. Molecular structure of $Ph_3PAuFeW(CO)_9^-$, a side view and along the C9–Fe–W–C1 bond axis. Selected distances (Å): Fe–W, 3.012 (3); Fe–Au, 2.520 (3); Au–P, 2.268 (5); W–C1, 1.880 (25); W–C2, –C3, –C4, –C5 (av) 1.942 (29); Fe–C9, 1.782 (26); Fe–C7, 1.756 (28); Fe–C8, 1.823 (23); Fe–C6, 1.780 (30). Angles (deg): Au–Fe–W, 82.7 (1); Fe–Au–P, 174.4 (2); C9–Fe–C6, –C7, –C8 (av) 100.7 (11); C7–Fe–C6, 102.0 (7); C8–Fe–C6, 101.7 (6); C8–Fe–C7, 144.1 (12); Au–Fe–C7, 78.7 (8); Au–Fe–C8, 74.7 (6); Fe–C9–O9, 178.1 (10); Fe–C6–O6, 176.8 (10); Fe–C7–O7, 171.6 (26); Fe–C8–O8, 171.7 (9).

The use of Ph_3PAu^+ as an ersatz H^+ has become a popular exercise of late.[7] Isolobal with H via an s, p_z, and d_{z^2} hybrid orbital, the Ph_3PAu ligand has low-lying p_x and p_y orbitals. The presence of the latter serve to explain the tendency (greater than that of H) of Ph_3PAu to form bridge bonds, either with other metals, hydrogen, or itself, as in $(OC)_4Fe(AuPPh_3)_2$ (strong Fe–Au bonds, partial Au- -Au interaction),[8] $(OC)_5V(AuPPh_3)_3$ (VAu_3 cluster with strong metal–metal bonds),[9] and $(OC)_5Cr–H–AuPPh_3$.[10] In fact there was, until the work reported herein, no example of a Ph_3PAu derivative of a bimetallic or cluster compound that has Ph_3PAu as a terminal ligand. Neither is there known an anionic complex $(OC)_xM–AuPPh_3^-$ analogous to the well-known anionic hydrides such as $HFe(CO)_4^-$ or $HW(CO)_5^-$.

This report is of the synthesis, X-ray crystal structure, and characterization of $Et_4N^+Ph_3PAuFeW(CO)_9^-$, a unique heterotrimetallic which again demonstrates the remarkable ability of $Fe^{\delta-}$ to dominate metal–metal′ donor–acceptor bond formation, permitting no bridging character to the Ph_3PAu ligand. The complex anion is a precise structural mimic of the $HFeW(CO)_9^-$ anion, and, in analogy, contains the $Ph_3PAuFe(CO)_4^-$ anion as ligand to $W(CO)_5{}^0$.

Synthesis of $Ph_3PAuFeW(CO)_9^-$ (2c). A schematic of the synthesis of Et_4N^+**2c** is given in eq 2 and 3 and details are available

$$Fe(CO)_5 \xrightarrow[-CO_2]{Et_4N^+OH^-} HFe(CO)_4^- \xrightarrow{THF\cdot W(CO)_5} \underset{\mathbf{1c}}{Et_4N^+\ HFeW(CO)_9^-} \quad (2)$$

$$Et_4N^+\ \mathbf{1c} \xrightarrow[-H_2O]{Et_4N^+OH^-} [Et_4N]_2FeW(CO)_9 \xrightarrow{Ph_3PAuCl} \underset{\mathbf{2c}}{Et_4N^+\ Ph_3PAuFeW(CO)_9^-} \quad (3)$$

as supplementary material.[11] Although the bright orange crystalline Et_4N^+**2c** was stable to moisture and showed only slow decomposition in the air, it was routinely manipulated under anaerobic conditions.

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(11) All group 6 derivatives of $HFeM(CO)_9^-$ (**1a**, M = Cr; **1b**, M = Mo; **1c**, M = W) have been characterized as well as the analogous $Ph_3PAuFeM(CO)_9^-$ anions, **2a**, **2b**, and **2c** where M = Cr, Mo, and W, respectively.

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