

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 $\text{C}_2\text{H}_5\text{CHO}$ formation.

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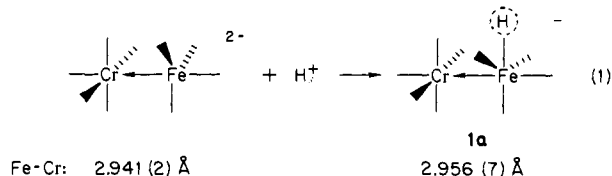
Comparisons of the Heterobimetallic and Heterotrimetallic Anions $\text{HFeW}(\text{CO})_9^-$ and $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$

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Recently we reported, without benefit of a neutron diffraction study and location of the hydride position, the molecular structure of $\text{PPN}^+\text{HFeW}(\text{CO})_9^-$, a mixed-metal adduct formed when $\text{HW}(\text{CO})_5^-$ reacted with $\text{Fe}(\text{CO})_5$ or when $\text{HFe}(\text{CO})_4^-$ was added to $\text{THF}\cdot\text{W}(\text{CO})_5$.¹ Because of the ^1H chemical shift (-11.8 ppm), the observation of W-H coupling ($J_{\text{WH}} = 15.0$ Hz), and the occurrence of hydride bridge bonding in both parents ($\mu_2\text{-H}(\mu_2\text{-CO})_2\text{Fe}_2(\text{CO})_6^-$ and $(\mu_2\text{-H})\text{W}_2(\text{CO})_{10}^{2-}$,^{2,3} we referred to this new heterobimetallic hydride as a "bridging" or "semibridging" hydride, possessing considerable Fe-H terminal character. Subsequent theoretical⁴ 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 $\text{HFeW}(\text{CO})_9^-$ 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 $\text{FeCr}(\text{CO})_9^{2-}$ dianion to yield $\text{HFeCr}(\text{CO})_9^-$ (**1a**) (eq 1; H^- represents unlocated hydride, expected position).⁶



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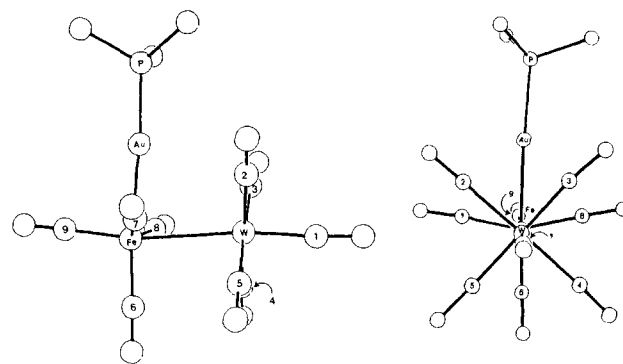
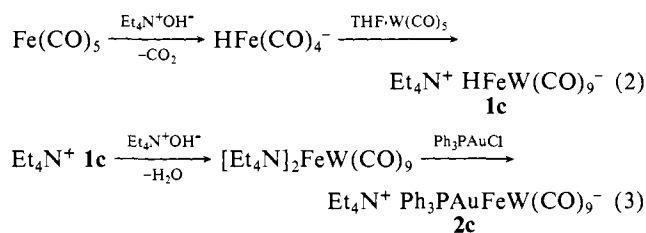


Figure 1. Molecular structure of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$, a side view and along the C9-Fe-W-C1 bond axis. Selected distances (\AA): Fe-W, 3.012 (3); Fe-Au, 2.520 (3); Au-P, 2.268 (5); W-C1, 1.880 (25); W-C2, -C3, -C4, -C5 (av) 1.942 (29); Fe-C9, 1.782 (26); Fe-C7, 1.756 (28); Fe-C8, 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 $(\text{OC})_4\text{Fe}(\text{AuPPh}_3)_2$ (strong Fe-Au bonds, partial Au-Au interaction),⁸ $(\text{OC})_5\text{V}(\text{AuPPh}_3)_3$ (VAu_3 cluster with strong metal-metal bonds),⁹ and $(\text{OC})_5\text{Cr-H-AuPPh}_3$.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 $(\text{OC})_x\text{M-AuPPh}_3^-$ analogous to the well-known anionic hydrides such as $\text{HFe}(\text{CO})_4^-$ or $\text{HW}(\text{CO})_5^-$.

This report is of the synthesis, X-ray crystal structure, and characterization of $\text{Et}_4\text{N}^+\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$, a unique heterotrimetallic which again demonstrates the remarkable ability of $\text{Fe}^{\delta-}$ 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 $\text{HFeW}(\text{CO})_9^-$ anion, and, in analogy, contains the $\text{Ph}_3\text{PAuFe}(\text{CO})_4^-$ anion as ligand to $\text{W}(\text{CO})_5^0$.

Synthesis of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ (2c**).** A schematic of the synthesis of $\text{Et}_4\text{N}^+\text{2c}$ is given in eq 2 and 3 and details are available



as supplementary material.¹¹ Although the bright orange crystalline $\text{Et}_4\text{N}^+\text{2c}$ 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 $\text{HFeM}(\text{CO})_9^-$ (**1a**, M = Cr; **1b**, M = Mo; **1c**, M = W) have been characterized as well as the analogous $\text{Ph}_3\text{PAuFeM}(\text{CO})_9^-$ anions, **2a**, **2b**, and **2c** where M = Cr, Mo, and W, respectively.

The complex $\nu(\text{CO})$ IR band patterns for $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ and $\text{HFeW}(\text{CO})_9^-$ are practically identical. All band positions of $\text{HFeW}(\text{CO})_9^-$ are displaced to higher frequencies by $\sim 20 \text{ cm}^{-1}$ from those of $\text{Et}_4\text{N}^+\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ (in THF, 2043 m, 1967 ms, 1917 s, 1895 sh, 1849 m). The lower field ^{13}C resonances of the carbonyl carbons of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ compared to $\text{HFeW}(\text{CO})_9^-$ are, like the comparative $\nu(\text{CO})$ IR data, consistent with greater negative charge on the carbonyl groups of the gold derivative.^{7b,12}

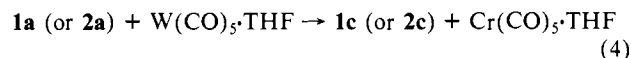
X-ray Crystal Structure.¹³ Two views of $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ (**2c**) shown in Figure 1, were selected to easily relate to those presented earlier for $\text{HFeW}(\text{CO})_9^-$. The Fe, W, and CO arrangements and distances are practically identical for the two structures. Tungsten is in a regular octahedral array in both. In **2c**, the iron center is six-coordinate and may be described as a highly distorted octahedron or as a bicapped tetrahedron. Carbonyls **7** and **8**, bound to Fe and mutually cis to both Au and W, are bent ($\angle\text{Fe-C-O}$ av 171.6 (26)^o). The Au-C7 and Au-C8 distances (2.776 (23) and 2.688 (28) Å, respectively) but not the W-C7 and W-C8 distances (3.201 (28) and 3.129 (29) Å, respectively) are within van der Waals radii. All other intermetal-ligand distances are > 3.3 Å.

The gross coordination environment about Fe is reminiscent of structures of $\text{Fe}(\text{CO})_4^{2-}$ which show hard cations penetrating the tetrahedral anion: $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5$ dioxane,¹⁴ [(dipy)- $\text{CdFe}(\text{CO})_4$]₃,¹⁵ and [$\text{CdFe}(\text{CO})_4$]₄·2 acetone.¹⁶ In the case of $\text{Na}_2\text{Fe}(\text{CO})_4$, the similar bent Fe-C-O and close $\text{Na}^+ \cdots \text{C}$ interaction distance (2.86 Å) are accepted as a way of gaining electrostatic interaction between Na^+ and Fe^{2-} via the electrons delocalized into C_{π^*} .¹⁴ The arrangement in $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ suggests a similar *inverse* direct donation¹⁷ of $\text{Fe}_{d\pi}$ electrons to Ph_3PAu^+ via C_{π^*} .

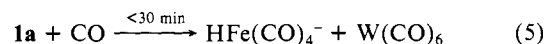
The W-Au distance of 4.12 Å rules out any bonding between these atoms. In contrast, the distance between Cr and Au in $(\text{OC})_5\text{Cr-H-AuPPh}_3$ is 2.770 Å,¹⁰ between W and Au in $(\text{OC})_2\text{W}(\mu\text{-CHR})\text{AuPPh}_3$ is 2.729 Å, and between Au atoms in $\text{Fe}(\text{CO})_4(\text{AuPPh}_3)_2$ is 3.028 (1) Å.⁸ The Fe-Au distance of 2.520 (3) Å is identical with that of the one known compound which has a terminal Fe-Au bond, $(\eta^3\text{-C}_3\text{H}_5)\text{Fe}(\text{CO})_3\text{AuPPh}_3$.¹⁸

In summary, the structure of **2c** is viewed as the interaction of $\text{Fe}(\text{CO})_4^{2-}$ with two metalloelectrophiles: one, 16-electron $\text{W}(\text{CO})_5$ forms a metal-metal donor-acceptor bond with the iron nucleophile; the second, the more demanding 12-electron Ph_3PAu^+ accepts electrons both directly from the iron and indirectly from the electron-rich iron carbonyl carbons. The extreme similarity of the metal carbonyl frameworks suggests the hydrogen in **1c**, like the Ph_3PAu in **2c**, to be a terminal ligand.

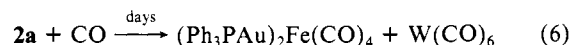
Despite identical Fe-W and nearly identical M-C bond distances in $\text{HFeW}(\text{CO})_9^-$ and $\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$, the latter is substantially more robust. The anions are reactive to both electrophiles and nucleophiles. For example, $\text{HFeCr}(\text{CO})_9^-$ reacts with $\text{THF} \cdot \text{W}(\text{CO})_5$ within time of mixing to generate **1c**. The analogous reaction of $\text{Ph}_3\text{PAuFeCr}(\text{CO})_9^-$ (**2a**) requires 2 h (eq 4). Carbon monoxide disrupts **1c** within minutes according to



eq 5. Complete reaction of **2a** with CO requires several days



and the iron-containing product is the neutral bis((triphenylphosphine)gold) complex (eq 6). Phosphines also cleave the



dimers, much more slowly than CO, with similar results. That is, the very stable $\text{HFe}(\text{CO})_4^-$ ligand is readily displaced from $\text{W}(\text{CO})_5^0$ whereas the $\text{Ph}_3\text{PAuFe}(\text{CO})_4^-$ "ligand" is unknown as an isolated species.^{19,20} Whether this fact bears on the reactivity, and indeed the mechanism of these cleavage reactions, warrants future study.

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Supplementary Material Available: Detailed synthesis, characterization, X-ray structural analysis, atomic positional and thermal parameters, all bond lengths and angles, anisotropic thermal parameters, and observed and calculated structure factors for $\text{Et}_4\text{N}^+\mathbf{2c}$ (27 pages). Ordering information is given on any current masthead page.

(19) Several attempts to prepare $\text{Ph}_3\text{PAuFe}(\text{CO})_4^-$, via reaction of Ph_3PAuCl with $\text{Fe}(\text{CO})_4^{2-}$, all resulted in formation of $(\text{Ph}_3\text{PAu})_2\text{Fe}(\text{CO})_4$. In contrast, we have good evidence for the anion *cis*- $\text{Ph}_3\text{PAuW}(\text{CO})_4\text{PMe}_2^-$ prepared via a similar route.²⁰

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Direct Observation of the Initial Insertion of an Unsaturated Hydrocarbon into the Titanium-Carbon Bond of the Soluble Ziegler Polymerization Catalyst, $\text{Cp}_2\text{TiCl}_2\text{-MeAlCl}_2^1$

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Despite more than 25 years of intensive study, the precise nature of the active center formed from the soluble, two-component ethylene polymerization catalyst $\text{Cp}_2\text{TiCl}_2\text{-R}_n\text{AlCl}_{3-n}$ has remained uncertain.²⁻⁵ We therefore are pleased to report that by using a highly substituted surrogate for ethylene, namely, trimethyl-(phenylethynyl)silane (**1**), we have been able, for the first time, to intercept, isolate, and determine the crystal structure of the initial insertion product formed in such a so-called Ziegler catalyst

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(13) Single crystals of $\text{Et}_4\text{N}^+\text{Ph}_3\text{PAuFeW}(\text{CO})_9^-$ were grown from THF/hexane. Data collection was carried out at 22 °C, using a Nicolet P3F automated diffractometer, Mo $K\alpha$ radiation. The space group is $P\bar{1}$ with $a = 13.008$ (5) Å, $b = 13.974$ (6) Å, $c = 14.110$ (7) Å, $\alpha = 99.14$ (4)^o, $\beta = 116.63$ (3)^o, $\gamma = 101.01$ (3)^o. Intensity data were collected for 5989 reflections of which 2766 were unique and measured $F_o^2 > 3\sigma F_o^2$ and were used for structure solution and refinement using SHELXTL. The last cycle of least-squares refinement gave residuals of $R = 0.0569$, $R_w = 0.068$, and a goodness of fit indicator of 1.786 for a fit of 419 variables to 2766 observations. Complete details of the refinement along with tables are available as supplementary material.

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