Å)[20] and (η^5-C$_5$H$_5$)(PPh$_3$)(NO)ReCH$_2$Ph (1.749 (7) Å)[26] and deserve no comment.

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Semibridging Interactions and Conformational Equilibria in Methoxymethylidyne Cluster Complexes. Syntheses, Spectroscopic, and X-ray Crystallographic Studies on CoFe$_2$(μ-H)(μ_3-COCH$_3$)(CO)$_7$(η-C$_5$H$_5$), Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$), and AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(PPh$_3$)(η-C$_5$H$_5$)

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Treatment of Fe$_3$(μ-H)(μ-COCH$_3$)(CO)$_{10}$ (1) in toluene at 363 K with either Co(CO)$_2$(η-C$_5$H$_5$) or [Ni-(CO)(η-C$_5$H$_5$)]$_2$ affords CoFe$_2$(μ-H)(μ_3-COCH$_3$)(CO)$_7$(η-C$_5$H$_5$) (2) or Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (3), respectively. Formation of **3** was accompanied by minor quantities of FeNi(μ-CO)$_2$(CO)(η-C$_5$H$_5$)$_2$ (4) and Fe$_3$(μ_3-COCH$_3$)(μ-CO)$_2$(CO)$_6$(η-C$_5$H$_5$) (5). Complexes **2–5** were characterized by IR, NMR, and mass spectroscopies, with single-crystal X-ray diffraction studies on **2** and **3**. Crystal data for **2**: P2$_1$/a, a = 13.901 (1) Å, b = 8.207 (1) Å, c = 14.725 (2) Å, β = 85.973 (8)°, Z = 4, final R (R$_w$) values 0.028 (0.036) for 1990 independent observed data. The CoFe$_2$ triangle is asymmetrically capped by a μ_3-COCH$_3$ group (Fe(1)–C(8) = 1.871 (4) Å; Fe(2)–C(8) = 1.877 (4) Å; Co(1)–C(8) = 2.001 (4) Å), the carbonyl group on Co(1) showing slight semibridging interactions with the two iron atoms (Fe(1)···C(7) = 2.559 (4) Å; Fe(2)···C(7) = 2.629 (5) Å). Crystal data for **3**: P1̄, a = 7.930 (3) Å, b = 8.338 (1) Å, c = 13.474 (2) Å, α = 96.97 (1)°, β = 98.97 (2)°, γ = 107.12 (2)°, Z = 2, final R (R$_w$) values 0.030 (0.040) for 3482 independent observed data. The NiFe$_2$ triangle is nearly symmetrically capped by a μ_3-carbonyl ligand (Ni(1)–C(7) = 1.944 (3) Å; Fe(1)–C(7) = 2.056 (3) Å; Fe(2)–C(7) = 2.065 (3) Å), the μ_3-COCH$_3$ group being approximately equidistant from the three metal atoms (Ni(1)–C(8) = 1.959 (3) Å; Fe(1)–C(8) = 1.902 (3) Å; Fe(2)–C(8) = 1.888 (3) Å). Treatment of **2** with AuCH$_3$(PPh$_3$) in toluene at 363 K afforded AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$-(PPh$_3$)(η-C$_5$H$_5$) (6), thereby replacing μ-H by μ-AuPPh$_3$. Crystal data for **6**: P2$_1$/n, a = 13.669 (3) Å, b = 14.313 (5) Å, c = 16.665 (4) Å, β = 103.12 (2)°, Z = 4, final R (R$_w$) values 0.024 (0.031) for 4257 independent observed data. The C(7)–Fe(1) and C(7)–Fe(2) interactions (2.322 (6) and 2.362 (6) Å, respectively) are noticeably greater than in **2**. Variable-temperature ^{13}C NMR spectra on **2**, **3**, and **6** indicate conformational equilibria in solution, with two distinct species observable in IR studies on **3**. These data indicate there to be a soft potential energy surface relating the μ_3 and semi μ_3 bonding configurations of the methoxymethylidyne group about the trimetallic cluster.

Introduction

There is currently great interest in the chemistry of cluster complexes containing alkylidyne ligands, due partly to the putative involvement of such intermediates in the catalytic reduction of CO by H$_2$,[1] with strong evidence also existing for similar species in the chemisorption of hydrocarbons at metal surfaces.[2] In contrast to the rapidly developing chemistry of cluster species containing the μ-CR (R = aryl, alkyl) ligand,[3] relatively little work has been

reported on corresponding alkoxy-substituted derivatives. This is in spite of the availability of facile, high yield synthetic routes to such complexes via O-alkylation of bridging carbonyl ligands in anionic clusters, e.g., reaction of [M$_3$(μ-H)(μ-CO)(CO)$_{10}^-$] with CH$_3$SO$_3$F to give M$_3$(μ-H)(μ-COCH$_3$)(CO)$_{10}$ (1a, M = Fe;[4] 1b, M = Ru;[5] 1c, M = Os[6]). Reports in the literature on the reactivity of cluster-bound μ-COR groups are sparse however. Shapley et al. have achieved alkylidyne carbon functionalization by

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(1. a M = Fe, 1. b M = Ru, 1. c M = Os)
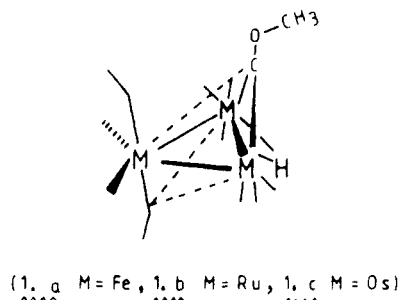
sequential treatment of **1b** or **1c** with a nucleophile (H⁻ or Ph⁻) followed by an electrophile (H⁺ or CH₃⁺) resulting in the interesting complexes $M_3(\mu\text{-H})(\mu\text{-CR})(CO)_{10}$ (M = Ru, R = H;[7] M = Os, R = H,[8] Ph[9]). Moreover C–C bond formation involving incorporation of COC_2H_5 or $COCH_3$ ligands into metallacyclic systems via reaction with alkynes has recently been demonstrated by Mathieu[10] and Keister.[11] The $\mu\text{-COCH}_3$ ligand may serve as a model for chemisorbed intermediates in the Fischer–Tropsch type formation of C_2 oxygenates,[12] particularly in view of studies by Keister et al.[13,14] on hydrogenolysis of **1b** whereby organic molecules such as $(CH_3)_2O$ and HCO_2CH_3 were detected.

Synthetically, transition-metal complexes containing μ-alkylidyne ligands have proved extremely useful precursors in the stepwise designed build up of heteronuclear cluster compounds,[3] due to the high reactivity of the metallacyclopropene ring. Our interest lay in examining the potential of complexes **1**, containing a μ-alkoxyalkylidyne linkage, as source materials for such syntheses. Earlier results have demonstrated that novel reaction pathways involving the $\mu\text{-COCH}_3$ ligand were possible. Thus although treatment of **1a** with $Pt(C_2H_4)_2(PPh_3)$ afforded[15] the expected tetranuclear complex $Fe_3Pt(\mu_3\text{-H})(\mu_3\text{-COCH}_3)(CO)_{10}(PPh_3)$ containing a triply bridging $COCH_3$ group, the corresponding reaction of **1c** with $Pt(C_2H_4)_2\text{-}(PCy_3)$ (Cy = $c\text{-}C_6H_{11}$) resulted[16] in an unusual pentanuclear cluster compound, $Os_3Pt_2(\mu\text{-H})(\mu_5\text{-C})(\mu\text{-OCH}_3)(\mu\text{-CO})(CO)_9(PCy_3)_2$. The μ_5-carbido and $\mu\text{-OCH}_3$ ligands in this compound presumably result from C–O bond cleavage of the $COCH_3$ moiety in the precursor, a reaction which occurs under mild conditions.

Herein we report cluster syntheses involving the complex $Fe_3(\mu\text{-H})(\mu\text{-COCH}_3)(CO)_{10}$ (**1a**) and discuss the structural features, in the solid state and solution, that these new compounds display.

Results and Discussion

Reaction of **1a** with a slight excess of $Co(CO)_2(\eta\text{-}C_5H_5)$ in toluene at 363 K affords the dark green-brown trinuclear mixed-metal complex $CoFe_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(CO)_7(\eta\text{-}$

Figure 1. Molecular geometry and atomic labeling scheme for the complex $CoFe_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(CO)_7(\eta\text{-}C_5H_5)$ (2).

Table I. Atomic Positional (Fractional Coordinate) Parameters with Estimated Standard Deviations in Parentheses for the Complex $CoFe_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(CO)_7(\eta\text{-}C_5H_5)$ (2)

atom	x	y	z
Fe(1)	0.13580 (4)	0.01000 (7)	0.66257 (4)
Fe(2)	0.06229 (4)	-0.02701 (7)	0.82815 (4)
Co(1)	0.06285 (4)	-0.25766 (6)	0.71485 (4)
O(1)	0.2477 (3)	-0.1724 (5)	0.5240 (3)
O(2)	0.0175 (3)	0.1997 (4)	0.5407 (3)
O(3)	0.2970 (3)	0.2284 (4)	0.6840 (3)
O(4)	0.0335 (3)	-0.2816 (5)	0.9638 (3)
O(5)	0.1738 (3)	0.1910 (5)	0.9350 (3)
O(6)	-0.1284 (3)	0.1274 (6)	0.8643 (3)
O(7)	-0.1003 (2)	-0.0726 (4)	0.6665 (2)
O(8)	0.25619 (18)	-0.17189 (38)	0.77746 (20)
C(1)	0.2023 (4)	-0.1025 (6)	0.5776 (3)
C(2)	0.0623 (3)	0.1246 (5)	0.5867 (3)
C(3)	0.2325 (3)	0.1498 (5)	0.6744 (3)
C(4)	0.0447 (3)	-0.1807 (6)	0.9102 (3)
C(5)	0.1292 (4)	0.1076 (6)	0.8938 (3)
C(6)	-0.0552 (3)	0.0659 (6)	0.8494 (3)
C(7)	-0.0295 (3)	-0.1262 (5)	0.6882 (3)
C(8)	0.1679 (3)	-0.1198 (5)	0.7604 (3)
C(9)	0.2752 (4)	-0.2196 (8)	0.8675 (4)
C(10)	0.1493 (4)	-0.4549 (5)	0.6782 (5)
C(11)	0.1043 (7)	-0.4814 (6)	0.7641 (4)
C(12)	0.0038 (6)	-0.4820 (7)	0.7540 (7)
C(13)	-0.0068 (4)	-0.4556 (7)	0.6649 (7)
C(14)	0.0793 (5)	-0.4403 (6)	0.6183 (4)
H(1)	0.574 (3)	0.385 (5)	0.743 (3)

Table II. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for the Complex $CoFe_2(\mu\text{-H})(\mu_3\text{-COCH}_3)(CO)_7(\eta\text{-}C_5H_5)$ (2)

Bond Lengths			
Fe(1)–Fe(2)	2.594 (1)	Fe(1)···C(7)	2.559 (4)
Fe(1)–Co(1)	2.517 (1)	Fe(2)···C(7)	2.629 (5)
Fe(2)–Co(1)	2.523 (1)	Co(1)–C(7)	1.742 (5)
Fe(1)–C(8)	1.871 (4)	C(7)–O(7)	1.144 (6)
Fe(2)–C(8)	1.877 (4)	C(9)–O(8)	1.424 (7)
Co(1)–C(8)	2.001 (4)	Fe–C_carbonyl(av)	1.785 [2]
C(8)–O(8)	1.340 (5)	Fe_carbonyl C–O(av)	1.134 [3]
Fe(1)–H(1)	1.66 (4)	CpC–C(av)	1.372 [5]
Fe(2)–H(1)	1.71 (4)	Co–C_Cp(av)	2.068 [3]

Bond Angles			
Fe(1)–Fe(2)–Co(1)	58.9 (1)	Co(1)–C(7)–O(7)	164.4 (4)
Fe(1)–Co(1)–Fe(2)	62.0 (1)	Fe(1)–C(8)–O(8)	126.7 (3)
Co(1)–Fe(1)–Fe(2)	59.1 (1)	Fe(2)–C(8)–O(8)	136.3 (3)
C(8)–O(8)–C(9)	119.6 (4)	Co(1)–C(8)–O(8)	125.6 (3)
Fe(1)–H(1)–Fe(2)	101 (2)	Fe–C–O(av)	177.8 [2]
Fe(1)–C(8)–Fe(2)	87.6 (2)		
Fe(1)–C(8)–Co(1)	81.0 (2)	C(2)–Fe(1)–C(3)	100.7 (3)
Co(1)–C(8)–Fe(2)	81.1 (2)	C(6)–Fe(2)–C(5)	98.3 (3)
		C(2)–Fe(1)–C(1)	97.1 (3)
		C(3)–Fe(1)–C(1)	92.6 (3)
		C(4)–Fe(2)–C(5)	97.2 (3)
		C(4)–Fe(2)–C(6)	96.0 (3)

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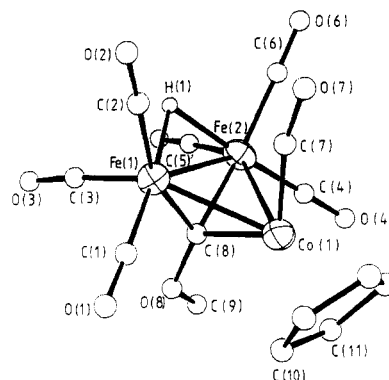(16) Farrugia, L. J.; Miles, A. D.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2437.

C_5H_5) (2), obtained as black crystals after chromatography and recrystallization from petroleum ether. Microanalytical data and particularly the observation, in a high resolution mass spectrum, of a parent ion at m/e 475.8343 (relative intensity 10.35, deviating 1.5 mmu from $C_{14}H_9O_8CoFe_2$) strongly support the above formulation. A ^1H NMR spectrum of 2 showed three signals at δ 5.03, 4.46, and –19.64 with appropriate relative intensities, due to the C_5H_5, $COCH_3$, and Fe(μ-H)Fe groups, respectively. Discussions of further spectroscopic properties of 2 will be deferred until a description of the structure has been given.

The molecular geometry of complex 2, as revealed by a single-crystal X-ray diffraction study is shown in Figure 1, while the results of the analysis are summarized in Tables I and II. Complex 2 contains a triangular array of one cobalt and two iron atoms capped with a μ_3-$COCH_3$ moiety. Each iron atom bears three terminal carbonyl groups, with a μ-hydrido ligand bridging the Fe(1)–Fe(2) vector, while the cobalt atom is ligated to one carbonyl ligand and a cyclopentadienyl group. Thus 2 can be thought of as being derived from 1a by replacement of the "Fe(CO)$_4$" fragment in the latter by the isolobal[17] moiety "Co(CO)(η-C_5H_5)". The reaction leading to the formation of 2 is thus a simple metal exchange reaction,[18] and Fe(CO)$_5$, the expected by product, was detected by IR spectroscopy. The cyclopentadienyl ring is inclined at an angle of 74.5° to the Fe$_2$Co plane. The two Fe(CO)$_3$ moieties are eclipsed relative to one another, with the relevant torsion angles close to zero: C(2)–Fe(1)–Fe(2)–C(6) = 0.2 (3)°; C(3)–Fe(1)–Fe(2)–C(5) = 3.2 (3)°; C(1)–Fe(1)–Fe(2)–C(4) = 6.6 (4)°.

Metal–metal internuclear separations are characteristic[19] of these elements in trinuclear systems. Thus the hydrido-bridged vector Fe(1)–Fe(2) = 2.594 (1) Å is identical, within error, to the corresponding internuclear distance of 2.597 Å in the presursor 1a. The two iron–cobalt separations Fe(1)–Co(1) = 2.517 (1) Å and Fe(2)–Co(1) = 2.523 (1) Å are closely similar and comparable with corresponding distances found in Co$_2$Fe(CO)$_6$(η-$C_5(CH_3)_5$)$_2$ (average 2.572 Å)[20] and Co$_2$Fe(CO)$_4$(η-$C_5(CH_3)_5$)$_2$(η-C_4H_4) (average 2.512 Å).[21] In the recently reported complex Co$_2$Fe(μ_3-CPh)$_2$(CO)$_3$(η-C_5H_5)$_2$, where the Co$_2$Fe triangle is capped by two μ_3-benzylidyne ligands, the Co–Fe separations (2.429 (2) and 2.469 (2) Å) are somewhat shorter.[22]

[The structural parameters of complex 1a described in this paper have been calculated from coordinates taken from ref 4a and obtained from the Databank of the Cambridge Crystallographic Centre, Cambridge, U.K. No errors are thus available. The idealized position of the (unobserved) hydrido ligand was determined by using the program Hydex.[24]]

The position of the hydride ligand H(1) in complex 2 was determined from a difference Fourier synthesis as the strongest remaining feature after inclusion of all non-hydrogen atoms. Free refinement of thermal and positional parameters of this atom resulted in a converged model where the Fe(1)–H(1) and Fe(2)–H(1) distances were 1.66 (4) and 1.71 (4) Å, respectively. These distances are com-

parable with the accurately known Fe–H separation in the anion [Fe$_3$(μ-H)(μ-CO)(CO)$_{10}$$^-$] of 1.693 (4) Å, as determined by a neutron diffraction study.[23] The position of H(1) also concurs with that calculated by using potential energy minimization procedures.[24] The Fe(1)–Fe(2)–H(1) plane is inclined at an angle of 144.2° to the Fe(1)–Fe(2)–Co(1) plane, while in 1a the corresponding interplanar angle (117.5°) involving the idealized hydrido ligand site is more acute.

The major facet of interest in the structure of 2 is that the methoxymethylidyne ligand adopts a μ_3 configuration, while in the isolobally related triiron precursor 1a a μ_2-bonding mode is observed. The alkylidyne carbon atom

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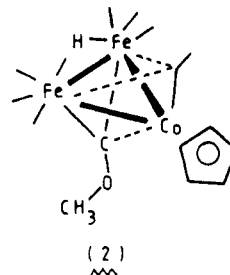
C(8) is asymmetrically bonded to the triangular face, with the Fe(1)–C(8) and Fe(2)–C(8) distances of 1.871 (4) and 1.877 (4) Å, respectively, identical within error. The Co(1)–C(8) vector of 2.001 (4) Å, however, is noticeably longer and suggestive of a weaker interaction between Co(1) and the alkylidyne ligand. In the complex Co$_2$Fe(μ_3-CPh)$_2$-(CO)$_3$(η-C_5H_5)$_2$, for example, the Co–C$_{alkylidyne}$ distances average 1.880 [7] Å, while the Fe–C$_{alkylidyne}$ separations are 1.973 (2) Å.[22] The C(8)–O(8) vector is inclined at an angle of 95.6° to the trimetal plane.

Interestingly, the carbonyl ligand C(7)-O(7) on the cobalt atom deviates markedly from linearity (Co(1)–C(7)–O(7) angle = 164.4 (4)°) with remaining Fe–C–O angles averaging 177.8 [2]°. In addition the Fe⋯C(7) contact distances are rather short (Fe(1)⋯C(7) = 2.559 (4) Å; Fe(2)⋯C(7) = 2.629 (5) Å). These factors are indicative of a weak μ_3 semibridge involving C(7), which presumably occurs in order to transfer excess electron density from the cobalt atom (formally with 19 electrons) to the nominally electron-deficient iron atoms ($17^1/_2$ electrons each). [The α values are 0.47 and 0.51, where α is defined as ($d_2 - d_1$)/d_1; d_2 and d_1 being the longer and shorter M–C values. Semibridging carbonyl ligands have an α value between 0.1 and 0.6. See ref 53.] Shriver[4] has proposed a similar "triple metal semibridge" arrangement of the $COCH_3$ ligand in complex 1a, although the interaction is evidently weaker than observed in 2 (Fe⋯C$_{alkylidyne}$ contact = 2.70 (1) Å). A terminal carbonyl, lying across the opposite face of the iron triangle, also shows a weak interaction with the other iron atoms. The relationship between the configuration found in 1a to that observed in 2 corresponds to a movement of the μ-$COCH_3$ unit across the triangular face, coupled with a complementary motion of a carbonyl ligand in the opposite direction. This is reminiscent of the "compensating" behavior shown by pairs of semibridging carbonyl ligands about metal–metal bonds.[25] Further motion along this coordinate is illustrated by the two structures described later in this paper. Semibridging interactions have been reported[26] in a related complex, Ru$_3$(μ-H)(μ_3-$COCH_3$)-

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$(CO)_8(1,3-C_6H_8)$, but here incipient μ_2- rather than μ_3-carbonyl bridges are involved.

The formation of semibridges involving alkylidyne ligands is the subject of recent interest. Shapley and co-workers have shown that the complex $Os_3(\mu-H)(\mu-CR)(CO)_{10}$ (**3a**, R = H;[8] **3b**, R = Ph[9]) have short contact distances between the unique osmium atom and the alkylidyne carbon [2.353 (10) Å for **3a**, 2.586 (10) Å for **3b**], while Green et al.[27] have reported a related complex (**3c**, R = $CH_2CH(CH_3)_2$) with a similar short contact of 2.640 (26) Å. It has been suggested that donation from the saturated 18-electron $Os(CO)_4$ center to the electrophilic alkylidyne carbon atom is responsible for the semi μ_3 interaction in these compounds[8,27] and that alkoxy substituents on the alkylidyne carbon, by a process of π donation, tend to alleviate such electron deficiency and hence reduce the μ_3 interaction.[8] The $O-C_{alkylidyne}$ distance is a measure of such π donation within the $COCH_3$ group, and the C(8)–O(8) separation of 1.340 (5) Å in $CoFe_2(\mu-H)(\mu_3-COCH_3)(CO)_7(\eta-C_5H_5)$ (**2**), representing a value intermediate with that expected for a C—O single and C=O double bond, is thus indicative of substantial π character. This distance in **2** may be compared with corresponding separations found in other complexes containing the μ_3-COCH_3 moiety, e.g. $Ru_3(\mu_3-COCH_3)(CO)_8(1,3-C_6H_8)$,[26] 1.357 (3) Å; $[Fe_4(\mu_3-COCH_3)(CO)_{12}^-]$,[28] 1.361 (5) Å; $Fe_3Pt(\mu_3-H)(\mu_3-COCH_3)(CO)_{10}(PPh_3)$,[15] 1.34 (1) Å; $Ru_3Au(\mu-H)_2(\mu_3-COCH_3)(CO)_9(PPh_3)$,[29] 1.376 (1) Å; $Ru_3Au_2(\mu-H)(\mu_3-COCH_3)(CO)_9(PPh_3)_2$,[30] 1.371 (15) Å (with the average value 1.361 [4] Å). For complexes containing a $\mu-COCH_3$ group the requisite distances are 1.299 (8)[5] and 1.305 (5) Å[26] for $Ru_3(\mu-H)(\mu-COCH_3)(CO)_{10}$, 1.31 (3) Å for $AuRu_3(\mu-COCH_3)(CO)_{10}(PPh_3)$,[29] and 1.30 (1) and 1.28 (1) Å for $AuOs_3(\mu-COCH_3)(CO)_{10}(PPh_3)$,[31] resulting in an average value of 1.301 [7] Å. The significance of the π-donor interaction from the oxygen to μ-alkylidyne carbon would be expected to diminish, in a synergic fashion, with the formation of a μ_3 or semi μ_3 bridge, due to lessening electron deficiency at this carbon atom induced by donation from the third metal center. This seems to be borne out by the limited data available, since the above figures illustrate a pronounced tendency toward shorter $O-C_{alkylidyne}$ distances in complexes containing $\mu-COCH_3$ groups. The relatively poor accuracy of some of these data preclude too detailed speculation however. Evidence for π donation in heteroatom-substituted alkylidyne complexes comes from various quarters, e.g., PES[32] and PES/MO[33] studies on $Co_3(\mu_3-CR)(CO)_9$ compounds, ^{59}Co NQR coupling constant correlations,[34] and dynamic NMR measurements on complexes **1b**[5] and **1c**.[6] Moreover Keister[35] and co-workers have recently attributed the labilization of the complexes $M_3(\mu_3-COCH_3)(\mu-H)_n(CO)_9$ (M = Ru, n = 3; M = Co, n = 0) to CO substitution as due to π-donor effects of the OCH_3 group.

Several recent theoretical studies have focused on the bonding in μ_3-alkylidyne cluster complexes.[33,36–38] A localized bonding description involving an essentially sp-hybridized alkylidyne carbon atom has been suggested,[33,36] with an orthogonal set of p orbitals on this carbon interacting with cluster MO's of π symmetry. It has been proposed[33] that the hybridization at the alkylidyne carbon remains essentially the same regardless of the bonding mode of the ligand. Bonding in the $COCH_3$ unit may be thus described in terms of an essentially sp^2-hybridized oxygen atom, with the filled p orbital acting as a π donor as shown. The bond angle of 119.6 (4)° at this oxygen
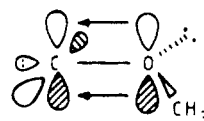
atom in complex **2** [i.e., the angle C(8)–O(8)–C(9)] is close to 120° (as it is in other methoxymethylidyne cluster complexes[4–6,26,28–30]) in line with proposed sp^2 hybridization. Ideas of flexible and extended π systems enunciated for $Co_3(\mu_3-CR)(CO)_9$ systems[33,39] may be applicable to other alkylidyne complexes containing substituents R capable of acting as π donors, e.g., X$^-$, aryl, etc. In this context it is interesting to note the Os$\cdots$C contact in complex **3b**[9] of 2.586 (10) Å is significantly greater than for **3a**,[8] suggesting that the π system of the phenyl ring in **3b** may be alleviating electron deficiency at this carbon by π donation although of course steric factors[9] may also be important.

Complex **2** is evidently fluxional in solution since a ^{13}C NMR spectrum at ambient temperature showed two broad resonances at δ 215.7 and 208.9 due to the Co–CO and $Fe(CO)_3$ groups, respectively. At 176 K, however, four signals in the same region δ 214.7, 211.8, 209.6, and 204.5 (relative intensity 1:2:2:2) revealed that the rotation of the $Fe(CO)_3$ groups was now slow relative to the NMR time scale. Another fluxional process must still be taking place, since there is effective mirror symmetry in the molecule. In the solid-state structure (Figure 1) the two $Fe(CO)_3$ units are inequivalent due to the orientation of the $COCH_3$ ligand. Static structures with distinct $M(CO)_3$ groups have been observed at low temperatures in dynamic NMR studies on complexes **1b**[5] and **1c**,[6] and processes involving either rotation of the OCH_3 group about the $O-C_{alkylidyne}$ bond[5] or inversion at oxygen giving linear $COCH_3$ intermediates[6] have been invoked to explain the fluxional behavior. Whatever the exact process, the activation energy appears to increase on descending a periodic group since for the osmium complex **1c** a value of 56 kJ mol^{-1} has been reported,[6] while for the iron compound **1a** even at 153 K fluxional motion is still rapid.[4b] Complex **2** with a reduced $O-C_{alkylidyne}$ bond order compared with **1a** should have an even lower activation energy, and indeed we were unable to observe static structures for **2** or the other complexes described later in this paper. In a ^{13}C{^{1}H coupled} NMR spectrum recorded at 176 K $^2J_{C-H}$ couplings with the hydrido ligand of 10, 7, and 5 Hz were seen on the signals at δ 320.6, 209.6, and 204.5, respectively, with trans and cis $^2J_{C-H}$ within the $Fe(CO)_3$ fragment of similar magnitude.

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It is of some significance that the chemical shift of the alkylidyne carbon displays noticeable temperature dependence, changing from δ 324.6 at ambient temperature to δ 320.6 at 176 K. Other signals in the spectrum shift by ca. 1 ppm or less. Temperature dependence of the chemical shifts of the semi μ_3-alkylidyne ligands in complexes 3b[9] and 3c[27] has also been reported, in both cases with a similar upfield shift at low temperatures. [We have also observed a temperature dependence of the alkylidyne resonance in complex 1a with an upfield shift of 2.7 ppm from ambient temperature to 208 K.] [13]C chemical shifts of alkylidyne carbon atoms have been found empirically to depend on the bonding mode,[4-6,15,20,40] since μ_3 ligands generally resonate in the region δ 250–300, while μ ligands usually appear at lower field, i.e., from δ 290 to 400. [Shifts as low as δ 502.5 have been reported in cationic μ-alkylidyne complexes.[41]] In complexes containing both μ- and μ_3-CR groups,[40a] signals due to μ ligands invariably appear at lower field. It is thus tempting to attribute the upfield shift of the alkylidyne resonance in complexes 2, 3b, and 3c at low temperatures as due to equilibria involving increasing concentrations of conformers with stronger μ_3 interactions, a suggestion already alluded to.[27] Such an increased interaction with the third metal atom would also be expected to lead to compensatory effects on the carbonyl ligand on the opposite metal face (i.e., ligand C-(7)–O(7) in complex 2) also leading to increasing μ_3 character. The fact that the lowest energy CO stretch in the IR solution spectrum of 2 at 1913 cm^{-1} is unusually broad (half-height width ca. 20 cm^{-1}, other bands 5–8 cm^{-1}) lends weight to the idea that there are a range of structures in solution involving a terminal carbonyl ligand in varying degrees of interaction with a second and third iron atom. There is however little temperature dependence of the chemical shift of the cobalt-bound carbonyl in the ^{13}C NMR spectrum of (2).

It was thus of some interest to synthesize other complexes related to 2 to probe any steric or electronic factors affecting the nature of bonding of the COCH$_3$ group. Treatment of 1a in toluene at 363 K with [Ni(CO)(η-C$_5$H$_5$)]$_2$ afforded a mixture of three complexes, the major product obtained as dark blue-green crystals in 45% yield, being identified as Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4). Microanalytical and high-resolution mass spectroscopic data (parent ion at m/e 473.8297, deviating 2.5 mmu from C$_{14}$H$_8$O$_8$Fe$_2$Ni) were in concordance with this formulation. An IR spectrum (hexane solution) in the region 2200–1600 cm^{-1} revealed, in addition to seven terminal bands between 2070 and 1964 cm^{-1}, two broad stretches in the bridging region at 1808 and 1762 cm^{-1}. In a ^{13}C NMR spectrum at 181 K however, only two resonances in the carbonyl region at δ 209.9 and 249.2 in the ratio 6:1 were observed, indicative of only one bridging carbonyl ligand. The chemical shift of the alkylidyne carbon was again observed to be temperature dependent [δ 331.8 (ambient), δ 326.2 (181 K)], but interestingly in this case there was a similar effect on the bridging carbonyl signal [δ 246.7 (246 K), δ 249.2 (181 K)]. The shift in the bridging carbonyl resonance is in the opposite direction to that
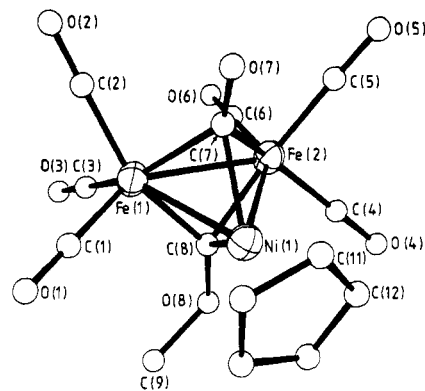
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Figure 2. Molecular geometry and atomic labeling scheme for the complex Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4).

Table III. Atomic Positional (Fractional Coordinate) Parameters with Estimated Standard Deviations in Parentheses for the Complex Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4)

atom	x	y	z
Ni(1)	-0.25951 (4)	0.22036 (4)	-0.16754 (2)
Fe(1)	-0.12962 (5)	0.42004 (4)	-0.27449 (3)
Fe(2)	-0.17872 (5)	0.09973 (4)	-0.31856 (3)
C(1)	-0.1959 (5)	0.5704 (4)	-0.1985 (3)
C(2)	0.1071 (4)	0.5490 (3)	-0.2563 (2)
C(3)	-0.1880 (5)	0.4793 (4)	-0.3963 (3)
C(4)	-0.3675 (5)	-0.0931 (4)	-0.3576 (3)
C(5)	-0.0201 (5)	-0.0112 (4)	-0.2834 (2)
C(6)	-0.1279 (5)	0.1280 (4)	-0.4404 (2)
C(7)	-0.0157 (4)	0.2725 (3)	-0.1923 (2)
C(8)	-0.3405 (3)	0.2258 (3)	-0.3117 (2)
C(9)	-0.5992 (5)	0.3128 (5)	-0.3430 (3)
C(11)	-0.2243 (7)	0.1508 (10)	-0.0239 (4)
C(12)	-0.3668 (11)	0.0318 (5)	-0.0888 (4)
C(13)	-0.4910 (6)	0.1022 (10)	-0.1154 (3)
C(14)	-0.4363 (11)	0.2598 (10)	-0.0745 (5)
C(15)	-0.2666 (11)	0.2993 (6)	-0.0158 (3)
O(1)	-0.2388 (4)	0.6667 (3)	-0.1505 (3)
O(2)	0.2535 (3)	0.6268 (3)	-0.2457 (2)
O(3)	-0.2239 (5)	0.5176 (4)	-0.4721 (2)
O(4)	-0.4860 (4)	-0.2124 (3)	-0.3823 (3)
O(5)	0.0746 (4)	-0.0838 (3)	-0.2584 (2)
O(6)	-0.0998 (5)	0.1476 (4)	-0.5192 (2)
O(7)	0.1214 (3)	0.2921 (3)	-0.1371 (2)
O(8)	-0.5088 (3)	0.1896 (3)	-0.3595 (2)

Table IV. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for the Complex Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4)

Bond Lengths			
Fe(1)–Fe(2)	2.563 (1)	Fe(1)–C(7)	2.056 (3)
Fe(1)–Ni(1)	2.438 (1)	Fe(2)–C(7)	2.065 (3)
Fe(2)–Ni(1)	2.419 (1)	Ni(1)–C(7)	1.944 (3)
Fe(1)–C(8)	1.902 (3)	C(7)–O(7)	1.173 (4)
Fe(2)–C(8)	1.888 (3)	C(8)–O(8)	1.317 (4)
Ni(1)–C(8)	1.959 (3)	C(9)–O(8)	1.431 (5)
Fe$_{carbonyl}$C–O(av)	1.130 [2]	Fe–C$_{carbonyl}$(av)	1.798 [2]
CpC–C(av)	1.339 [5]	Ni–C$_{Cp}$(av)	2.080 [3]

Bond Angles			
Fe(1)–Fe(2)–Ni(1)	58.5 (1)	Ni(1)–C(7)–O(7)	130.9 (3)
Fe(1)–Ni(1)–Fe(2)	63.7 (1)	Fe(1)–C(7)–O(7)	136.6 (3)
Fe(2)–Fe(1)–Ni(1)	57.8 (1)	Fe(2)–C(7)–O(7)	137.3 (3)
Fe(1)–C(8)–O(8)	137.3 (2)	Fe(1)–C(8)–Fe(2)	85.1 (2)
Fe(2)–C(8)–O(8)	130.3 (2)	Fe(1)–C(8)–Ni(1)	78.3 (1)
Ni(1)–C(8)–O(8)	126.0 (2)	Fe(2)–C(8)–Ni(1)	77.9 (1)
C(8)–O(8)–C(9)	118.7 (3)		
Fe–C–O(av)	178.8 [2]		

observed for the alkylidyne signal (i. e., to a *lower* field at *lower* temperatures) and is consistent with the proposition of a stronger μ_3 interaction at lower temperatures, since it is well established that the ^{13}C chemical shift of μ_3 carbonyls is to low field of μ-carbonyl ligands.[42]

The molecular structure of complex 4, illustrated in Figure 2, was determined from a single-crystal X-ray diffraction study, the results of this analysis being summarized in Tables III and IV. Complexes 4 and 2 are rather similar in general ligand disposition, but as 4 lacks a hydrido ligand, there are some subtle discrepancies between the two structures. Thus the Fe(1)–Fe(2) distance of 2.563 (1) Å in (4) is slightly shorter than observed in 2, a consequence of the bond-lengthening effect[23] of the hydrido ligand in the latter compound. There is also noticeable asymmetry within the cluster, not attributable to any obvious cause, with the two Fe–Ni distances of 2.438 (1) and 2.419 (1) Å significantly different though normal[19] for these metals in trinuclear complexes. In [Fe$_2$Ni(μ_3-C$_2$Ph$_2$)(CO)$_6$(η-C$_5$H$_5$)$^-$] for example Fe–Ni separations of 2.453 (1), 2.474 (1) Å are found.[43] In addition, and in contrast to the situation in complex 2, the two Fe(CO)$_3$ units in (4) are skewed as evident from the torsion angles C(2)–Fe(1)–Fe(2)–C(5) = 27.6 (2)°, C(3)–Fe(1)–Fe(2)–C(6) = 28.9 (2)°, and C(1)–Fe(1)–Fe(2)–C(4) = 50.3 (3)°.

The most significant difference between the structures of 2 and 4 however lies in the greater μ_3 character of both the COCH$_3$ ligand and the μ-carbonyl moiety in the nickel compound, as indeed suspected from the spectroscopic data. Thus C(7) is almost symmetrically disposed about the Fe$_2$Ni triangle (Fe(1)–C(7) = 2.056 (3) Å; Fe(2)–C(7) = 2.065 (3) Å; Ni(1)–C(7) = 1.944 (3) Å) with the Ni(1)–C(7)–O(7) angle of 130.9 (3)° considerably more acute than the corresponding angle in the cobalt analogue 2. Similarly C(8) is essentially equidistant from the three metal atoms (C(8)–Fe(1) = 1.902 (3) Å; C(8)–Fe(2) = 1.888 (3) Å; C(8)–Ni(1) = 1.959 (3) Å). The C(7)–O(7) and C(8)–O(8) vectors are inclined at angles of 6.5° and 5.9°, respectively, to the Fe$_2$Ni plane. The C(8)–O(8) distance of 1.317 (4) Å is somewhat shorter than the average observed in several similar structures (vide supra).

The structure of the complex Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4) represents a further departure along the coordinate describing the relationship between the structures of 1a and 2, one where the μ-COCH$_3$ in 1a has now become an essentially symmetrically bonded μ_3-ligand. Concomitant with this is the conversion of a weak semi-bridged carbonyl in 1a[4a] to a full triply bridged group in complex 4. Although, to our knowledge, no similar example of a complex containing symmetric μ_3-CO and μ_3-COCH$_3$ ligands has been described, the compound Ru$_3$(μ_3-NOCH$_3$)(μ_3-CO)(CO)$_9$, containing an O-methylated nitrosyl group, has a closely analogous structure.[44] Coupled with the movement of the ligands across the triangular face, there is a tilt involving the angle between the cyclopentadienyl unit and the trimetal plane in going from the cobalt complex 2, 74.5°, to the nickel compound 4, 90.9°.

Although in the solid-state complex 4 shows only one band at 1716 cm^{-1} in the IR due to the bridging carbonyl ligand, in solution two broad stretches were observed, which indicates that at least two distinct structures are adopted in this phase. Such structures are evidently involved in rapid interchange, since the ^{13}C NMR signal at δ 249.2 (181 K), representing an *averaged* bridging carbonyl environment, is not significantly broadened relative to other resonances. A variable-temperature solution IR study was undertaken to investigate any equilibria in solution. The IR spectra, between 2125 and 1700 cm^{-1} and
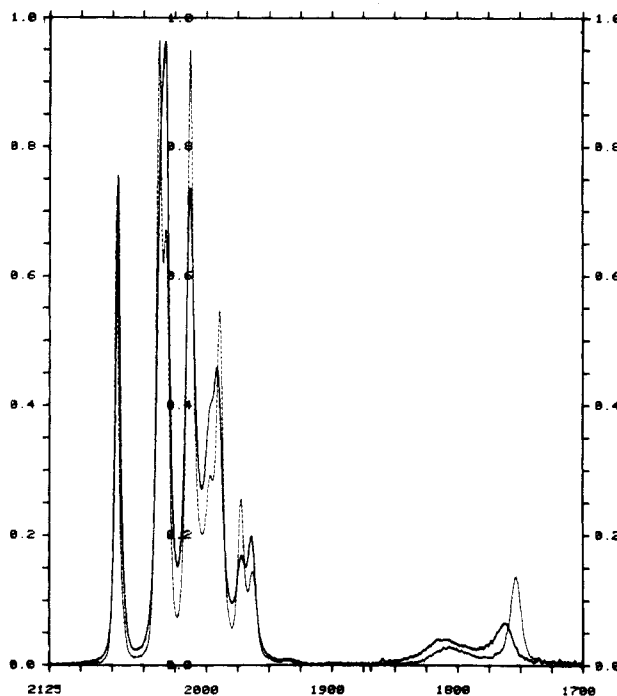

Figure 3. Solution IR spectrum (hexane) for the complex Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$): (i) solid trace 298 K; (ii) broken trace 193 K.

recorded in hexane solution at 298 and 193 K, are illustrated in Figure 3. In general there is increased resolution due to narrower band widths at the lower temperature, but significant relative intensity changes were also observed. At 193 K the broad band at 1808 cm^{-1} diminishes in intensity relative to the lower frequency band, while this latter band sharpens considerably, increases in absolute intensity, and shifts to lower wavenumber (from 1762 cm^{-1} at 298 K to 1753 cm^{-1} at 193 K). This shift may be due partly to band deconvolution[45] at the lower temperature, though this is unlikely to account for such a large effect. Changes in relative intensity are also observable for several bands in the terminal region, notably those pairs at 1964, 1972 cm^{-1} and 1997, 1991 cm^{-1}. We take this evidence to indicate that two main conformers of complex 4, in equilibrium with each other, are present in solution. Assuming that the band at 1753 cm^{-1} is due to a structure in solution 4i resembling that found in the solid state (the lower ν(μ_3-CO) in the solid suggests that they are not identical), then the second conformer 4ii must have a semi μ_3-carbonyl and presumably also a semi μ_3-COCH$_3$ ligand arrangement. A double minimum in the potential energy
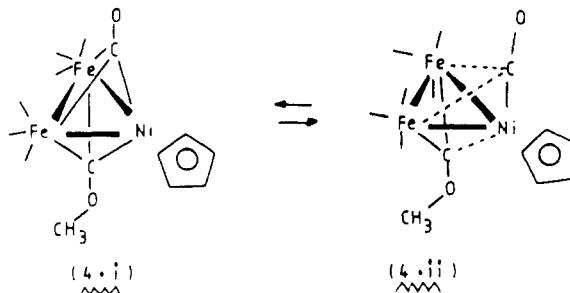
surface for the semi μ_3 to μ_3 transformation is implied by the two distinct bridging carbonyl bands, and we tentatively suggest there may be other minor configurational differences between conformers 4i and 4ii. One possible

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difference lies in the relative orientations of the $Fe(CO)_3$ groups, bearing in mind the solid-state structures of **4** and **2**. Clearly the energy difference between the conformers is small, and it may be pertinent to note that even at 181 K, ^{13}C NMR shows complex **4** with a single environment for the six carbonyls on iron, while at 223 K the fluxional equivalence within the $Fe(CO)_3$ groups is frozen out for **2**.

In the reaction of $Fe_3(\mu\text{-H})(\mu\text{-COCH}_3)(CO)_{10}$ with [Ni-$(\mu\text{-CO})(\eta\text{-C}_5H_5]_2$ leading to the formation of complex **4**, two other compounds were isolated in low yield. These have been identified, by spectroscopic means, as the known[46] species $FeNi(\mu\text{-CO})_2(CO)(\eta\text{-C}_5H_5)_2$ (**5**) and the new compound $Fe_3(\mu_3\text{-COCH}_3)(\mu\text{-CO})_2(CO)_6(\eta\text{-C}_5H_5)$ (**6**). Both

(6)
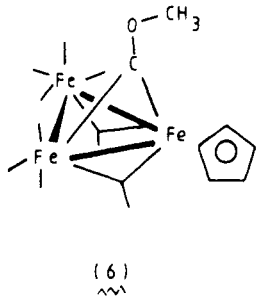
complexes gave parent ions in high-resolution mass spectra, with **6** displaying six bands in the terminal and two bands (1866 and 1826 cm^{-1}) in the bridging region of a solution IR spectrum. A ^{13}C NMR spectrum of **6** at 180 K showed the alkylidyne resonance at δ 338.9 (again temperature dependent, with δ 341.4 at 298 K) and four signals in the carbonyl region at δ 248.6, 212.7, 211.5, and 204.0 (2:2:2:2 ratio). The structure proposed is consistent with the data, but in view of the above results, it is difficult to ascertain the exact extent of interaction of the $\mu\text{-COCH}_3$ ligand with the cluster.

Although complexes **2** and **4** are closely related, the lack of a hydrido ligand in **4** will have electronic[37,47,48] as well as steric consequences.[23] Attempts to protonate **4** or deprotonate **2** to give isoelectronic complexes with *identical* ligand spheres but differing in charge have so far proved unsuccessful. In view of the known isolobal connection between the $\mu\text{-H}$ and $\mu\text{-AuPR}_3$ fragments[49,50] and the demonstrated structural similarities in complexes containing these ligands,[51,52] the effects of replacement of the $Fe(\mu\text{-H})Fe$ moiety in complex **2** with a $Fe(\mu\text{-AuPPh}_3)Fe$ group were investigated, to determine the effect on the disposition of the $COCH_3$ unit.

Treatment of **2** with $AuCH_3(PPh_3)$ in toluene at 363 K afforded $AuCoFe_2(\mu_3\text{-COCH}_3)(\mu_3\text{-CO})(CO)_6(PPh_3)(\eta\text{-C}_5H_5)$ (**7**) in moderate yield, characterized by spectroscopic methods and X-ray diffraction. A solution IR spectrum revealed that the structures of **7** and **2** were not analogous, since **7** displayed four rather broad bands from 2030 to 1938 cm^{-1} and a very broad weak stretch at 1810 cm^{-1} (in the solid state 1773 cm^{-1}). ^{1}H and ^{31}P NMR spectra confirmed the presence of the $COCH_3$, C_5H_5, and PPh_3 lig-

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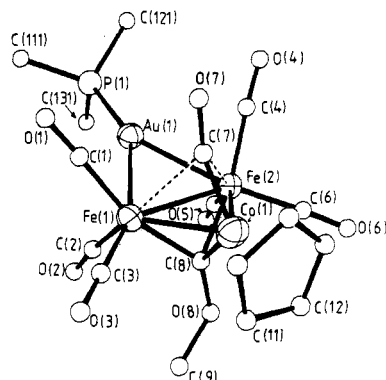**Figure 4.** Molecular geometry and atomic labelling scheme for the complex $AuCoFe_2(\mu_3\text{-COCH}_3)(\mu_3\text{-CO})(CO)_6(PPh_3)(\eta\text{-C}_5H_5)$ (**7**). Phenyl rings omitted for clarity, with point of contact carbons only shown.
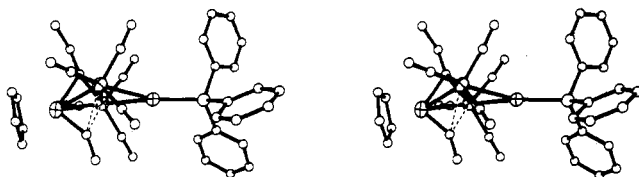

Figure 5. Stereoview of $AuCoFe_2(\mu_3\text{-COCH}_3)(\mu_3\text{-CO})(CO)_6$-$(PPh_3)(\eta\text{-C}_5H_5)$, showing disposition of phenyl rings.

ands, while ^{13}C NMR spectra showed signals due to the alkylidyne ligand [δ 325.5 (298 K), δ 320.4 (176 K)] and a bridging carbonyl [δ 241.6 (233 K), δ 243.9 (176 K)] which were again noticeably temperature dependent. **7** shows similar fluxional behavior to **2** with one broad resonance for all seven carbonyls at δ 212.9 observed at ambient temperatures and four signals (δ 243.9, 214.6, 214.1, 208.4) at 176 K.

The molecular structure of **7** is shown in Figure 4 with a stereoview in Figure 5. Important bond lengths and angles are given in Table VI. The major effect of replacing the $\mu\text{-H}$ ligand in **2** is to increase the μ_3 character of both the $COCH_3$ and $\mu\text{-CO}$ moieties. Thus the Fe(1)–C(8) and Fe(2)–C(8) distances of 1.925 (5) and 1.887 (5) Å, respectively, are slightly longer, and the Co(1)–C(8) separation of 1.932 (5) Å slightly shorter than the corresponding distances in complex **2**. Similarly the Fe(1)–C(7) and Fe(2)–C(7) vectors (2.322 (6) and 2.362 (6) Å, respectively) are ca. 0.25 Å shorter than those in **2**, while the Co(1)–C(7) distance (1.774 (6) Å) is marginally longer. The interaction of C(7) with the iron atoms is best described as a semi μ_3 bridge (α value = 0.31) with the geometry observed in complex **7** intermediate between that previously shown for complexes **2** and **4**.

Apart from these factors, the perturbation of replacing $\mu\text{-H}$ by $\mu\text{-AuPPh}_3$ has relatively minor effects on the geometry of the rest of the molecule. Thus the two Co–Fe separations, 2.486 (1) and 2.493 (1) Å, are ca 0.03 Å shorter than those in **2** while the Fe(1)–Fe(2) distance (2.643 (1) Å) is 0.05 Å longer. The angle between the Fe_2Au and Fe_2Co planes is 155.4°, more obtuse than the corresponding angle involving the hydrido ligand in **2**. The two $Fe(CO)_3$ units are essentially eclipsed with torsion angles C(1)–Fe(1)–Fe(2)–C(4) = 2.8 (3)°, C(2)–Fe(1)–Fe(2)–C(5) = 3.7 (3)°, and C(3)–Fe(1)–Fe(2)–C(6) = 9.2 (5)°. The cyclopentadienyl group is inclined at an angle of 81.2° to the trimetal plane (viz., 74.5° in **2** and 90.9° in **4**).

Although the $AuPPh_3$ unit is evidently much larger than a hydrido ligand, its steric influence on the disposition of the *primary* ligating atoms of the Fe_2Co cluster [i.e., the carbonyl carbons and C(8)] is only marginally greater. The "splay-back" angles C(1)–Fe(1)–C(2) and C(4)–Fe(2)–C(5)

Table V. Atomic Positional (Fractional Coordinate) Parameters with Estimated Standard Deviations in Parentheses for the Complex AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(PPh$_3$)(η-C$_5$H$_5$) (7)

atom	x	y	z
Au(1)	-0.07731 (1)	0.06749 (1)	0.21511 (1)
Co(1)	0.24687 (5)	0.07068 (5)	0.24265 (5)
Fe(1)	0.08062 (5)	0.05276 (4)	0.14554 (4)
Fe(2)	0.10184 (5)	0.14385 (4)	0.28639 (4)
P(1)	-0.24471 (8)	0.05691 (7)	0.21505 (7)
O(1)	-0.0112 (3)	-0.1338 (3)	0.1307 (3)
O(2)	-0.0584 (3)	0.1750 (3)	0.0347 (3)
O(3)	0.1984 (3)	0.0011 (3)	0.0271 (3)
O(4)	0.0382 (3)	0.0534 (3)	0.4253 (2)
O(5)	-0.0378 (4)	0.2986 (3)	0.2404 (3)
O(6)	0.2474 (4)	0.2664 (4)	0.3879 (3)
O(7)	0.1467 (3)	-0.0784 (3)	0.3055 (3)
O(8)	0.1694 (3)	0.2474 (2)	0.1611 (2)
C(1)	0.0211 (4)	-0.0607 (4)	0.1383 (3)
C(2)	-0.0087 (4)	0.1246 (4)	0.0771 (3)
C(3)	0.1524 (4)	0.0216 (4)	0.0736 (3)
C(4)	0.0610 (3)	0.0861 (3)	0.3704 (3)
C(5)	0.0142 (4)	0.2355 (4)	0.2603 (3)
C(6)	0.1930 (4)	0.2162 (4)	0.3507 (4)
C(7)	0.1617 (4)	-0.0087 (4)	0.2722 (4)
C(8)	0.1511 (3)	0.1640 (3)	0.1908 (3)
C(9)	0.1932 (5)	0.2535 (4)	0.0827 (4)
C(11)	0.3699 (4)	0.0889 (6)	0.1891 (5)
C(12)	0.3786 (4)	0.1486 (5)	0.2575 (6)
C(13)	0.3823 (5)	0.0893 (8)	0.3251 (5)
C(14)	0.3763 (5)	-0.0028 (7)	0.3017 (6)
C(15)	0.3672 (5)	-0.0037 (5)	0.2168 (6)
C(111)	-0.3125 (3)	-0.0338 (3)	0.1502 (3)
C(112)	-0.2610 (4)	-0.1130 (4)	0.1370 (4)
C(113)	-0.3108 (6)	-0.1840 (4)	0.0872 (5)
C(114)	-0.4114 (6)	-0.1773 (4)	0.0526 (4)
C(115)	-0.4640 (5)	-0.1004 (5)	0.0665 (4)
C(116)	-0.4152 (4)	-0.0264 (4)	0.1143 (3)
C(121)	-0.2689 (3)	0.0367 (3)	0.3164 (3)
C(122)	-0.2030 (4)	0.0751 (3)	0.3843 (3)
C(123)	-0.2170 (4)	0.0615 (4)	0.4623 (3)
C(124)	-0.2940 (5)	0.0085 (4)	0.4748 (3)
C(125)	-0.3584 (5)	-0.0305 (4)	0.4097 (4)
C(126)	-0.3487 (4)	-0.0163 (4)	0.3289 (3)
C(131)	-0.3098 (3)	0.1642 (3)	0.1783 (3)
C(132)	-0.3814 (4)	0.2042 (3)	0.2140 (3)
C(133)	-0.4296 (4)	0.2856 (4)	0.1820 (4)
C(134)	-0.4069 (4)	0.3282 (4)	0.1152 (4)
C(135)	-0.3366 (4)	0.2875 (4)	0.0788 (4)
C(136)	-0.2879 (4)	0.2064 (4)	0.1099 (3)

[104.0 (3) and 102.6 (3)°, respectively] are only slightly larger than the corresponding ones in complex 2, where C(2)–Fe(1)–C(3) is 100.7 (3)° and C(6)–Fe(2)–C(5) is 98.3 (3)°. Nonbonded contacts between Au(1) and the nearest carbon atoms average 2.732 [2] Å with Au(1)···C(7) at 3.370 (5) Å some 23% greater. In complex 2 nearest-neighbor H(1)···C contacts average 2.35 [2] Å, but here H(1)···C(7) is 2.62 (4) Å, i.e., only 11% greater. There is *relatively* closer contact between H(1) and C(7) in 2 than there is between C(7) and Au(1) in 7. From Figure 5 it is evident that the phenyl groups will only have close intramolecular contacts with the carbonyl oxygens, and the shortest contact is H(112)···O(1) at 2.533 (4) Å.

Electronic factors may be responsible for the greater μ_3 character of the CO and COCH$_3$ ligands in complex 7. The gold–iron bond is more polar than the corresponding hydrido–iron interaction, a consequence of the a$_1$ hy(s-z) orbital of gold lying to higher energy than the hydrogen 1s.[50] Charge redistribution leads to greater electron density at the transition metals, this being borne out by the generally lower carbonyl stretches observed in 7 as compared with 2. This excess electron density may then be dissipated by the carbonyl bridge and greater interaction of the alkylidyne ligand with the cobalt atom.

Table VI. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for the Complex AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(PPh$_3$)(η-C$_5$H$_5$) (7)

Bond Lengths

Fe(1)–Fe(2)	2.643 (1)	Au(1)–P(1)	2.293 (2)
Fe(1)–Au(1)	2.681 (1)	P(1)–C(111)	1.805 (5)
Fe(2)–Au(1)	2.698 (1)	P(1)–C(121)	1.817 (5)
Fe(1)–Co(1)	2.486 (1)	P(1)–C(131)	1.811 (5)
Fe(2)–Co(1)	2.493 (1)	Fe(1)–C(8)	1.925 (5)
Co(1)–C(7)	1.774 (6)	Fe(2)–C(8)	1.887 (5)
Fe(1)–C(7)	2.322 (6)	Co(1)–C(8)	1.932 (5)
Fe(2)–C(7)	2.362 (6)	C(7)–O(7)	1.183 (7)
C(8)–O(8)	1.337 (6)		
C(9)–O(8)	1.419 (8)	Fe–C$_{carbonyl}$(av)	1.789 [2]
CpC–C(av)	1.396 [6]	Co–C$_{Cp}$(av)	2.083 [3]
C–O(carbonyl)(av)	1.133 [3]		

Bond Angles

Fe(1)–Fe(2)–Co(1)	57.8 (1)	C(8)–O(8)–C(9)	119.8 (5)
Fe(1)–Co(1)–Fe(2)	64.1 (1)	Fe(1)–Au(1)–P(1)	153.7 (1)
Co(1)–Fe(1)–Fe(2)	58.1 (1)	Fe(2)–Au(1)–P(1)	146.4 (1)
Fe(1)–Au(1)–Fe(2)	58.9 (1)		
Au(1)–Fe(1)–Fe(2)	60.9 (1)	Fe–C–O(av)	175.9 [2]
Au(1)–Fe(2)–Fe(1)	60.2 (1)		
Co(1)–C(7)–O(7)	149.9 (5)	C(1)–Fe(1)–C(2)	104.0 (3)
Fe(1)–C(7)–O(7)	130.4 (5)	C(4)–Fe(2)–C(5)	102.6 (3)
Fe(2)–C(7)–O(7)	129.2 (5)	C(1)–Fe(1)–C(3)	92.2 (3)
Co(1)–C(8)–O(8)	128.2 (4)	C(2)–Fe(1)–C(3)	96.7 (3)
Fe(1)–C(8)–O(8)	135.4 (4)	C(4)–Fe(2)–C(6)	95.5 (3)
Fe(2)–C(8)–O(8)	125.6 (4)	C(5)–Fe(2)–C(6)	93.4 (3)

Conclusions

The complexes CoFe$_2$(μ-H)(μ_3-COCH$_3$)(CO)$_7$(η-C$_5$H$_5$) (2) and Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) (4) have been synthesized via metal exchange reactions on Fe$_3$(μ-H)(μ-COCH$_3$)(CO)$_{10}$, whereas previous cluster syntheses utilizing μ-alkylidyne complexes have normally involved metal addition.[3] This is presumably due to weaker metal–metal bonds in the first-row transition series. Complexes 2, 7, and 4 illustrate steps along a structural coordinate leading to increasing μ_3 interaction of a μ-COCH$_3$ and μ-CO ligand with a trinuclear cluster. Spectroscopic data suggest that a similar molecular motion occurs in solution for each of these complexes. The nature of the alkylidyne ligand bonding mode[26] in cluster complexes clearly depends on both steric and electronic considerations, but the occurrence in solution of at least two conformers of Fe$_2$Ni(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(η-C$_5$H$_5$) suggests these factors may be very finely balanced. It may prove possible to examine the relevant ligand–ligand nonbonded interactions in these cluster complexes using the molecular graphics techniques recently described.[54]

Experimental Section

All manipulations were carried out under dry, oxygen-free nitrogen, using standard vacuum line/Schlenk tube techniques. Reactions performed at 363 K were carried out in Carius tubes fitted with Teflon stoppers. Solvents were deoxygenated and freshly distilled prior to use; petroleum ether refers to that fraction with a boiling point of 40–60 °C. ^{1}H and ^{31}P NMR measurements were obtained on a Varian XL100 spectrometer operating in the Fourier transform mode. ^{13}C NMR spectra (recorded in the presence of Cr(acac)$_3$[55]) were obtained on a Bruker WP 200SY instrument. Chemical shifts were measured relative to internal solvent signals and referenced to Me$_4$Si for ^{1}H and ^{13}C and 85% H$_3$PO$_4$ for ^{31}P. Infrared spectra were obtained on a Perkin-Elmer 983, with low-temperature measurements made by using a 0.5-mm cell with sapphire windows. High-resolution mass spectra were recorded on a MS 902S (Kratos) mass spectrometer. Elemental

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Table VII. Experimental Data for Crystallographic Studies[a]

	2	4	7
formula	$C_{14}H_9O_8CoFe_2$	$C_{14}H_8O_8Fe_2Ni$	$C_{32}H_{23}O_8AuCoFe_2P$
M_r	475.7	474.4	934.1
space group	$P2_1/a$ (no. 14, C_{2h}^5)	$P\bar{1}$ (no. 2, C_i^1)	$P2_1/n$ (no. 14, C_{2h}^5)
cryst system	monoclinic	triclinic	monoclinic
$a/\text{Å}$	13.901 (1)	7.930 (3)	13.669 (3)
$b/\text{Å}$	8.207 (1)	8.338 (1)	14.313 (5)
$c/\text{Å}$	14.725 (2)	13.474 (2)	16.665 (4)
α/deg		96.97 (1)	
β/deg	85.973 (8)	98.97 (2)	103.12 (2)
γ/deg		107.12 (2)	
$V/\text{Å}^3$	1676.0 (8)	827.3 (9)	3175 (1)
Z	4	2	4
$D_{calcd}/\text{g cm}^{-3}$	1.88	1.90	1.95
$F(000)$	944	472	1808
$\mu(\text{Mo K}\alpha)/\text{cm}^{-1}$	27.2	29.0	61.1
T/K	298	298	298
scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
θ range/deg	$1.5 < \theta < 25$	$1.5 < \theta < 30$	$2 < \theta < 25$
cryst size/mm	$0.19 \times 0.30 \times 0.51$	$0.14 \times 0.35 \times 0.22$	$0.50 \times 0.72 \times 0.40$
cryst faces		$\langle 01\bar{1}\rangle, \langle 001\rangle, \langle 10\bar{1}\rangle, \langle 1\bar{1}0\rangle$	
abs correctn method	DIFABS	GAUSSIAN	DIFABS
range of transmissn coeff/correctn	0.825–1.188	0.486–0.676	0.910–1.717
no. of data collected	3303	5142	6039
no. of unique data	2951	4817	5541
R_{merge} (before abs correctn)	0.045	0.017	0.141
R_{merge} (after abs correctn)	0.032	0.015	0.017
std reflctns	$7\bar{3}1, \bar{8}2\bar{3}, \bar{3}3\bar{9}$	$41\bar{4}, 3\bar{4}5, 331$	$\bar{4}73, 1\bar{4}8, 0\bar{8}0$
observability criterion n; $I > n\sigma(I)$	2.5	2.5	2.5
no. of data used in refinement	1990	3482	4257
region collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
no. of refined parameters	230	226	406
final R	0.028	0.030	0.024
R_w	0.036	0.040	0.031
largest remaining features in electron density difference map, e Å^{-3}	+0.30 (max) −0.35 (min)	+0.27 (max) −0.58 (min)	+0.56 (max) −0.92 (min)
shift/esd in last cycle of refinement			
max	0.341	0.144	0.344
av	0.013	0.019	0.068

[a] Diffractometer, Enraf-Nonius CAD4F, graphite-monochromated X radiation; λ = 0.710 69 Å.

(C/H) analyses were performed by the Microanalytical Unit in the Department of Chemistry, University of Glasgow. Column chromatography was carried out by using Florosil (BDH 100–200 mesh) in hexane, with hexane or hexane/dichloromethane mixtures as eluants. $CF_3SO_3CH_3$ (Aldrich) was distilled at atmospheric pressure prior to use. $Co(CO)_2(\eta\text{-}C_5H_5)$ was used as supplied by Strem Chemicals and $NEt_3H^+[Fe_3(\mu\text{-}H)(CO)_{11}^-],^{56}$ $[Ni(CO)\text{-}(\eta\text{-}C_5H_5)]_2,^{57}$ and $AuCH_3(PPh_3)^{58}$ were prepared from literature methods. $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ was prepared by a modification of the method of Shriver[4] et al. described below.

Preparation of $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$. $NEt_3H^+[Fe_3(\mu\text{-}H)(CO)_{11}^-]$ (8.18 g, 14.1 mmol) was washed with petroleum ether, until the washings were colorless, to remove $Fe_3(CO)_{12}$. Petroleum ether (80 mL) followed by $CF_3SO_3CH_3$ (2 mL, 17.7 mmol) (*care: extreme carcinogen*) was added. The resultant mixture was stirred for 2 days. Removed of solvent in vacuo, followed by extraction with petroleum ether (3 × 50 mL), gave an intensely colored purple-red solution. The solution was passed down a short column (3 × 6 cm) of Florosil using petroleum ether as eluant. The solvent was removed in vacuo and the crystalline residue redissolved in the minimum volume of petroleum ether. Overnight standing at −30 °C afforded black crystals of the complex $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (5.50 g, 79% yield).

Preparation of $CoFe_2(\mu\text{-}H)(\mu_3\text{-}COCH_3)(CO)_7(\eta\text{-}C_5H_5)$ (2). $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (4.0 g, 8.1 mmol) and $Co(CO)_2(\eta\text{-}C_5H_5)$(1.63 g, 9.1 mmol) in toluene (40 mL) were heated, in vacuo, in a Carius tube at 363 K for 8 h. Removal of volatiles, followed by extraction with light petroleum gave a dark-brown solution. Chromatography afforded, in order of elution, green $Fe_3(CO)_{12}$ (trace), red-purple unreacted $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (0.45 g),

orange $Fe(CO)_5$ (identified from IR spectrum) with excess $Co(CO)_2(\eta\text{-}C_5H_5)$, a dark green-brown band, and traces of an unidentified purple product. Recrystallization of the green-brown band from petroleum ether (−30 °C) afforded $CoFe_2(\mu\text{-}H)(\mu_3\text{-}COCH_3)(CO)_7(\eta\text{-}C_5H_5)$ (1.95 g, 4.1 mmol 56.8% based on starting material consumed): mass spectrum, m/e 475.8343 (M^+, ^{56}Fe); IR (hexane) ν_{CO} 2070 (s), 2041 (vs), 2029 (w), 2007 (vs), 1995 (m), 1985 (s), 1972 (s), 1946 (vw, br), 1913 (w, br) cm^{-1}; IR (KBr disk) ν_{max} 3120 (w), 3020 (w), 2985 (w), 2940 (w), 2838 (w), 2064 (s), 2035 (s), 1982 (s), 1971 (s), 1963 (s), 1911 (s) cm^{-1}; ^{1}H NMR (CDCl$_3$, ambient) δ 5.03 (s, 5 H, C$_5$H$_5$), 4.46 (s, 3 H, OCH$_3$), −19.64 (s, 1 H, Fe(μ-H)Fe); ^{13}C{^{1}H} NMR (CDCl$_3$), ambient) δ 324.6 (s, 1 C, COCH$_3$), 215.7 (s, br, 1 C, CoCO), 208.9 (s, br, 6 C, FeCO), 89.7 (s, 5 C, C$_5$H$_5$), 69.0 (s, 1 C, COCH$_3$); ^{13}C{^{1}H coupled} NMR (CDCl$_3$, 176 K) δ 320.6 (d, 1 C, J_{CH} = 10 Hz), 214.7 (s, 1 C, CoCO), 211.8 (s, 2 C, FeCO), 209.6 (d, 2 C, FeCO, J_{CH} = 7 Hz), 204.5 (d, 2 C, FeCO, J_{CH} = 5 Hz), 89.2 (d, 5 C, C$_5$H$_5$, J_{CH} = 179 Hz), 68.9 (q, 1 C, OCH$_3$, J_{CH} = 146 Hz). Anal. Calcd for $C_{14}H_9O_8CoFe_2$: C, 35.35; H, 1.91. Found: C, 35.43; H, 1.61%.

Reaction of $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ with $[Ni(CO)(\eta\text{-}C_5H_5)]_2$. $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (1.62 g, 3.3 mmol) and $[Ni(CO)(\eta\text{-}C_5H_5)]_2$ (1.0 g, 3.3 mmol) in toluene (50 mL) were heated in a Carius tube under vacuum for 6 h. A nickel mirror was formed and the solvent removed from the dark brown solution. Extraction with petroleum ether followed by chromatography, and recrystallization of each band from petroleum ether afforded unreacted $Fe_3(\mu\text{-}H)(\mu\text{-}COCH_3)(CO)_{10}$ (0.2 g), blue-green $Fe_2Ni\text{-}(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)$ (0.62 g, 45% on starting material consumed), brown $FeNi(\mu\text{-}CO)_2(CO)(\eta\text{-}C_5H_5)_2$ (0.08 g, 3.5% based on Ni), and brown $Fe_3(\mu_3\text{-}COCH_3)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)$ (0.05 g, 3.4% on material consumed). Traces of an orange and a purple product were unidentified.

$Fe_2Ni(\mu_3\text{-}COCH_3)(\mu_3\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)$ (4): mass spectrum, m/e 473.8297 (M^+, ^{56}Fe, ^{58}Ni, relative intensity 22.7); IR (hexane) ν_{CO} (298K) 2070 (s), 2038 (sh), 2033 (vs), 2013 (s), 1997 (sh), 1991

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(m), 1972 (w), 1964 (w), 1808 (w, br), 1762 (w, br) cm^{-1}; IR (193 K) ν_{CO} 2071 (s), 2038 (vs), 2032 (s), 2013 (vs), 1997 (m), 1989 (s), 1972 (m), 1963 (w), 1806 (w, br), 1753 (m) cm^{-1}; IR (KBr disk, selected bands) ν_{max} 3120 (w), 3020 (vw), 2942 (w), 2843 (w), 2067 (s) 2030 (s), 2011 (s), 1996 (s), 1984 (s), 1963 (s), 1927 (s), 1716 (s), 1443 (m), 1408 (w), 1339 (w), 1191 (vs) 1113 (m) cm^{-1}; ^{1}H NMR (CDCl$_3$, ambient δ 5.35 (s, 5 H, C$_5$H$_5$), 4.44 (s, 3 H, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$, ambient) δ 331.8 (s, 1 C, COCH$_3$), 212.0 (s, br, 7 C), 95.4 (s, 5 C, C$_5$H$_5$), 72.0 (s, 1 C, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$/CH$_2$Cl$_2$, 181 K) δ 326.8 (s, 1 C, COCH$_3$), 249.2 (s, 1 C, μ-CO), 209.9 (s, 6 C, CO), 94.5 (s, 5 C, C$_5$H$_5$), 71.5 (s, 1 C, OCH$_3$). Anal. Calcd for C$_{14}$H$_8$O$_8$Fe$_2$Ni: C, 35.45; H, 1.70. Found: C, 35.50; H, 1.15.

FeNi(μ-CO)$_2$(CO)(η-C$_5$H$_5$) (5): mass spectrum, m/e 327.9341 (M$^+$, ^{56}Fe, ^{58}Ni, relative intensity 9.3); IR (hexane) ν_{CO} 2004 (s), 1960 (vw), 1857 (vw), 1825 (s), 1794 (vw) cm^{-1}.

Fe$_3$(μ_3-COCH$_3$)(μ-CO)$_2$(CO)$_6$(η-C$_5$H$_5$) (6): mass spectrum, m/e 499.8213 (M$^+$, ^{56}Fe, relative intensity 5.8); IR (hexane) ν_{CO} 2070 (s), 2025 (vs), 2015 (s), 1990 (w), 1981 (m), 1968 (m), 1866 (m), 1826 (w) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, amb) δ 4.99 (s, 5 H, C$_5$H$_5$), 4.63 (s, 3 H, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, ambient) δ 341.4 (s, 1 C, COCH$_3$), 93.8 (s, 5 C, C$_5$H$_5$), 70.8 (s, 1 C, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 180K) δ 338.9 (s, 1 C, COCH$_3$), 248.6 (s, 2 C, μ-CO), 212.8 (s, 2 C, CO), 211.5 (s, 2 C, CO), 204.0 (s, 2 C, CO), 93.0 (s, 5 C, C$_5$H$_5$), 70.4 (s, 1 C, OCH$_3$). Anal. Calcd for C$_{15}$H$_8$O$_9$Fe$_3$: C, 36.05; H, 1.61. Found: C, 36.06; H, 1.43.

Preparation of AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$-(PPh$_3$)(η-C$_5$H$_2$). CoFe$_2$(μ-H)(μ_3-COCH$_3$)(CO$_7$)(η-C$_5$H$_5$) (0.7 g, 1.47 mmol) and AuCH$_3$(PPh$_3$) (0.7 g, 1.47 mmol) in toluene (50 mL) were heated in vacuo for 6 h. Removal of solvent and extraction with the minimum volume CH$_2$Cl$_2$ followed by chromatography gave a dark brown-green band. Recrystallization from CH$_2$Cl$_2$/hexane afforded black crystals of AuCoFe$_2$(μ_3-COCH$_3$)(μ_3-CO)(CO)$_6$(PPh$_3$)(η-C$_5$H$_5$) (0.87 g, 63%): IR (cyclohexane) ν_{CO} 2030 (w), 2000 (s), 1961 (s), 1938 (sh), 1810 (w, br) cm^{-1}; IR (KBr disk, selected bands) ν_{max} 3055 (w), 2935 (w), 2834 (w), 2028 (s), 1993 (vs), 1957 (vs), 1944 (vs), 1773 (m, br), 1434 (m), 1198 (s), 1150 (s) cm^{-1}; ^{1}H NMR (CD$_2$Cl$_2$, ambient) δ 7.5 (m, 15 H, C$_6$H$_5$), 5.32 (s, 5 H, C$_5$H$_5$), 4.38 (s, 3 H, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, ambient) δ 325.5 (s, 1 C, COCH$_3$), 212.9 (s, br, 7 C, CO), 134.1–129.1 (m, C$_6$H$_5$), 89.9 (s, 5 C, C$_5$H$_5$), 68.2 (s, 1 C, OCH$_3$); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 176 K) δ 320.4 (s, 1 C, COCH$_3$), 243.9 (s, 1 C, μ-CO), 214.6 (s, 2 C, CO), 214.1 (s, 2 C, CO), 208.4 (s, 2 C, CO), 133.4–128.9 (m, C$_6$H$_5$), 89.4 (s, 5 C, C$_5$H$_5$), 67.9 (s, 1 C, OCH$_3$); ^{31}P{^{1}H} NMR (CDCl$_3$, ambient) δ 55.1. Anal. Calcd for C$_{32}$H$_{23}$O$_8$AuCoFe$_2$P: C, 41.14; H, 2.46. Found: C, 40.46; H, 2.22.

Crystal Structure Determinations

Details of data collection procedures, structure solution, and refinement are given in Table VII. Data were collected on an Enraf-Nonius CAD4F automated diffractometer. Standards were measured every 2 h during data collection. No significant decay in intensities was observable. Lorentz, polarization, and absorption corrections were applied to all data sets. For complexes 2 and 7 the empirical absorption/extinction (DIFABS) correction method of Walker and Stuart[59] was applied, while for compound 4 a correction by Gaussian quadrature[60] was computed. Structures were solved by standard methods (Patterson function for 4 and 7; direct methods (MITHRIL)[61] for 2, electron density difference syntheses revealing the positions of all non-hydrogen atoms. Hydrogen atoms were included at calculated positions for the phenyl and cyclopentadienyl rings (C–H = 1.084 Å) and methyl groups (C–H= 1.073 Å) and the positional and thermal parameters (0.05 Å^3) fixed during refinement. The hydrido ligand in complex 2 was detected in a final difference Fourier synthesis and allowed free thermal and positional motion during refinement. During initial stages of the refinement block-diagonal least squares was applied, with final cycles of full-matrix least squares. For complex 7 it was necessary to divide the parameter list into two blocks and apply full-matrix methods to these separately. The function minimized during least squares was $\sum w(|F_o| - |F_c|)^2$, with the weighting function $w = [\sigma^2(F_o)]^{-1}$ used and judged satisfactory. $\sigma(F_o)$ was estimated from counting statistics. All non-hydrogen atoms were allowed anisotropic thermal motion. Scattering factors were taken from ref 62, with corrections applied for anomalous dispersion. All calculations were carried out on the in-house Gould-SEL 32/27 mini computer, using the GX suite of programs.[63]

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