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Tungsten Iron Heterobimetallic Complexes: Preparation and Reactions

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Organometallic cyclopentadienyl-substituted phosphines $(\eta^5\text{-}C_5H_4PPh_2)Fe(CO)_2CH_3$ (**3**) and $(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3CH_3$ (**4**) were prepared from $(\eta^5\text{-}C_5H_5)M(CO)_nCH_3$ (M = Fe, n = 2; M = W, n = 3) by lithiation of the cyclopentadienyl ring followed by reaction with chlorodiphenylphosphine. Complexes **3** and **4** were used to synthesize heterobimetallic compounds $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)WCH_3(CO)_2Cp$ (**5**) and $CH_3(CO)_3W(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)Fe(COCH_3)(CO)Cp$ (**8**), whose X-ray structures were determined. $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)WCl(CO)Cp$ (**6**) was also prepared by the substitution of a carbonyl ligand on $Cp(CO)_3WCl$ by **3**. The reaction of **3** with $[Cp(CO)_3W]^+BF_4^-$ gave the heterobimetallic cation $[CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)W(CO)_3Cp]^+BF_4^-$ (**7**). The reduction of **6** with sodium amalgam gave the heterobimetallic anion, and although this anion could be alkylated with methyl iodide to yield **5**, protonation of the anion did not produce the hydride. The reaction of the heterobimetallic cation **7** with methyllithium produced $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)W(COCH_3)(CO)Cp$ (**12**). Reaction of **7** with excess sodium borohydride gave low yields of the tungsten hydride heterobimetallic complex $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2\text{-}\mu)W(H)(CO)_2Cp$ (**10**).

Introduction

Dinuclear transition-metal complexes can be considered to represent the simplest model of metal surfaces and have the potential, through cooperativity of the metal centers, to effect unique transformations of simple organic substrates not possible by single metal centers.[1] Heterodinuclear complexes are particularly interesting in this regard since each metal may be able to effect a reaction that is not possible for the other, or both metals in concert could orchestrate a transformation unavailable to either metal alone.

Because early transition metals are strong hydride donors[2] and are oxophilic[3] while late transition metals readily coordinate carbon monoxide and effect its "insertion" into a metal–carbon bond,[4] the rational design of a heterobimetallic catalyst for carbon monoxide reduction appeared to include early and late metal centers. Although there are a number of ways in which two dissimilar transition metals may be brought together, we initially chose to bridge the two metals by a cyclopentadienylphosphine ligand, which has been employed to bridge a variety of dinuclear complexes.[5]

Results and Discussion

Synthesis. Organometallic phosphines $(\eta^5\text{-}C_5H_4PPh_2)Fe(CO)_2CH_3$ (**3**) and $(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3CH_3$ (**4**) were prepared in high yield by the lithiation of $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$ (**1**) and $(\eta^5\text{-}C_5H_5)W(CO)_3CH_3$ (**2**), respectively, followed by reaction with chlorodiphenyl phosphine (Scheme I).[6] Complexes **3** and **4** were moderately air- and moisture-sensitive crystalline complexes that were conveniently purified by flash column chromatography.

The tungsten(methyl)–iron(methyl) heterobimetallic complex **5** was prepared by the displacement of coordinated THF from the intermediate $Cp(CO)_2W(THF)CH_3$, generated by the photolysis[7] of **2** in the coordinating solvent. Complex **5** could also by purified by flash column chromatography and recrystallized. The infrared stretching frequencies of the carbonyl groups coordinated to tungsten in **2** were shifted to lower wavenumbers on formation of **5**, consistent with the complexation of tungsten to the phosphine donor. The stretching frequencies of the carbonyls on iron remained unchanged, suggesting no interaction with tungsten. The NMR spectrum of **5** showed the protons on the cyclopentadienyl ring coordinated to tungsten as doublets coupled to phosphorus and two sets of multiplets for the cyclopentadienyl protons of the (diphenylphosphino)cyclopentadienyl ligand. The tungsten–methyl appeared as a doublet. The ^{31}P NMR showed a shift from −20.2 ppm in **3** to 28.7 ppm on complexation with tungsten in **5**.

The geometry of complex **5** with respect to the groups coordinated to tungsten could be assigned as trans. First, in the infrared spectrum the antisymmetric ν_{CO} stretch at 1839 cm^{-1} was more intense than the symmetric ν_{CO} stretch at 1926 cm^{-1}.[8] Further, the ^1H NMR spectrum showed a $^3J_{PH}$ coupling constant of 1.6 Hz, consistent with a trans geometry.[9] The ^{31}P chemical shift at 28.7 ppm also was consistent with the trans assignment.[10] Thus, in solution, only the trans isomer is observed, and at no time during the course of the reaction or in the workup was any evidence of the cis isomer observed.

The tungsten(chloro)–iron(methyl) complex **6** was synthesized by the trimethylamine *N*-oxide promoted substitution[11] of cyclopentadienylchlorocarbonyltungsten[12] by

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(1) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*, Wilkinson, G., Able, E.; Eds.; Pergamon Press: Oxford, England, 1982; Chapter 40.

(2) (a) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25. (b) Pearson, R. G. *Chem. Rev.* **1985**, *85*, 41.

(3) See, for example: (a) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. (b) Gaus, P. L.; Kao, S. C.; Youngdahl, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (c) Tooley, P. A.; Ovalles, C.; Kao, S. C.; Darensbourg, D. J.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465 and references therein.

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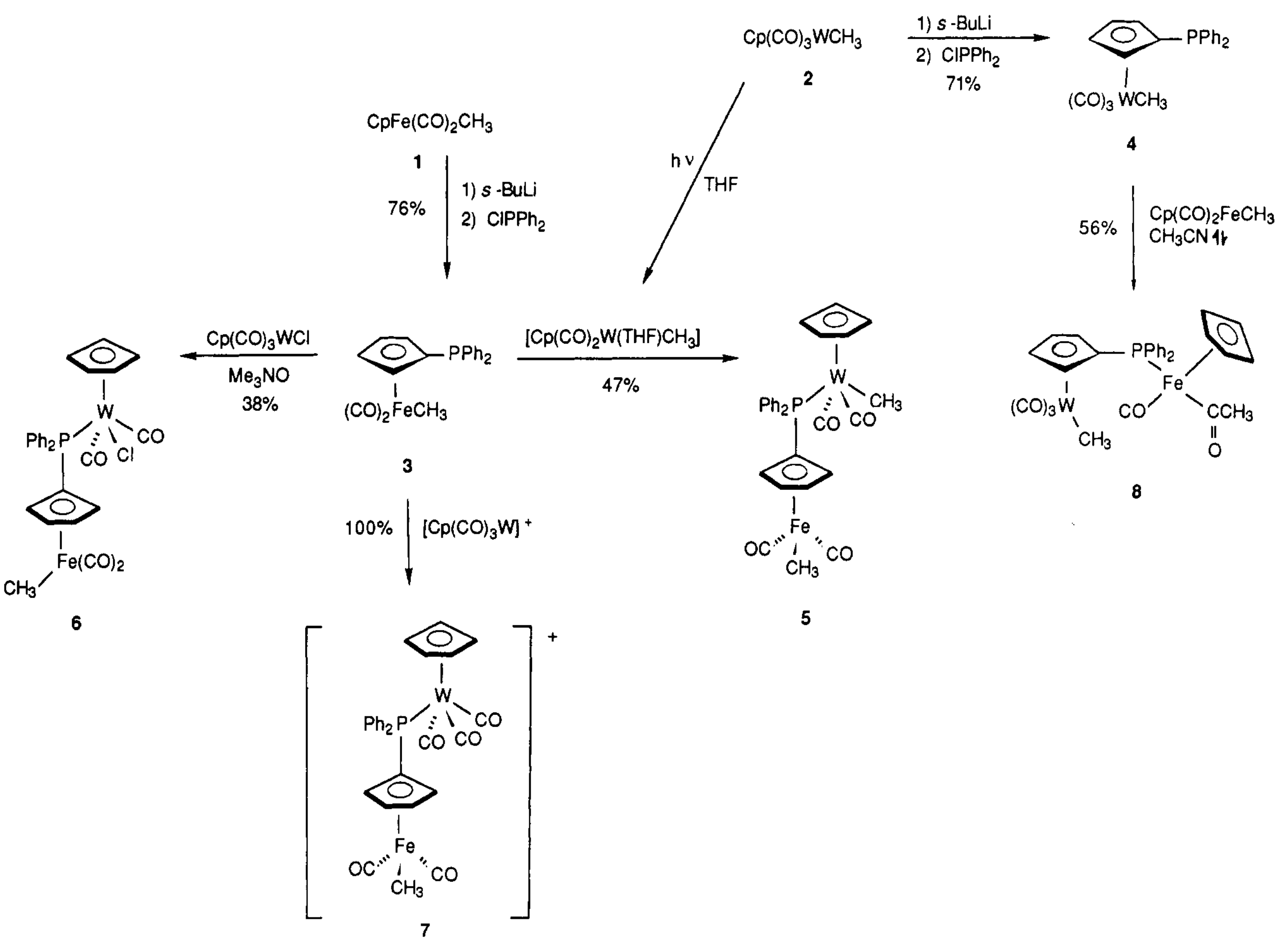
Scheme I



3. The cis geometry was assigned on the basis of the position of the ν_{CO} stretch and the ^{31}P NMR peak at 10.97 ppm. In this reaction, there was no evidence of the reaction of 3 with itself, even though its ν_{CO} bands are at 2010 and 1960 cm^{-1}. Generally, trimethylamine *N*-oxide will promote substitution on carbonyl complexes having ν_{CO} > 2000 cm^{-1}.[11]

The addition of the iron–methyl complex 3 to a solution of cyclopentadienyltricarbonyltungsten tetrafluoroborate gave the (diphenylphosphino)cyclopentadienyl-bridged heterobimetallic cation 7. The cyclopentadienyltricarbonyltungsten cation was prepared by reaction[13] of cyclopentadienyltricarbonylhydridotungsten[14] with the triphenylmethyl cation. Although tetrafluoroborate, hexafluorophosphate, and hexafluoroarsenate salts were prepared, the tetrafluoroborate salt was utilized in subsequent reactions.

The heterobimetallic cation 7 was stable in air for short periods (<3 h) and in carefully dried, degassed solvents (~1 day). The ^1H NMR spectrum showed that the methyl group on iron (δ 0.13 ppm) had not shifted, indicating that the charge was localized on tungsten. The ^{31}P NMR of 7 showed a singlet at 5.57 ppm (J_{PW} = 196 Hz), unambiguous proof of the tungsten–phosphorus link.

The yield of 7 was quantitative (NMR), and an 86% isolated yield was realized. Although $[Cp(CO)_3M]^+$ cations (M = Mo, W) form adducts with a carbonyl-containing metal center[15] and $[Cp(CO)_3Mo]^+$ reacts with $FpCH_3$ by promoting methyl migration onto an iron carbonyl complexed to the molybdenum cation, this reaction path was not observed with 3.

Heterobimetallic complex 5 showed no tungsten–(iron ligand) or iron–(tungsten ligand) interactions, either in solution or in the solid state (vide infra). In an attempt to induce such an intramolecular interaction, the tungsten(methyl)–iron(acetyl) complex 8 was synthesized.

The reaction of 4 with $FpCH_3$ (1) was carried out under the usual conditions to promote CO insertion into the iron–methyl bond by phosphine.[16] The reaction was monitored both by solution infrared (appearance of an acyl at 1590 cm^{-1}) and ^{31}P NMR (disappearance of uncomplexed P at δ −17 ppm and appearance of complexed phosphorus at δ 70.5 ppm). The reaction was stopped when the ratio of starting material to product reached 1:16. There was no evidence of a similar self reaction of 4 (absence of ^{183}W satellites in the ^{31}P spectrum[18]). The reaction of 4 with itself would not be expected, however, since $WpCH_3$ (2) is resistant to this CO insertion reaction.[17]

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Table I. Details of the Crystallographic Experiment and Computations for 5 and 8

	5	**8**
mol formula	$C_{28}H_{25}FeO_4PW$	$C_{29}H_{25}FeO_5PW$
f w	696.15	724.99
cryst system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
lattice constants		
a, Å	10.630 (3)	11.946 (3)
b, Å	15.567 (2)	14.940 (3)
c, Å	16.910 (5)	15.378 (3)
β, deg	103.25 (2)	106.67 (2)
V, Å^3	2724	2629.2
temp, °C	20	21
Z	4	4
$F(000)$	1496	1416
ρ(calcd), g cm^{-3}	1.70	1.83
cryst dimens, mm	0.46 × 0.20 × 0.35	0.46 × 0.16 × 0.20
radiatn	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
monochromator	graphite	graphite
μ, cm^{-1}	50.73	52.9
scan type	ω (Wyckoff)	$\theta/2\theta$
geometry	bisecting	bisecting
scan speed, deg min^{-1}	4.88–29.30	1.98–29.30
2θ range, deg	3.5–50	4–50
index restrictns	$-13 \le h \le 13$, $-19 \le k \le 0$, $-21 \le l \le 0$	$0 \le h \le 15$, $0 \le k \le 18$, $-19 \le l \le 19$
total no. of reflctns	4329	5277
no. of unique, obsd reflctns	3449	4234
obsd reflctn criterion	$\lvert F_o\rvert > 2.5\sigma(\lvert F_o\rvert)$	$\lvert F_o\rvert > 2.55\sigma(\lvert F_o\rvert)$
no. of least squares parameters	298	340
data/parameter ratio	11.57	12.45
R[a]	0.0406	0.0342
R_w[a]	0.0428	0.0346
GOF[a]	1.126	1.42
g (not refined)	0.001	0.000 33
slope, normal probability plot[b]	1.028	1.251

[a] $R = (\sum\lvert F_o - F_c\rvert)/(\sum F_o)$; $R_w = ((\sum w\lvert F_o - F_c\rvert^2)/(\sum w(F_o)^2))^{1/2}$; GOF $= ((\sum w\lvert F_o - F_c\rvert)^2/(N_{data} - N_{params}))^{1/2}$. [b] Abrahams, S. C. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 261–268.

Both the solution and mull infrared spectra showed ν_{CO} for the acetyl carbonyl at 1590 cm^{-1} and the ^{13}C NMR of 8 showed the acetyl carbonyl as a singlet at δ 275, both indicating little or no interaction of the iron acetyl with tungsten. Considerable oxycarbenoid character has been observed with a similar molybdenum–acetyliron heterobimetallic complex.[19]

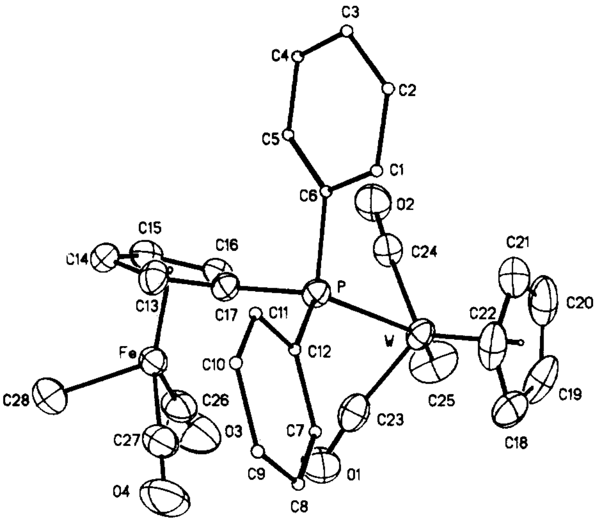

Figure 1. Molecular structure of dimethyl heterobimetallic complex 5. (Phenyl ring carbons are depicted as spheres of arbitrary radius.)

Table II. Selected Bond Distances (Å)[a] and Angles (deg)[a] for Dimethyl Heterobimetallic Compound 5

Bond Distances

W–P	2.448 (2)	C6–P	1.845 (6)	Fe–C26	1.73 (1)
W–C23	1.935 (11)	C12–P	1.845 (5)	Fe–C27	1.75 (1)
W–C24	1.955 (9)	C17–P	1.833 (6)	Fe–C28	2.06 (1)
W–C25	2.295 (12)			Fe–Cp	1.726
W–Cp	1.997				

Bond Angles

P–W–C23	81.3 (3)	C26–Fe–C27	92.7 (5)
P–W–C24	80.8 (2)	C26–Fe–C28	87.3 (5)
P–W–C25	137.1 (4)	C27–Fe–C28	86.1 (5)
C23–W–C24	107.8 (4)	Fe–C26–O3	178 (1)
C23–W–C25	73.8 (5)	Fe–C27–O4	176 (1)
C24–W–C25	74.5 (4)		
W–C23–O1	172.1 (8)		
W–C24–O2	176.8 (9)		

[a] Estimated standard deviations in the least significant digits are given in parentheses.

Crystal Structures of 5 and 8. The solid state structure of 5, as determined by a single-crystal X-ray diffraction study, verified the structure expected on the basis of spectroscopic data and showed the orientation of the two metal centers with respect to each other (Figure 1, Table I). The phosphorus coordinated to tungsten is trans to the methyl group. The distance between the two metal atoms, 4.970 Å, is clearly prohibitive for any direct W–Fe interaction, although in solution, with rotation about the phoshorus–carbon(cyclopentadienyl) and/or tungsten–phosphorus bonds, the two centers could approach considerably closer.

All of the bond lengths and angles (Table II) associated with the ((diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron portion are the expected values, comparing closely to unsubstituted cyclopentadienylorganoiron complexes such as $[Cp(CO)_2Fe]_2$[19] as well as other cyclopentadienyl organometallic compounds.[20-22]

For the $Cp(CO)_2PWCH_3$ fragment of 5, the W–Cp centroid distance is in agreement with that found in $[Cp(CO)_3W]_2$.[23] The bond distances and angles for the other ligands on tungsten are normal for a "piano stool" complex of this type.[23-26]

The solid-state structure of the tungsten(methyl)–iron(acetyl) heterobimetallic complex 8 was consistent with the

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Table III. Selected Bond Distances (Å)[a] and Angles (deg)[a] and Torsion Angles for Tungsten(Methyl)–Iron(Acetyl) Complex 8

		Bond Distances			
W–C6	1.989 (5)	P–C10	1.834 (5)	Fe–C27	1.775 (7)
W–C7	1.965 (6)	P–C16	1.830 (5)	Fe–C28	1.908 (6)
W–C8	2.028 (7)	P–C3	1.830 (5)	C28–C29	1.59 (1)
W–C9	2.288 (7)			O5–C28	1.146 (7)
W–Cp	2.014			Fe–P	2.197 (1)
				Fe–Cp	1.743
		Bond Angles			
C6–W–C8	77.3 (2)	W–C6–O1	176.5 (6)	C27–Fe–C28	93.5 (3)
C6–W–C9	72.4 (2)	W–C7–O2	179.0 (4)	P–Fe–C27	94.8 (2)
C7–W–C28	77.6 (3)	W–C8–O3	179.1 (6)	P–Fe–C28	92.3 (2)
C7–W–C9	74.9 (3)	O4–C27–Fe	170.8 (7)	Fe–P–C23	118.1 (2)
C6–W–C7	101.2 (2)			O5–C28–Fe	131.8 (6)
C8–W–C9	133.6 (2)			O5–C28–C29	112.7 (6)
				C29–C28–Fe	115.5 (5)
		Torsion Angles			
Fe–P–C3–C4	−177.0	Fe–P–C16–C17	33.8	Fe–P–C10–C11	−99.3
Fe–P–C3–O2	15.7	Fe–P–C16–C21	−150.1	Fe–P–C10–C11	73.6

[a] Estimated standard deviation in the least significant digits are given in parentheses.

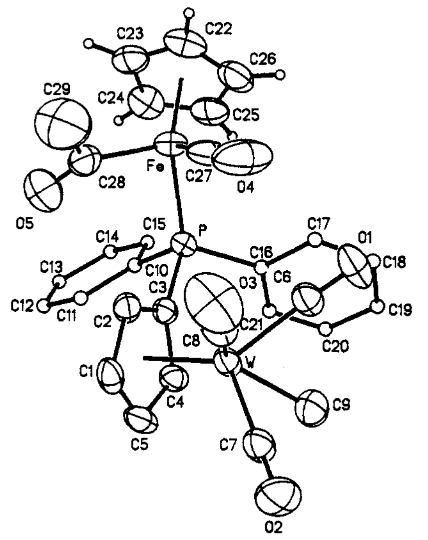

Figure 2. Molecular structure of tungsten(methyl)–iron(acetyl) heterobimetallic complex 8. (Phenyl ring carbons are depicted as spheres of arbitrary radius.)

solution structure assigned from the interpretation of the spectral data, showing the Fe–P linkage and the acyl ligand, the product of the phosphine-induced CO insertion (Figure 2, Table I).

The coordination geometry about the tungsten atom is essentially unchanged from the distorted square-pyramidal structure expected for $Cp(CO)_3MR$ compounds.[27] The methyl substituent is located directly under a cyclopentadienyl carbon, as is generally the case in the parent complexes.[28] Slight distortion of the idealized square-pyramidal geometry about tungsten in 8 leads to a wider angle of 133.6 (2)° between the carbonyl group and the methyl group trans to it and a smaller angle of 101.2 (2)° about tungsten and the two carbonyl groups trans to each other (Table III). The bond distances and angles are consistent with other cyclopentadienylmetal compounds.[20,23] The "$Cp(CO)PFe(COCH_3)$" fragment of 8 contains bond angles and lengths that are the expected values.[19,24c,29]

The O5–C28–Fe–C27 torsion angle θ of 8 is 138°, giving an anti arrangement of the acetyl oxygen atom and carbon monoxide ligand. Conformational analyses of $Cp(CO)PPh_3Fe(COR)$ compounds predicted that complexes with $\theta = 0°$ (syn) should be more stable than those with $\theta = 180°$ (anti), in direct contrast to X-ray diffraction results.[30]

The acyl ligand at the iron center of 8 exhibts a peculiar geometry. The Fe–C28–O5 bond angle of 131.8 (6)° is significantly distorted from idealized "ketone" sp^2 geometry and is also larger than that found in other iron–acyl complexes.[22,32] The only reported compound that exhibits a larger M–C–O angle is the metal formyl compound $[(C_6H_5O)_3P(CO)_3FeCHO]^-[NEt_4]^+$.[33] While the C28–C29 bond length (1.591 (1) Å) of 8 is expected, the remaining bond lengths of the acyl ligand are unusual. The Fe–C28 and C28–O5 bond distances of 1.908 (6) and 1.146 (7) Å, respectively, are the shortest of the Fe–C_α and C_α–O bond distances reported.[22,23] The Fe–C28 distance is similar to Fe–C distances of σ-bound acetylene–iron compounds[22] and the C-O bond length is similar to those found in terminal carbonyl compounds.[19,20]

The relatively short formyl CO bond and wide Fe–C–O angle of $(C_6H_5O)_3P(CO)_3FeCHO$ has been attributed to the hydride donor ability of the formyl ligand.[33] This cannot be the case with 8; significant carbene-type hybridization must be present, shortening the Fe–C28 and C28–O5 bonds and opening up the Fe–C28–O5 bond angle.

This unusually large angle seems to be related to the twist of the rings around the phosphorus atom of the ((diphenylphosphino)cyclopentadienyl)organotungsten ligand. The monometallic iron acyl compounds of the type $Cp(CO)PPh_3Fe(COR)$ all exhibit the structural feature of having one phenyl ring located under the OC–Fe–C_α plane and parallel to that plane, with the other two rings splayed. One of these two rings is in an orientation such that an ortho hydrogen atom is pointing directly at the acetyl oxygen atom.[29,30] In 8, the ring located under the OC–Fe–C_α plane is the substituted cyclopentadienyl ring coordinated to the tungsten atom with its other ligands. This ring is not parallel to the OC–Fe–C_α plane, but perpendicular. This orientation is dictated by the bulk.of the organotunsten fragment which apparently prevents the

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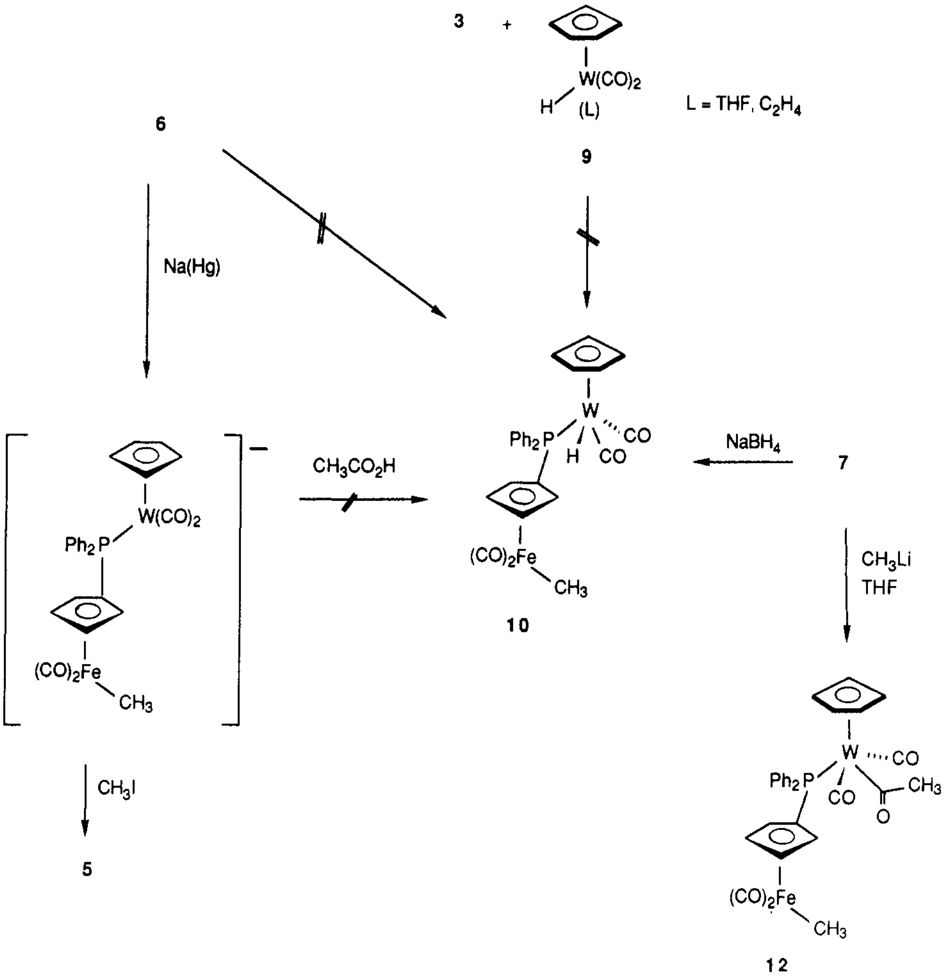
Scheme II



ring from adopting the parallel conformation. The bulk associated with the organotungsten-substituted cyclopentadienyl ring also has the effect of twisting the two phenyl rings into unusual angles compared to those of $Cp(CO)PPh_3Fe(COR)$. The C10–C15 phenyl ring of **8**, which should be the ring involved in the phenyl ring hydrogen atom–acetyl oxygen atom interaction, is twisted such that there is a C11–O5 intramolecular interaction (distance = 3.17 Å). It is this interaction that may be causing the Fe–C28–O5 angle of **8** to be unexpectedly large. With the widened angle comes concomitant O5–C28 and C28–Fe bond contraction.

The solution and mull phase infrared spectra of **8** both show the ν_{CO} for the acetyl ligand at ca. 1590 cm^{-1}, indicating that a similar steric argument could be invoked to explain the solution spectral results. In solution, with free rotation about the $P–C_{ipso}$ and Fe–P bonds, the ((diphenylphosphino)cyclopentadienyl)organotungsten ligand is very sterically demanding, almost completely shielding the C27–Fe–C28–O5 face of the molecule. The effect of this is to make the Fe–C28–O5 angle > 120° in solution, without lowering the ν_{CO} frequency for the acetyl ligand.

Reactions. The photolysis of either the tungsten(methyl)–iron(methyl) (**5**) or the tungsten(methyl)–iron(acetyl) (**8**) complex did not yield reductive elimination products such as methane, ethane, or acetone but only a complex mixture of metal-containing decomposition products. Thermolysis in either the absence or the presence of triphenylphosphine also failed to generate volatile elimination products. Triphenylphosphine, for example, displaced the bridging phosphine in **5** to yield **3** and $Cp(CO)_2Ph_3PWCH_3$.

Because the heterobimetallic tungsten hydride **10** contains an early-transition-metal hydride, an oxophilic tungsten, and an iron carbonyl capable of CO insertion reactions, its synthesis was an important goal. The photolysis of $Cp(CO)_3WH$ at −30 °C in THF-d_8 proceeded with the evolution of CO and the formation of **9** (L = THF).[34] Addition of **3** to this solution did not produce the heterobimetallic hydride **10**. The preparation of **9** (L = C_2H_4) was carried out by the photolysis of $CpW(CO)_3H$ in the presence of ethylene,[35] but **3** failed to displace the ethylene ligand from **9** (L = C_2H_4).

The tungsten(chloro)–iron(methyl) complex **6** could not be reduced cleanly to **10** by sodium borohydride, although a characteristic metal hydride at δ −6.60 ppm (d, $^2J_{PH}$ = 60 Hz) was observed in the mixture of products. The reaction of **6** with tributyltin hydride under radical conditions did not yield the desired hydride. Reaction of **6** with sodium amalgam generated the heterobimetallic anion **11** which could be quenched with methyl iodide to give **5** in a 43% isolated yield. Quenching the anion with acetic acid produced decomposition products. Again, the presence of **10** in the mixture was indicated in the NMR spectrum of the mixture.

The reaction of the tungsten(tricarbonyl)–iron(methyl) cation **7** with methyllithium in THF at −78 °C gave the tungsten(acetyl)–iron(methyl) complex in 62% yield. Only the trans isomer was observed as shown by the greater

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[34] Mahmoud, K. A.; Rest, A. J.; Alt, H. G. *J. Chem. Soc., Dalton Trans* **1984**, 187.

[35] Alt, H. G.; Eichner, M. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 121.

intensity of the antisymmetric infrared stretching frequency (1840 cm^{-1}) compared to the symmetric stretching frequencies at 1925 cm^{-1}. The acyl carbonyl stretch appeared at 1590 cm^{-1}. In addition, the ^{1}H NMR exhibited a doublet for the tungsten cyclopentadienyl protons at δ 5.05 ppm ($^3J_{PH}$ = 0.93 Hz). The ^{1}H NMR chemical shifts for the acyl methyl (δ 2.60 ppm), the tungsten cyclopentadienyl ring, and the infrared frequencies were identical with those reported for trans $Cp(CO)_2(PPh_3)W(COCH_3)$.[36]

Triethylborohydride reduces the cation $[Cp(CO)_3(Ph_3P)W]^+$ to the formyl complex $Cp(CO)_2(PPh_3)WCHO$.[37] The reduction of cation **7** with lithium triethylborohydride (superhydride) at −40 °C in THF-d_8 gave a mixture that showed a formyl proton in the ^{1}H NMR at δ +14.5 ppm and at ambient temperature ν_{CO} at 1630 cm^{-1} in the infrared. This species could not be isolated pure. The major product from this reaction, however, was $(\eta^5\text{-}C_5H_4PPh_2)Fe(CO)_2CH_3$ (**3**). The formyl proton persisted at room temperature; acetaldehyde could not be detected as a reductive elimination product.

Addition of sodium borohydride to cation **7** in THF/methanol at −78 °C gave a reaction on warming to −20 °C, the major product of which was the monometallic iron complex **3** and its BH_3 adduct. Chromatography and recrystallization of the minor product gave cis **10** which could not be obtained analytically pure because of decomposition during purification, the disappearance of the hydride signal being observed on continued manipulation. The ^{1}H NMR spectrum showed the hydride at δ −6.8 ppm and the tungsten cyclopentadienyl protons as a doublet at δ 5.31 ($^3J_{PH}$ = 1.3 Hz). The iron methyl group was shifted upfield to δ −0.05 ppm. Two multiplets (δ 5.20 and 5.05 ppm) are characteristic of the AA′BB′ cyclopentadienyl protons of the diphenyl cyclopentadienyl ligand. The ^{31}P spectrum showed an unresolved (for J_{PW}) peak at δ 26.00 ppm. On the basis of the spectral data and by comparison with the spectra of $Cp(CO)_2(PPh_3)WH$[38] complex **10** was assigned the cis geometry.

From the reaction of the heterobimetallic cation **7** with tetrabutylammonium hydroxide neither the carboxylate nor the hydride (the product of decarboxylation) could be detected.

Experimental Section

Proton NMR spectra were recorded on an IBM WP 270 (270 MHz) or IBM WP 200 (200 MHz) spectrometer in the deuterated solvent indicated using residual protons in the solvent as internal standard: $CHCl_3$, δ 7.24; benzene, δ 7.15; tetrahydrofuran (THF), δ 3.58; acetone, δ 2.04. Carbon-13 NMR spectra were recorded on an IBM WP 270 (68 MHz) or an IBM WP 200 (50.23 MHz) in the solvent indicated using solvent as internal standard: $CHCl_3$, δ 77.0; THF, δ 67.4; dichloromethane, δ 53.8. A 4-s run delay was used. Phosphorus-31 NMR were recorded on an IBM WP200 (81.02 MHz) in 10-mm tubes. Chemical shifts were referenced in 85% H_3PO_4, positive chemical shifts being downfield. Carbon-13 and phosphorus-31 NMR spectra were run in the broad band decoupled mode. Infrared spectra were recorded on a Beckman 4250 or Beckman Acculab spectrometer. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA. High-resolution mass spectrum (HRMS) was performed by the Midwest Center for Mass Spectrometry in Lincoln, NE.

Tetrahydrofuran (THF), benzene, pentane (containing diglyme), and diethyl ether were freshly distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride and stored in an amber bottle over activated 4-Å sieves. Carbon tetrachloride was distilled from phosphorus pentoxide and used immediately. Toluene was distilled from sodium and acetonitrile from calium hydride at water aspirator pressure. Hexanes for chromatography were distilled from $KMnO_4$; ethyl acetate was stored over calcium chloride. Solvents were degassed either by four freeze-pump-thaw cycles or by bubbling Ar into the solvent. Deuterated solvents were purified in a similar manner. Acetone-d_6 was stored over activated 3-Å molecular sieves.

Cyclopentadienyldicarbonylmethyliron (**1**) was prepared according to the Na/Hg amalgam literature procedure.[6] Cyclopentadienyltricarbonylmethyltungsten[6] (**2**) and cyclopentadienyltricarbonyl hydridotungsten[14] were prepared by the reaction of tungsten hexacarbonyl with sodium cyclopentadienide (DME)[39] in refluxing THF for 12 h. The resulting solution was cooled to 0 °C and quenched with methyl iodide or acetic acid. In the hydride preparation, all manipulations were performed in the dark. Both the iron and tungsten organometallic alkyl compounds **1** and **2** were purified by flash column chromatography (silica gel, hexanes). The hydridotungsten compound was isolated by Schlenk filtration, dried under reduced pressure (0.1 mmHg) overnight, and purified by sublimation (0.1 mmHg, 55 °C, water cooled cold finger). Proton NMR and infrared spectra agreed with literature values.[6,14] Cyclopentadienyltricarbonylchlorotungsten was prepared by a modification of the literature procedure.[12] Cyclopentadienyltricarbonylhydridotungsten was dissolved in carbon tetrachloride. The next day the chloride was isolated by filtration. Spectral data agreed with the literature values.[12]

General Procedure for the Preparation of ((Diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron (3) and ((Diphenylphosphino)cyclopentadienyl)tricarbonylmethyltungsten (4). A THF solution of starting unsubstituted cyclopentadienyl organometallic alkyl compound (**1** or **2**)[6] was cooled to −78 °C. *sec*-Butyllithium (1.01 equiv) was added by syringe. The solution was allowed to react for 10 min at −78 °C at which time chlorodiphenylphosphine (1.0 equiv based on alkyl lithium) was added by syringe. The cold bath was removed, and the solution was warmed to room temperature. After 2 h the solvent was removed by rotary evaporation. The crude material was purified by flash column chromatography (silica gel; short column). Starting material (**1** or **2**) eluted first with hexanes, followed by the ((diphenylphosphino)cyclopentadienyl)organometallic compound (**3** or **4**) (hexanes/EtOAc; 95/5).

((Diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron (3): waxy orange crystals (76%): mp 76–78 °C; IR ($CHCl_3$) ν_{CO} 2015 (s), 1960 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.55–7.25 (m, 10 H, Ph), 4.81 (m, $J \approx 2$ Hz, 2 H, C_5H_4P), 4.68 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 0.12 (s, 3 H, CH_3); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 216.4 (s, CO), 137.0 (d, J_{PC} = 4.7 Hz, ipso C_6H_5P), 133.5 (d, J_{PC} = 17.8 Hz, *o*-C_6H_5P), 129.0 (s, *p*- or *m*-C_6H_5P), 128.4 (s, *p*- or *m*-C_6H_5P), 92.1 (d, J_{PC} = 6.7 Hz, C2, C2′ C_5H_4P), 86.5 (s, C3, C3′ C_5H_4P), −22.2 (s, CH_3); ^{31}P NMR ($CDCl_3$) δ 20.1. Anal. Calcd for $C_{20}H_{17}O_2FeP$: C, 63.85; H, 4.56. Found: C, 63.65; H, 4.63.

((Diphenylphosphino)cyclopentadienyl)tricarbonylmethyltungsten (4): yellow crystals (71%); mp 113–115 °C; IR (CH_2Cl_2) ν_{CO} 2003 (s), 1929 (s) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.35–7.25 (m, 10 H, Ph), 5.51 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 5.15 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 0.28 (s, 3 H, CH_3); ^{13}C NMR (50.32 MHz, THF/THF-d_8) δ 228.5, 215.8 (1:2 ratio, CO), 137.7 (d, J_{PC} = 12.2 Hz, ipso C_6H_5P), 133.5 (d, J_{PC} = 19.5 Hz, *o*-C_6H_5P), 129.2 (s, *p*-C_6H_5P), 128.5 (d, J_{PC} = 7.4 Hz, *m*-C_6H_5P), 103.5 (d, J_{PC} = 20 Hz, ipso C_6H_5P), 96.6 (d, J_{PC} = 12.2 Hz, C2, C2′ C_5H_4P), 95.0 (s, C3, C3′ C_5H_4P), −34.6 (s, CH_3); ^{31}P NMR ($CDCl_3$) δ −17.2. Anal. Calcd for $C_{21}H_{17}O_3PW$: C, 47.39; H, 3.22. Found: C, 47.47; H, 3.29.

Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienyl-*trans*-dicarbonylmethyltungsten (5). A flask equipped with a magnetic stir bar was charged with cyclopentadienylmethyltricarbonyltungsten[6] (**2**) (0.348 g, 1.00 mmol) and 250 mL of THF and was capped with a septum. The resulting yellow solution was cooled to −40 °C and

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photolyzed for 2 h under an Ar atmosphere, during which time the solution became brown. A THF solution of ((diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron (**3**) (0.376 g, 1.00 mmol) cooled to −40 °C was added by cannula to the photolyzed tungsten compound. The reaction flask was wrapped with aluminum foil, and the reaction solution was brought to room temperature. After being stirred at room temperature for 1 h, the solution was filtered through Celite and solvent was removed by rotary evaporation. The resulting orange oil was chromatographed on alumina, activity II. Elution with hexanes gave unreacted **2** and hexanes/EtOAc (95/5) gave unreacted **3**. The heterobimetallic product **5** was eluted with hexanes/EtOAc (70/30); 0.327 g, 0.47 mmol, 47%; IR (neat) ν_{CO} 2015 (s), 1960 (br s), 1926 (m), 1839 (s) cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6) δ 7.6–7.5 (m, 4 H, Ph), 7.10–7.0 (m, 6 H, Ph), 4.75 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 4.36 (d, $^3J_{PH}$ = 1.6 Hz, 5 H, WCp), 4.05 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 0.95 (d, $^3J_{PH}$ = 2.7 Hz, 3 H, WCH_3), 0.14 (s, 3 H, $FeCH_3$); ^{31}P NMR (C_6D_6) δ 28.7 (s, J_{PW} = 260 Hz).

Compound **5** also was prepared from cyclopentadienyltricarbonylchlorotungsten (0.532 g, 0.742 mmol) by its addition to an excess of 3% Na amalgam in THF at 0 °C. The reaction mixture was warmed to room temperature and allowed to stir overnight. The resulting yellow solution was cannulated away from the amalgam and cooled to 0 °C. Methyl iodide (0.05 mL, 0.80 mmol) was added by syringe, and the reaction was warmed to room temperature. Solvent was removed by rotary evaporation. Column chromatography as above afforded **5** (0.222 g, 43%).

Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienylchloro-*cis*-dicarbonyltungsten (6). Cyclopentadienyltricarbonylchlorotungsten[12] (0.369 g, 1.00 mmol) and ((diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron (**3**) (0.940 g, 2.50 mmol) were dissolved in 10 mL of dichloromethane. Under a heavy counter argon flow trimethylamine *N*-oxide (0.150 g, 2.00 mmol) was added, and the argon was bubbled vigorously for ca. 3 min. The solution was stirred for 9 h at room temperature, and then the solvent was removed by rotary evaporation. Column chromatography (alumina, activity III) with hexanes/EtOAc (95/5) gave unreacted **3**. Elution with hexanes/EtOAc (80/20) afforded **6** as a red solid (0.272 g, 38% yield based on tungsten starting material): mp 86–89 °C; IR (neat) ν_{CO} 2050, 1950 (v br), 1865 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) δ 7.65–6.90 (m, 10 H, Ph), 5.01 (d, $^3J_{PH}$ = 0.40 Hz, 5 H, WCp), 4.93 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 4.83 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 0.15 (s, 3 H, CH_3); ^{13}C NMR (68 MHz, $CDCl_3$) δ 254.2 (d, J_{PC} = 26 Hz, WCO), 243.3 (d, J_{PC} = 4 Hz, WCO), 214.3 (s, FeCO), 131.4–122.3 (overlapping multiplets, C_6H_5P), 93.1 (br s, C3, C3′ C_5H_4P), 92.5 (s, WCp), 91.2 (br s, C2, C2′ C_5H_4P), −21.6 (s, $FeCH_3$); ^{31}P NMR (C_6D_6) δ 10.97 (s, J_{PW} = 272 Hz); HRMS exact mass for $C_{27}H_{22}{}^{56}FeO_4ClP{}^{184}W$ calcd *m/z* 715.9805, found *m/z* 715.9836. This compound could be converted to **5** (vide infra).

Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienyltricarbonyltungsten Tetrafluoroborate (7). A solution of triphenylcarbenium tetrafluoroborate (0.500 g, 1.51 mmol) in 8 mL of dichloromethane was cooled to −30 °C. Under a heavy counter argon flow solid cyclopentadienyltricarbonylhydridotungsten[14] (0.504 g, 1.51 mmol) was added. An immediate color change to deep violet indicated formation of cyclopentadienyltricarbonyltungsten tetrafluoroborate.[13] The cation was not isolated but was used as the dichloromethane solution. ((Diphenylphosphino)cyclopentadienyl)dicarbonylmethyliron (0.568 g, 1.51 mmol) was then added as a solid. The temperature was raised to −20 °C, and the mixture was allowed to react at this temperature for 4 h. Solvent was removed by vacuum transfer at −20 °C. The resulting red oil was washed (2 × 5 mL) with benzene at room temperature to remove triphenylmethane. The orange glass thus obtained was, by proton NMR, pure bimetallic cation **7** (1.03 g, 86%): mp 82–97 °C dec; IR (neat) ν_{CO} 2080 (s), 2040 (s), 1960 (s) cm^{-1}; ^{1}H NMR (270 MHz, CD_3COCD_3) δ 7.73–7.62 (m, 10 H, Ph), 6.15 (d, $^3J_{PH}$ = 0.69 Hz, 5 H, WCp), 5.52 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 5.27 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 0.13 (s, 3 H, CH_3); ^{13}C NMR (50.32 MHz, CH_2Cl_2/CD_2Cl_2) δ 214.2 (s, $W(CO)_2$), 214.0 (s, FeCO), 213.5 (s, FeCO), 212.7 (s, WCO), 132.9–126.4 (overlapping multiplets C_6H_5P), 94.5 (s, WCp), 92.3 (br s, C3, C3′ C_5H_4P), 90.3 (d, J_{PC} = 8.4 Hz, C2, C2′ C_5H_4P), ipso C not observed, −20.7 (s, CH_3); ^{31}P NMR (CH_2Cl_2/CD_2Cl_2) δ 5.57 (s, J_{PW} = 196 Hz); ^{31}P NMR (THF/THF-d_8) δ 9.33 (s, J_{PW} = 196 Hz); HRMS exact mass for $C_{28}H_{22}O_5P{}^{56}Fe{}^{182}W$ calcd *m/z* 707.0237, found *m/z* 707.0046 ($M^+ - BF_4$).

Methyltricarbonyltungsten(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienylacetylcarbonyliron (8). ((Diphenylphosphino)cyclopentadienyl)methyltricarbonyltungsten (**4**) (1.83 g, 3.44 mmol) and cyclopentadienyldicarbonylmethyliron[6] (**1**) (0.62 g, 5.01 mmol) were dissolved in 18 mL of acetonitrile. The solution was brought to reflux and allowed to react for 16 h. The reaction mixture was cooled to room temperature, filtered through Celite, and chromatographed using alumina, activity III. Elution with hexanes gave unreacted **1**, with hexanes/EtOAc (95/5) gave unreacted **4**, and with hexanes/EtOAc (85/15) gave after solvent removal by rotary evaporation **8** as an orange powder (1.40 g, 56%). Recrystallization from $CHCl_3$/pentane gave analytically pure material: mp 140–143 °C dec; IR ($CHCl_3$) ν_{CO} 2000 (s), 1900 (v br s), 1590 (m) cm^{-1}; IR (Nujol) ν_{CO} 2005 (s), 1900 (v br s), 1595 (m) cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.6–7.3 (m, 10 H, Ph), 5.54 (m, $J \sim 1.5$ Hz, 1 H, C_5H_4P), 5.46 (m, $J \sim 1.3$ Hz, 1 H, C_5H_4P), 5.34 (m, $J \sim 1.3$ Hz, 1 H, C_5H_4P), 5.11 (m, $J \sim 1.3$ Hz, 1 H, C_5H_4P), 4.44 (d, $^3J_{PH}$ = 0.97 Hz, 5 Hz, FeCp), 2.21 (s, 3 H, $COCH_3$), 0.11 (s, 3 H, CH_3); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 275.0 (br s, $COCH_3$), 227.2 (s, WCO), 220 (d, J_{PC} = 12 Hz, FeCO), 214.2 (s, $W(CO)_2$), 139.21, 137.52, 134.67, 133.54, 130.30, 128.13, 127.89 (multiplets, C_6H_5P), 108.53 (d, J_{PC} = 29.5 Hz, ipso C_5H_4P), 98.83 (d, J_{PC} = 10.31 Hz, C2 C_5H_4P), 98.44 (d, J_{PC} = 7.05 Hz, C2′ C_5H_4P), 92.44 (d, J_{PC} = 4.78 Hz, C3 C_5H_4P), 92.04 (br s, C3′ C_5H_4P), 51.68 (d, J_{PC} = 5.17 Hz, $COCH_3$), −33.0 (s, CH_3); ^{31}P NMR ($CDCl_3$) δ 70.48 (s). Anal. Calcd for $C_{29}H_{25}O_5FePW$: C, 48.04; H, 3.48. Found: C, 48.09; H, 3.51.

Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienylacetyl-*trans*-dicarbonyltungsten (12). Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienyltricarbonyltungsten tetrafluoroborate (**7**) (0.536 g, 0.673 mmol) was dissolved in 10 mL of THF and the mixture cooled to −78 °C. Methyllithium (0.480 mL, 0.673 mmol) was added to the orange solution by syringe, where upon the mixture turned deep red. The reaction was stirred at −78 °C for 10 min. The cooling bath was removed, and the solution was warmed to room temperature. Solvent was removed by rotary evaporation to yield a red oil. Chromatographic separation on alumina (activity II) using hexanes/EtOAc (7/1) gave **12** as an orange solid (0.302 g, 62%): IR (neat) ν_{CO} 1995 (m), 1955 (m), 1925 (m), 1835 (s), 1590 (m) cm^{-1}; ^{1}H NMR (270 MHz, C_6D_6) δ 7.6–7.4 (m, 4 H, Ph), 7.1–6.9 (m, 6 H, Ph), 4.88 (d, $^3J_{PH}$ = 1.45 Hz, 5 H, WCp), 4.83 (m, $J \sim 1.8$ Hz, 2 H, C_5H_4P), 4.16 (m, $J \sim 2$ Hz, 2 H, C_5H_4P), 3.08 (s, 3 H, $COCH_3$), 0.23 (s, 3 H, H_3); ^{13}C NMR (68 MHz, $CDCl_3$) δ 230.0 (s, WCO), 214.8 (s, FeCO), 95.6 (s, WCp), 90.25 (d, J_{PC} = 9.86 Hz, C2, C2′ C_5H_4P), 89.79 (d, J_{PC} = 6.03 Hz, C3, C3′ C_5H_4P), 58.1 (s, $COCH_3$), −21.6 (s, CH_3); ^{31}P NMR (C_6D_6) δ 26.3 (s, J_{PW} = 244 Hz). Anal. Calcd for $C_{29}H_{25}O_5FePW$: C, 48.10; H, 3.48. Found: C, 48.16; H, 3.56.

Dicarbonylmethyliron(μ-(diphenylphosphino)cyclopentadienyl)cyclopentadienyldicarbonylhydridotungsten (10). To a solution of heterobimetallic cation **7** (0.618 g, 0.776 mmol) in THF/methanol (10/1, v/v) at −78 °C was added sodium borohydride (0.89 g, 2.35 mmol). The cold bath was removed and the solution allowed to warm to room temperature and stirred for 30 min. Acetone or saturated $NaHCO_3$ solution was added to the mixture which was then extracted with diethyl ether, dried ($MgSO_4$), and filtered. Solvent was removed by rotary evaporation to afford a yellow solid. Rapid column chromatography (alumina, activity III) using hexanes/EtOAc (75/25) gave impure (ca. 80% of total collected) **10** (0.056 g) as an orange solid: IR (neat) ν_{CO} 2000, 1960, 1930, 1850 cm^{-1}; ^{1}H NMR (200 MHz, CD_3COCD_3) δ 7.6–7.2 (m, 18 H, Ph), 5.31 (d, $^3J_{PH}$ = 1.3 Hz, 5 H, WCp), 5.20 (br m, *J* not resolved, ~2 H,C_5H_4P), 5.05 (br m, *J* not resolved, ~2 H, C_5H_4P), −0.05 (s, 3 H, $FeCH_3$), −6.8 (d, $^2J_{PH}$ = 65 Hz, $^1J_{WH}$ not resolved, 1 H, hydride); ^{31}P NMR (CD_3COCD_3) δ 26.00 (br s, s/n prevented J_{PW} observation).

X-ray Data Collection and Structure Determination for 5. Crystals of $CH_3(CO)_2Fe(\eta^5\text{-}C_5H_4PPh_2)WCp(CO)_2CH_3$ (**5**) suitable for the X-ray diffraction experiment were obtained by layering pentane on a dichloromethane solution of **5** and cooling for 5 days at −20 °C. The orange, clear crystal chosen for the experiment was coated with epoxy in order to retard decomposition and placed in the beam of the Nicolet R3m diffractometer. Unit-cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections (2θ(av) = 17.88°). Details of the crystallographic experiment and computations for 5 are listed in Table I. All data processing was performed on a DG Eclipse/S140 computer using the SHELXTL program library, version 5.1.[40] An empirical absorption correction was performed by using the azimuthal data from 13 ψ-scan reflections collected in 12° increments; maximum transmission factor was 0.030, minimum transmission factor was 0.015. Neutral atom scattering factors and anomalous scattering contributions[41] were used for all non-hydrogen atoms.

Analysis of the Patterson map established the positions of the iron and tungsten atoms. Subsequent ΔF electron density maps revealed all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Hydrogen atoms placed in idealized positions (C–H = 0.96 Å, $U_H = 1.2U_{iso}$, C). In the final ΔF map, the highest peak (1.16 e Å^{-3}) was located 0.85 Å from tungsten. Final fractional atomic coordinates and thermal parameters with esd's are listed in Tables S-1–5. A table of calculated vs observed structure factors is available as supplementary material, Table S-6.

X-ray Data Collection and Structure Determination for 8. Crystals of $CH_3(CO)_3W(\eta^5\text{-}C_5H_4PPh_2)FeCp(CO)(COCH_3)$ (8) suitable for X-ray diffraction measurements were obtained by layering pentane on a dichloromethane solution of 8 and cooling for 5 days at −20 °C. The orange, clear crystal chosen for the experiment was coated with epoxy in order to retard decomposition. Unit-cell dimensions were obtained from a least-squares fit to the setting angles for 25 reflections (2θ(av) = 24.04°). Details of the crystallographic experiment and computations for 8 are listed in Table III. An empirical absorption correction was performed by using the azimuthal data from 15 ψ-scan reflections collected in 15° increments, maximum transmission factor was 0.768, minimum transmission factor was 0.522.

Analysis of the Patterson map established the positions of the iron and tungsten atoms. Subsequent ΔF electron density maps revealed all non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters.

Hydrogen atoms were placed in idealized positions. In the final ΔF map, the highest peak (1.3 e Å^{-3}), was located 0.87 Å from tungsten. Final fractional atomic coordinates and thermal parameters with esd's are listed in Tables S-7–11. A table of calculated vs observed structure factors is available as supplementary material (Table S-12).

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Supplementary Material Available: Table S-1, atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$)^a for 5, Table S-2, bond lengths (Å) for 5, Table S-3, bond angles (deg) for 5, Table S-4, anisotropic thermal parameters ($\text{Å}^2 \times 10^3$) for 5, Table S-5, hydrogen coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for 5, Table S-7, atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$) for 8, Table S-8, bond lengths (Å) for 8, Table S-9, bond angles (deg) for 8, Table S-10, anisotropic thermal parameters ($\text{Å}^2 \times 10^3$) for 8, and Table S-11, hydrogen coordinates ($\times 10^4$) and thermal parameters ($\text{Å}^2 \times 10^3$) for 8 (13 pages); Table S-6, observed and calculated structure factors for 5, and Table S-12, observed and calculated structure factors for 8 (45 pages). Ordering information is given on any current masthead page.

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Cluster-Bound Ylides Derived from CCO. Conversion of $[Fe_2Co(CO)_9(CCO)]^-$ to $[Fe_2Co(CO)_9(CPR_3)]^-$

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The ketenylidene-containing cluster $[PPN][Fe_2Co(CO)_9(CCO)]$ (1) reacts with a variety of simple phosphines to produce cluster-bound phosphorus ylides. The reactions proceed by a two-step process in which initial substitution at the Co metal center to give $[PPN][Fe_2Co(CO)_8(PR_3)(CCO)]$ (**2a–f**) is followed by phosphine migration to generate the organometallic ylides $[PPN][Fe_2Co(CO)_9(CPR_3)]$ (**3a–e**) (**a**, R = PMe_3; **b**, R = PMe_2Ph; **c**, R = $PMePh_2$; **d**, R = PEt_3; **e**, R = $P(OMe)_3$; **f**, R = $P(OPh)_3$). The substitution reaction does not occur for the bulky phosphines PPh_3 and PCy_3. The rate of the migration step appears sensitive to phosphine basicity. The compound $[PPN][Fe_2Co(CO)_9(CPMe_3)]$ (**3a**) undergoes protonation at the metal framework to give $HFe_2Co(CO)_9(CPMe_3)$, whereas the reaction with $Co_2(CO)_8$ generates a butterfly carbide cluster, $Fe_2Co_2(C)(CO)_{11}(PMe_3)$. Treatment of 1 with dmpm (dmpm = bis(dimethylphosphino)methane) produces $[PPN][Fe_2Co(CO)_7(dmpm)(CCO)]$ (6), which retains the ketenylidene moiety. This cluster undergoes CO exchange and electrophilic attack more readily than 1. The X-ray crystal structures of **3a** and **6**$\cdot CH_2Cl_2$ have been determined. Crystal data for **3a**: space group $P2_1/c$, a = 14.370 (3) Å, b = 18.761 (2) Å, c = 17.621 (3) Å, β = 94.21 (2)°, V = 4738 (2) Å^3, Z = 4. Crystal data for $6\cdot CH_2Cl_2$: space group $P\bar{1}$, a = 16.398 (2) Å, b = 16.858 (2) Å, c = 9.478 (2) Å, α = 94.89 (1)°, β = 99.11 (1)°, γ = 93.06 (1)°, V = 2572 (1) Å^3, Z = 2.

Introduction

Ketenylidene-containing clusters undergo a variety of ligand transformations upon treatment with nucleophiles and electrophiles.[1–7] In these processes, molecular charge plays a key role in determining how the cluster will react toward different substrates. We have previously described

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