$[Cp(H)Re(\mu\text{-}CO)_2Rh(PPh_3)_2]$ (1). THF (10 mL) was condensed onto a mixture of $(Ph_3P)_3RhCl$ (419 mg, 0.453 mmol) and $K[CpRe(CO)_2H]$ (159 mg, 0.458 mmol) at −78 °C. The solution was stirred at ambient temperature for 15 min. THF was evaporated under vacuum; the residue was dissolved in 24 mL of CH_2Cl_2, and the resulting solution was filtered. When hexane was added and the solution was cooled to −78 °C, a dark brown, microcrystalline solid precipated. Recrystallization from CH_2Cl_2/hexane gave **1** as a brown, air-sensitive solid (192 mg, 45%). ^1H NMR (C_6D_6, 270 MHz): δ 7.6–6.9 (m, 30 H), 4.73 (s, 5 H), −13.33 (s, 1 H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 0.07 M $Cr(acac)_3$): δ 234.7 (d, J_{RhC} = 32 Hz, μ-CO), 134.6 (ipso), 133.7 (ortho), 129.3 (para), 127.7 (meta), 81.25 (C_5H_5). $^{31}P\{^1H\}$ NMR (C_6D_6, 23 °C): δ 33.1 (d, J_{RhP} = 182 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −89 °C): δ 39.8 (dd, J_{RhP} = 183 Hz, $^2J_{PP}$ = 35 Hz), 26.3 (dd, J_{RhP} = 170 Hz, J_{PP} = 35 Hz). IR (CH_2Cl_2): 1735 cm^{-1}. Anal. Calcd for $C_{43}H_{36}O_2P_2ReRh$: C, 55.19; H, 3.88; P, 6.62. Found: C, 54.25; H, 3.63; P, 6.07.

Reaction of $(Ph_3P)_3RhH_2Cl$ with $K[CpRe(CO)_2H]$. $(Ph_3P)_3RhH_2Cl$ was prepared in situ by dissolving 13 mg (14 μmol) of $(Ph_3P)_3RhCl$ in THF-d_8 under 1 atm of H_2. A THF-d_8 solution of $K[CpRe(CO)_2H]$ (5 mg, 14 μmol) was then added at −78 °C. The ^1H NMR spectrum of the solution at −85 °C indicated the presence of resonances at δ 5.11 (s, 5 H) and δ −13.91 (s, 1 H) due to **1**. No resonances attributable to a trihydride species were observed.

$[(COD)Rh(\mu\text{-}H)(\mu\text{-}Cl)TaCp_2]$ (4). A solution of $[(COD)RhCl]_2$ (151 mg, 0.306 mmol) and Cp_2TaH_3 (170 mg, 0.541 mmol) in 7 mL of toluene was stirred at ambient temperature for 2 h and filtered. The filtrate was evaporated to give a dark green solid. The solid was dissolved in 100 mL of hexane, and the resulting solution was filtered and evaporated to dryness to give **4** as a dark green, air-sensitive powder (104 mg, 34%). ^1H NMR (C_6D_6): δ 4.83 (br m, 2 H, HC=CH), 4.71 (d, J = 0.46 Hz, 10 H, C_5H_5), 4.64 (br m, 2 H, HC=CH), 2.1–1.8 (m, 8 H, CH_2), −15.96 (d, J_{RhH} = 26 Hz, 1 H). ^{13}C NMR (C_6D_6): δ 86.64 (d, J_{CH} = 177 Hz, C_5H_5), 82.28 (dd, J_{RhC} = 10 Hz, J_{CH} = 156 Hz, HC=CH), 72.67 (dd, J_{RhC} = 14 Hz, J_{CH} = 156 Hz, HC=CH), 30.95 (t, J_{CH} = 129 Hz, CH_2), 29.67 (t, J_{CH} = 127 Hz, CH_2). Anal. Calcd for $C_{18}H_{23}ClRhTa$: C, 38.71; H, 4.15. Found: C, 38.48; H, 4.25.

$[Cp_2Ta(\mu\text{-}H)(\mu\text{-}Cl)Rh(Ph_2PCH_2CH_2PPh)]$ (5). A suspension of $[(Ph_2PCH_2CH_2PPh_2)RhCl]_2$ (183 mg, 0.17 mmol) in 8 mL of a benzene solution of Cp_2TaH_3 (102 mg, 0.32 mmol) was stirred for 2 days at 48 °C and then filtered. The filtrate was concentrated under vacuum to 4 mL, and 4 mL of hexane was added. The resulting air-sensitive, dark brown precipitate was filtered out, washed with hexane (3 × 2 mL), and dried under vacuum to yield **5** (80 mg, 30%). ^1H NMR (C_6D_6, 270 MHz): δ 7.9–7.0 (m, 20 H), 4.68 (s, 10 H), 1.7 (br, d, 4 H), −12.61 (ddd, $^2J_{PH}$ = 61, J_{RhH} = 24 Hz, $^2J_{PH}$ = 15 Hz, 1 H). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 79.0 (dd, J_{RhP} = 201 Hz, $^2J_{PP}$ = 43 Hz), 43.0 (dd, J_{RhP} = 175 Hz). ^{31}P NMR (C_6D_6, aromatic region selectively decoupled): δ 79.0 (ddd, J_{RhP} = 201 Hz, $^2J_{PP}$ = 43 Hz, $^2J_{PH}$ = 15 Hz), 43.0 (ddd, J_{RhP} = 175, $^2J_{PH}$ = 61 Hz).

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$P_{10}Fe$, a Phosphorus Analogue of Ferrocene?

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In 1984 theoretical calculations on the P_5^- molecule suggested the possibility of its isolation under appropriate experimental conditions.[1] Three years later Scherer[2] reported the synthesis and characterization of the mixed-sandwich complex $[(\eta^5\text{-}P_5)\text{-}FeCp^*]$ (**1**). Recently,[3] the synthesis of naked P_5^- gives further support for the possible preparation of $[(\eta^5\text{-}P_5)_2Fe]$ (**2**), the phosphorus analogue of ferrocene. This note explores different geometrical possibilities for those systems by molecular orbital calculations at the extended Hückel level.

Table I. Overlap Population and Stabilization Energy (eV)

species	overlap pop. Fe–P_5	overlap pop. Fe–Cp	stabilizn from interacn of e_1'' and P_5Fe LUMO[a]
$(\eta^5\text{-}P_5)Fe$	0.95^b		
$(\eta^1\text{-}P_5)Fe$	0.85^c		
$(\eta^5\text{-}P_5)FeCp$ (**1**)	0.55^b	0.65	1.72
$(\eta^1\text{-}P_5)FeCp$ (**3**)	0.84^c	0.70	1.1
$(\eta^5\text{-}P_5)_2Fe$ (**2**)	-0.13^b		−0.98
$(\eta^1\text{-}P_5)(\eta^5\text{-}P_5)Fe$ (**6**)	$0.25,^b$ 0.78^c		0.6
$(\eta^1HP_5)_2Fe$	0.85^c		

[a] Stabilization as the energy difference between the Cp and P_5 π (MO) e_1'' and the molecular orbital in the final compound. A positive value indicates stabilization. [b] For all P atoms in one ring. [c] Only for one P atom in one ring.

An energy diagram comparing **1** (we used Cp instead of Cp* in the calculation and a staggered conformation) and the hypothetical molecules **2** and $[(\eta^1\text{-}P_5)FeCp]$ (**3**) appears in Figure 1. The levels are traced to show their parentage in the MOs of the ring and P_5Fe fragments.

We start our study with a fragment analysis by partitioning the molecular orbitals. Transforming Cp^- into P_5^- (both D_{5h} symmetry) changed the ordering of the MOs. As a consequence, the e_1'' π donor type orbital which constitutes the HOMO of Cp^- lies below the occupied e_1' and e_2' σ types. In P_5^- the e_1 HOMO is a result of a combination of atomic orbitals lying in the molecular plane (p_x and p_y). The HOMO in P_5 is therefore a lone-pair level; hence it is possible to get a σ interaction with Fe to obtain an $(\eta^1\text{-}P_5)Fe$ fragment.

The HOMO of $(\eta^1\text{-}P_5)Fe$ showed a large contribution of metal d_{yz} character. The LUMO is d_{xz} antibonding to the P_5 ring. The orbitals of the isolated fragment $(\eta^5\text{-}P_5)Fe$ are similar to those of the well-known CpM fragment.[4] There are three relatively low-lying occupied orbitals, a_1 and e_2, originating primarily from the metal d_{z^2}, $d_{x^2-y^2}$, and d_{xy}. The LUMO, an e_1'' acceptor orbital from d_{xz} and d_{yz} metal orbitals, is ideally prepared for interaction with another system.

The energy level diagram of **1** showed a splitting pattern analogous to that of ferrocene[5] due to the similar nature of the HOMO and LUMO of the Cp^- and $(\eta^5\text{-}P_5)Fe$ fragments. The main difference appears in the ordering $e_2 < e < a$ in **1** compared to $e_{2g} < a_g < e_g$ in ferrocene.

A similar analysis for the hypothetical compound **2** showed however large differences in comparison to ferrocene. Here the HOMO is actually predicted to be the antibonding combination of e_1 in P_5 and the LUMO of the $(\eta^5\text{-}P_5)Fe$ fragment. An overlap population analysis (Table I) shows the lack of bonding in this compound between Fe and the two P_5 rings. The π interaction between the LUMO of the $(\eta^5\text{-}P_5)Fe$ fragment and the low-lying e_1'' orbital of P_5 is weak, and e_1'' is actually destabilized by lower orbitals in the $(\eta^5\text{-}P_5)Fe$ stack. The gap between these orbitals corresponds to 3.81 eV, and we found a destabilization energy of 0.98 eV for this interaction compared to a stabilization of −1.72 eV in **1**. Hence, these calculations strongly suggest that the possibility of isolating **2** would be difficult.

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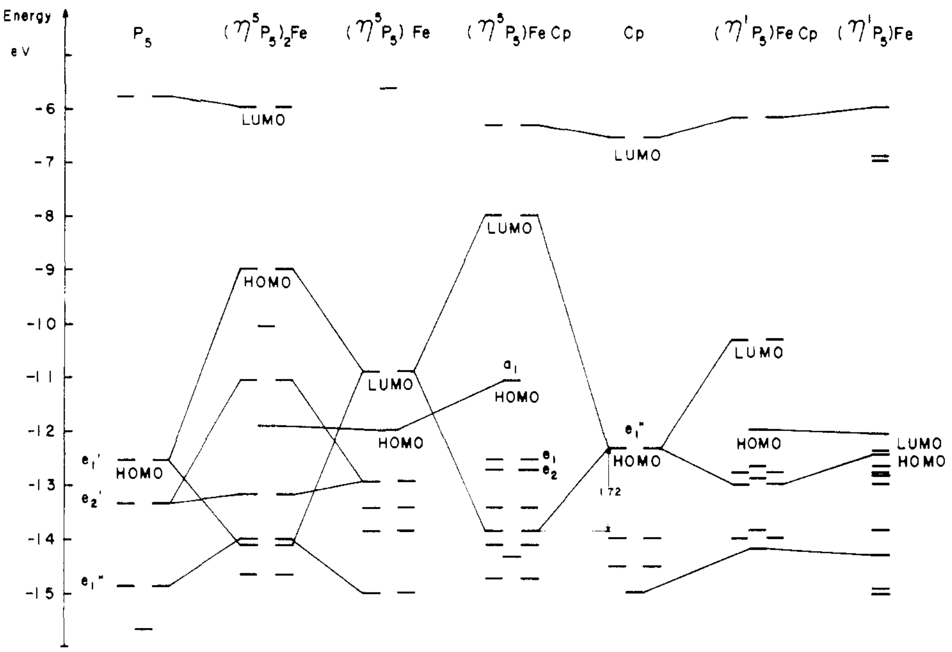


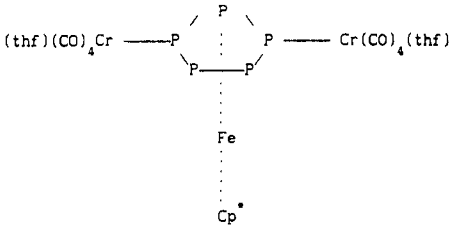
Figure 1. Interaction energy level diagram for the complexes.

Table II. Extended Hückel Parameters

atom	orbital	H_{ii}, eV	ζ_1	ζ_2	C_1^a	C_2
P	3s	−18.6	1.75			
	3p	−14.0	1.30			
Fe	4s	−9.17	1.90			
	4p	−5.37	1.90			
	3d	−12.70	5.35	1.80	0.5366	0.6678
Cr	4s	−8.66	1.70			
	4p	−5.24	1.70			
	3d	−11.22	4.95	1.80	0.5060	0.6750

[a] Contraction coefficients used in the double-ζ expansion.

It is possible, however, to get a σ bond between the P_5 ring and Fe. In this direction Scherer reported[6] that the P_5 ring in **1** interacts with two molecules of $H[Cr(CO)_5(thf)]$ to give compound **4**. Preliminary results of calculations with **4** indicate an overlap population of 0.4 for each σ Cr–P bond.



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Hence, $[(\eta^1\text{-}P_5)FeCp]$ (**3**) can be interpreted in a way similar to that for **1** and **2** as the result of a π interaction between the $(\eta^1\text{-}P_5)Fe$ fragment and the e_1'' Cp HOMO. Here the stabilization energy is 1.1 eV, in other words 0.62 eV less than that computed for **1**. An overlap population analysis for **3** showed the formation of an important σ Fe–P bond. This remains if the interaction between Fe and the two P_5 rings is σ, as is shown in Table I for $[(\eta^1\text{-}P_5)_2Fe]$ (**5**). Furthermore, we have considered a mixed species with both σ and π bonds, $[(\eta^1\text{-}P_5)Fe(\eta^5\text{-}P_5)]$ (**6**). It is interesting to note that the overlap population for the σ bond is a little less than in **3** but the π bond is dramatically reduced compared with the other cases. The stabilization energy for this species, as can be seen in Table I, is computed to be higher than that for **2**. Hence, if we compare only the overlap populations, the results of these calculations indicate that the most favorable isomer is **5** followed by **6**, while the phosphorus analogue to ferrocene appears to be improbable.

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Appendix

All calculations were performed by using the extended Hückel method[7] with the weighted H_{ii} formula.[8] The bond lengths reported by Scherer were used for compounds **1**–**3** and **6**. The P–Cr bond length of 2.18 Å was used in compound **4**, and 2.22 Å was used for all the σ P–Fe bonds. The values for the H_{ii} and orbital exponents are listed in Table II. The parameters of C and H are the standard ones.[7]

Registry No. **1**, 124716-07-0; **2**, 124687-20-3.

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Reactions of 4-Acetylpyridine with $[(RH)W(CO)_5]$ Intermediates (RH = Cyclohexane, Methylcyclohexane) Produced via Pulsed Laser Flash Photolysis

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Pulsed laser flash photolysis studies of $W(CO)_6$ in the presence of 4-acetylpyridine (4-acpy) in methylcyclohexane (MCH) solution (eq 1), reported several years ago,[1] revealed the presence of a

$$W(CO)_6 + \text{4-acpy} \xrightarrow[\text{MCH}]{h\nu} \text{(4-acpy)}W(CO)_5 + CO \qquad (1)$$

reactive $[(MCH)W(CO)_5]$ intermediate with an absorption

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