[Cp(H)Re(μ-CO)₂Rh(PPh₃)₂] (1). THF (10 mL) was condensed onto a mixture of (Ph₃P)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 CH₂Cl₂, and the resulting solution was filtered. When hexane was added and the solution was cooled to −78 °C, a dark brown, microcrystalline solid precipitated. Recrystallization from CH₂Cl₂/hexane gave **1** as a brown, air-sensitive solid (192 mg, 45%). ^{1}H NMR (C₆D₆, 270 MHz): δ 7.6–6.9 (m, 30 H), 4.73 (s, 5 H), −13.33 (s, 1 H). ^{13}C{^{1}H} NMR (CD₂Cl₂, 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 (C₅H₅). ^{31}P{^{1}H} NMR (C₆D₆, 23 °C): δ 33.1 (d, J_{RhP} = 182 Hz). ^{31}P{^{1}H} NMR (CD₂Cl₂, −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 (CH₂Cl₂): 1735 cm⁻¹. Anal. Calcd for C₄₃H₃₆O₂P₂ReRh: C, 55.19; H, 3.88; P, 6.62. Found: C, 54.25; H, 3.63; P, 6.07.

Reaction of (Ph₃P)₃RhH₂Cl with K[CpRe(CO)₂H]. (Ph₃P)₃RhH₂Cl was prepared in situ by dissolving 13 mg (14 μmol) of (Ph₃P)₃RhCl in THF-*d₈* under 1 atm of H₂. A THF-*d₈* solution of K[CpRe(CO)₂H] (5 mg, 14 μmol) was then added at −78 °C. The ^{1}H 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(μ-H)(μ-Cl)TaCp₂] (4). A solution of [(COD)RhCl]₂ (151 mg, 0.306 mmol) and Cp₂TaH₃ (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%). ^{1}H NMR (C₆D₆): δ 4.83 (br m, 2 H, *HC*=CH), 4.71 (d, *J* = 0.46 Hz, 10 H, C₅H₅), 4.64 (br m, 2 H, HC=C*H*), 2.1–1.8 (m, 8 H, CH₂), −15.96 (d, J_{RhH} = 26 Hz, 1 H). ^{13}C NMR (C₆D₆): δ 86.64 (d, J_{CH} = 177 Hz, C₅H₅), 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, CH₂), 29.67 (t, J_{CH} = 127 Hz, CH₂). Anal. Calcd for C₁₈H₂₃ClRhTa: C, 38.71; H, 4.15. Found: C, 38.48; H, 4.25.

[Cp₂Ta(μ-H)(μ-Cl)Rh(Ph₂PCH₂CH₂PPh)] (5). A suspension of [(Ph₂PCH₂CH₂PPh₂)RhCl]₂ (183 mg, 0.17 mmol) in 8 mL of a benzene solution of Cp₂TaH₃ (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%). ^{1}H NMR (C₆D₆, 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{^{1}H} NMR (C₆D₆): δ 79.0 (dd, J_{RhP} = 201 Hz, $^2J_{PP}$ = 43 Hz), 43.0 (dd, J_{RhP} = 175 Hz). ^{31}P NMR (C₆D₆, 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).

Contribution from the Facultad de Química,
Instituto de Investigación en Materiales,
and Instituto de Química,
Universidad Nacional Autónoma de México,
Ciudad Universitaria 04510, México, DF

P₁₀Fe, a Phosphorus Analogue of Ferrocene?

José A. Chamizo,*,† Marina Ruiz-Mazón,† Roberto Salcedo,*,‡ and Rubén A. Toscano§

In 1984 theoretical calculations on the P₅⁻ molecule suggested the possibility of its isolation under appropriate experimental conditions.[1] Three years later Scherer[2] reported the synthesis

Table I. Overlap Population and Stabilization Energy (eV)

species	overlap pop.		stabilizn from interacn of e₁″ and P₅Fe LUMO[a]
	Fe–P₅	Fe–Cp	
(η⁵-P₅)Fe	0.95[b]		
(η¹-P₅)Fe	0.85[c]		
(η⁵-P₅)FeCp (1)	0.55[b]	0.65	1.72
(η¹-P₅)FeCp (3)	0.84[c]	0.70	1.1
(η⁵-P₅)₂Fe (2)	−0.13[b]		−0.98
(η¹-P₅)(η⁵-P₅)Fe (6)	0.25,[b] 0.78[c]		0.6
(η¹HP₅)₂Fe	0.85[c]		

[a] Stabilization as the energy difference between the Cp and P₅ π (MO) e₁″ 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.

and characterization of the mixed-sandwich complex [(η⁵-P₅)-FeCp*] (1). Recently,[3] the synthesis of naked P₅⁻ gives further support for the possible preparation of [(η⁵-P₅)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.

An energy diagram comparing **1** (we used Cp instead of Cp* in the calculation and a staggered conformation) and the hypothetical molecules **2** and [(η¹-P₅)FeCp] (3) appears in Figure 1. The levels are traced to show their parentage in the MOs of the ring and P₅Fe fragments.

We start our study with a fragment analysis by partitioning the molecular orbitals. Transforming Cp⁻ into P₅⁻ (both D_{5h} symmetry) changed the ordering of the MOs. As a consequence, the e₁″ π donor type orbital which constitutes the HOMO of Cp⁻ lies below the occupied e₁′ and e₂′ σ types. In P₅⁻ the e₁ HOMO is a result of a combination of atomic orbitals lying in the molecular plane (pₓ and p_y). The HOMO in P₅ is therefore a lone-pair level; hence it is possible to get a σ interaction with Fe to obtain an (η¹-P₅)Fe fragment.

The HOMO of (η¹-P₅)Fe showed a large contribution of metal d_{yz} character. The LUMO is d_{xz} antibonding to the P₅ ring.

The orbitals of the isolated fragment (η⁵-P₅)Fe are similar to those of the well-known CpM fragment.[4] There are three relatively low-lying occupied orbitals, a₁ and e₂, originating primarily from the metal d_{z²}, d_{x²-y²}, and d_{xy}. The LUMO, an e₁″ 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 (η⁵-P₅)Fe fragments. The main difference appears in the ordering e₂ < e < a in **1** compared to e₂g < 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 e₁ in P₅ and the LUMO of the (η⁵-P₅)Fe fragment. An overlap population analysis (Table I) shows the lack of bonding in this compound between Fe and the two P₅ rings. The π interaction between the LUMO of the (η⁵-P₅)Fe fragment and the low-lying e₁″ orbital of P₅ is weak, and e₁″ is actually destabilized by lower orbitals in the (η⁵-P₅)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.

† Facultad de Química.
‡ Instituto de Investigación en Materiales.
§ Instituto de Química.

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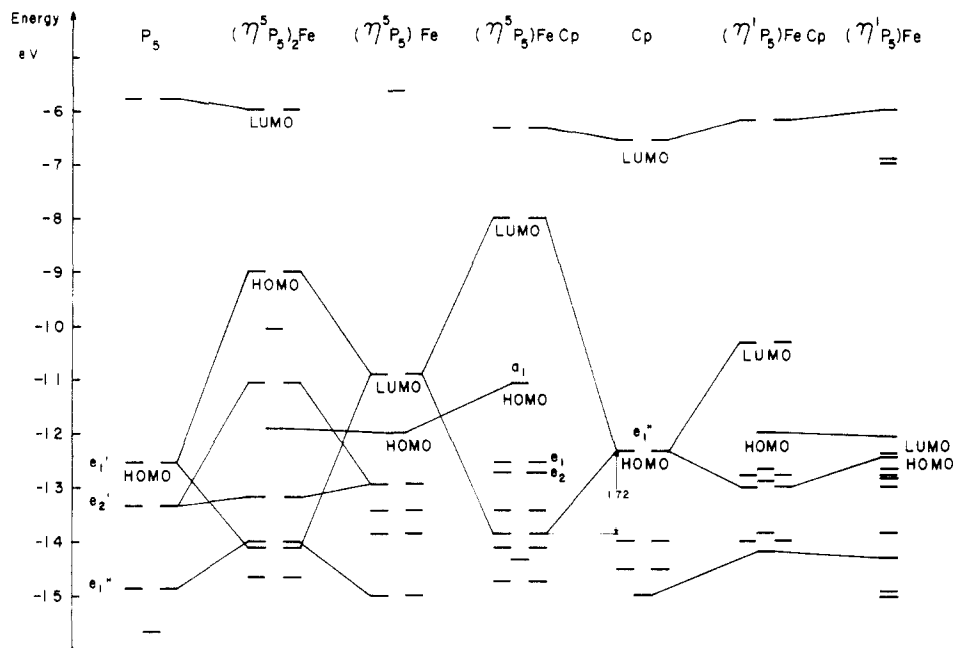(5) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

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.

4
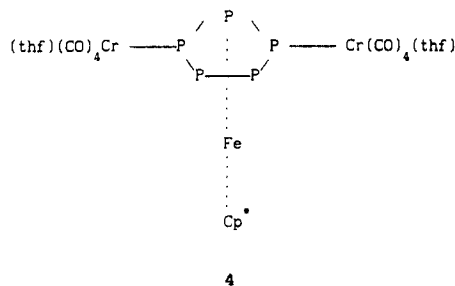
Hence, $[(\eta^1\text{-}P_5)FeCp]$ (**3**) can be interpreted in a way similar to that for **1** and **2** as the result of a π interaction between the $(\eta^1\text{-}P_5)$Fe fragment and the e_1'' Cp HOMO. Here the stabilization energy is 1.1 eV, in other words 0.62 eV less than that computed for **1**. 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.

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]

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Contribution from the Department of Chemistry
and Center for Organometallic Research,
University of North Texas, Denton, Texas 76203-5068

Reactions of 4-Acetylpyridine with [(RH)W(CO)5] Intermediates (RH = Cyclohexane, Methylcyclohexane) Produced via Pulsed Laser Flash Photolysis

Gerard R. Dobson* and Michael D. Spradling

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

$$W(CO)_6 + 4\text{-acpy} \xrightarrow[\text{MCH}]{h\nu} (4\text{-acpy})W(CO)_5 + CO \quad (1)$$
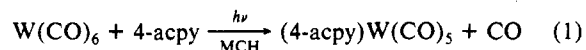
reactive $[(MCH)W(CO)_5]$ intermediate with an absorption

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