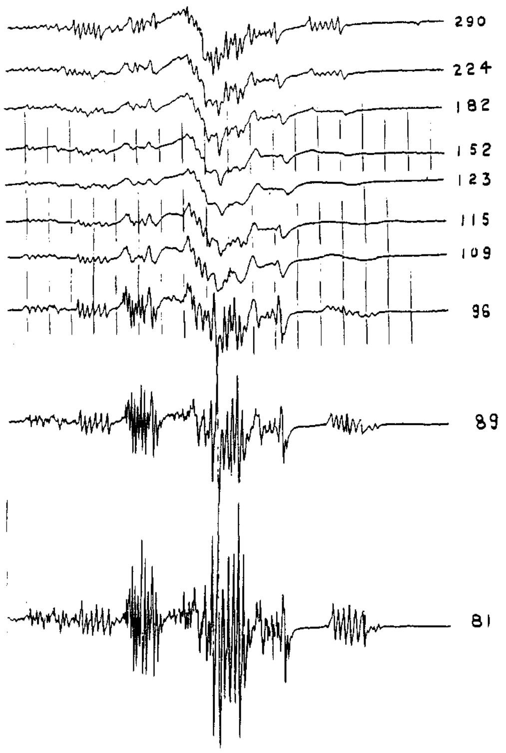

Figure 4. EPR spectra at different temperatures for an orientation of the crystal in which the magnetic field is rotated approximately 10–20° from the z principal axis of one of the two magnetic sites.

for the reduction of D_{eff} relative to the value of D found from the powder measurements.

The temperature study was repeated for several orientations slightly off from the z principal axis where the sensitivity of the two sextets to the magnetic field orientation was much greater than that found when the magnetic field is aligned with the z principal axis. The results of one run are shown in Figure 4. In this run, the separation of the upper sextet into at least two sextets is quite striking as is the relative change in intensity of the two. In particular, note the nearly equal intensity of the two sextets at 96 K in the high-field fine structure line and compare this with the spectrum taken at 81 K.

We have also mounted a crystal in a finger Dewar with the magnetic field aligned nearly parallel with one of the z principal axes at room temperature. Liquid N_2 was then added to cool the crystal rapidly to 77 K. After cooling, the sextets were considerably downfield from their room-temperature positions. It took a rotatio of nearly 30° to obtain a maximum zero-field splitting of a magnitude comparable to what the powder measurements of D would predict. This rotation study showed the supper sextet to be split into two resonances of nearly equal intensity.

Discussion

While there is some magnetic broadening of all lines as the temperature is lowered, it is clear that the earlier explanation[7] of the broadening in the spin-crossover transition region cannot be correct. Instead, we must consider some mechanism involving variation of the ZFS parameters (D, E, and the direction of the principal axes associated with them) over various sites from Mn(II). If the sites for the paramagnetic and diamagnetic iron atoms are randomly distributed, we could expect a random distribution of ZFS parameters for the manganese atoms throughout the crystal lattice. This should introduce a broadening of the sort seen in our studies here and the random distribution of environments would give a Gaussian line shape. However, attempts to simulate the broadening of the sextet suggest that the line shape is closer to Lorentzian than Gaussian. Further, the appearance of two or three distinct sextets below the transition whose relative intensities vary with temperature suggest a specific set of ZFS parameters rather than a random distribution. In some temperature runs at certain orientations, we have seen multiple sextets in the high-field sextet at temperatures above the transition temperature T_c as well as below.

The large change in the orientation of the principal z axis observed in the low-temperature phase does not mean the iron or manganese complexes have experienced such large rotations. Crystallographic studies,[15] in fact, show a change of 1–2° in the orientation of the ligand planes between the high-spin and low-spin structures. The iron(II), and therefore the Mn(II), ion lies in a site with no point group symmetry, and there is no symmetry requirement for the orientation of the principal axes of the ZFS matrix. The high-spin lattice is a "good" host for the Mn(II) defect as the Fe–N bond lengths should be similar to the Mn–N bond lengths. The Mn(II) complexes should sit in a relatively "relaxed" state, with little added strain energy. The contraction in the unit cell in the low-spin state associated with the shorter Fe–N bond lengths for the low-spin complex should exert forces on the ligands around the Mn(II) ion, causing distortions that show up as a change in the orientation of the principal axes for the ZFS interaction.

The most likely explanation of everything we have observed is one that assumes the transition involves at least three or more domains. For example there could be three domains of the following types: (1) all high spin; (2) half high spin and half low spin; (3) all low spin. Each of these phases would have a particular set of ZFS parameters for the impurity Mn(II), and there would be a gradual change in the quantity of each phase as the temperature changes through the crossover region. It is interesting to note that Meissner et al.[19] have found the transition in $[Fe(2\text{-pic})_3]Cl_2{\cdot}C_2H_5OH$ to be a double transition with two T_c's. There could, of course, be more than three phases, but we see no other way to explain our results but to assume that the Mn(II) ion finds itself in a limited number of distinct lattices during the course of the spin-crossover transition.

Conclusions

The use of Mn(II) EPR as a probe to study the spin crossover in single crystals of $[Fe(II)(2\text{-pic})_3]Cl_2{\cdot}C_2H_5OH$ has provided new information on the nature of the transition. We have interpretated the results as showing that the Mn(II) complex exists in several distinct lattices (domains) in which the ZFS parameters differ both in magnitude and in the orientation of the principal axis relative to the unit cell axes. The intensity of the resonance associated with each domain varies with the temperature. These results along with earlier EPR studies[9,10] from this laboratory demonstrate the unique structural information that can be obtained about the spin-crossover transformation from single-crystal EPR that are not obtainable from the techniques conventionally used to study these systems.

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(19) Köppen, H.; Müller, E. W.; Kohler, C. P.; Spiering, H.; Meissner, E.; Gütlich, P. *Chem. Phys.* **1982**, *91*, 348.

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Synthesis of Rhodium-Containing Heterobimetallic Hydride Complexes

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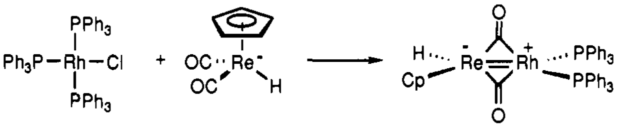
There has been a great deal of recent interest in the synthesis of heterobimetallic dihydrides[1] in the hope that these compounds might show novel reduction chemistry. For example, we have recently prepared the platinum rhenium dihydride complex Cp(CO)$_2$HRePtH(PPh$_3$)$_2$[2] and have studied its use in alkene and alkyne reduction.[3] During synthetic attempts aimed at preparing heterobimetallic dihydrides, we have isolated three heterobimetallic monohydride complexes containing Rh bound to either Re or Ta. Here we report the synthesis, characterization, and reactivity of these heterobimetallic compounds.

Results and Discussion

Rhodium-Rhenium Hydride. The reaction of (Ph$_3$P)$_3$RhCl with K[CpRe(CO)$_2$H][4] in THF led to the isolation of the rhodium-rhenium monohydride Cp(H)Re(μ-CO)$_2$Rh(PPh$_3$)$_2$ (1) in 45% yield as a brown solid, which was recrystallized from CH$_2$Cl$_2$/hexane. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of 1 demonstrated that it was a homogeneous material of >98% purity. However, because of the extreme air sensitivity of the compound, we were unable to obtain fully satisfactory elemental analysis after several attempts (see Experimental Section). Dark red needles of 1 were grown from CH$_2$Cl$_2$, but due to poor crystal quality only a partial X-ray structural determination was achieved. Only the four coplanar atoms P1, P2, Rh, and Re were located with certainty. A Re-Rh distance of about 2.54 Å was estimated.[5]

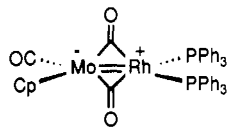


1

Because of the difficulties outlined above, the structure of 1 was established spectroscopically. The ^{1}H NMR spectrum of 1 exhibits a singlet at δ −13.3 coupled to neither Rh nor P that must be assigned to a terminal hydride on rhenium. The IR spectrum of 1 shows the presence of only bridging carbonyl ligands (1785 and 1765 cm^{-1} in KBr; 1765 cm^{-1} in CH$_2$Cl$_2$). The ^{31}P{^{1}H} NMR spectrum of 1 in CD$_2$Cl$_2$ at −89 °C exhibits resonances for two inequivalent phosphorus atoms at δ 39.8 (dd, J_{PP} = 35 Hz, J_{PRh} = 183 Hz) and 26.3 (dd, J_{PP} = 35 Hz, J_{PRh} = 170 Hz). The strong P-Rh coupling demonstrates that both phosphines are bound to rhodium.

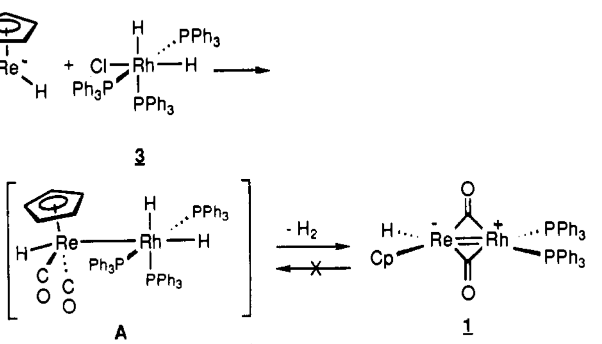
The temperature-dependent ^{31}P NMR spectrum of 1 provides evidence for a fluxional process that interconverts the phosphine environments without loss of rhodium coupling. At ambient temperature, rapid interchange of phosphine environments gives rise to a single resonance at δ 33.3 (d, J_{PRh} = 182 Hz). A coalescence temperature of −42 °C was observed. ΔG^* of 10.6 kcal mol^{-1} was calculated from the coalescence data. The presence of inequivalent phosphines at low temperature taken together with the equivalence of the bridging carbonyls requires the geometry shown for 1.

The structure of 1 is similar to that of the molybdenum-rhodium complex 2, which was determined by X-ray crystallography. Carlton[6] has formulated 2 as having a molybdenum-rhodium double bond to explain the short metal-metal distance and to obtain an 18-electron environment at molybdenum. In analogy with 2, we prefer to formulate 1 with a rhodium-rhenium double bond, which depicts rhenium in an 18-electron environment and rhodium in a 16-electron environment.



2

Oxidative addition of H$_2$ to the Rh center of 1 was pursued as a possible route to a heterobimetallic trihydride A. However, solutions of 1 under 1 atm of H$_2$ at 25 °C exhibited only ^{1}H NMR resonances assignable to the monohydride 1. Compounds containing Mo-Rh bonds have also been found to be resistant to oxidative addition of H$_2$ even under high pressures and temperatures.[7] An alternative synthesis of the desired bimetallic trihydride was attempted from reaction of K[CpRe(CO)$_2$H] with (Ph$_3$P)$_3$RhH$_2$Cl (3),[8] generated in situ from (Ph$_3$P)$_3$RhCl under 1 atm of H$_2$ in THF-d_8. However, this resulted in formation of the monohydride 1 as monitored by ^{1}H NMR spectroscopy at −85 °C. No evidence for complex A was obtained by ^{1}H NMR spectroscopy. If compound A is formed by this route, it undergoes fast reductive elimination of H$_2$. Alternatively, 1 might be formed by reductive elimination of H$_2$ from rhodium dihydride 3 to give (Ph$_3$P)$_3$RhCl, which we have shown to react with K[Cp(CO)$_2$ReH] to produce 1.



3

A

1

The reaction of 1 with 1 atm (5 equiv) of CO led to formation of the homonuclear products CpRe(CO)$_3$[9] and [(Ph$_3$P)$_2$Rh(CO)]$_2$,[10] identified by ^{1}H NMR and infrared spectroscopy. This reaction is proposed to proceed by CO addition to the rhodium center of 1, followed by simultaneous transfer of hydride from rhenium to rhodium and transfer of CO from rhodium to rhenium. This would produce CpRe(CO)$_3$ and Rh(PPh$_3$)$_2$(CO)H, which is known to decompose to [(PPh$_3$)$_2$Rh(CO)]$_2$ and H$_2$.[10] The reaction of Cp(CO)$_2$ReH$_2$ with Ir(CO)(PPh$_3$)$_2$Cl and CO that produces CpRe(CO)$_3$ and Ir(CO)(PPh$_3$)$_2$ClH$_2$ has been proposed to proceed by a similar mechanism.[2]

Rhodium-Tantalum Hydrides. The reaction of Cp$_2$TaH$_3$[11] with [(COD)RhCl]$_2$[12] (COD = 1,5-cyclooctadiene) in toluene at ambient temperature produces the extremely air- and water-sensitive complex Cp$_2$Ta(μ-H)(μ-Cl)Rh(COD) (4) in 34% yield. The

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[1] (a) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167 and references therein. (b) Albinati, A.; Togni, A.; Venanzi, L. M. *Organometallics* **1986**, *5*, 1785. (c) Chaudret, B.; Dahan, F.; Sabo, S. *Organometallics* **1985**, *4*, 1490. (d) Breen, M. J.; Geoffroy, G. L.; Rheingold, A. L.; Fultz, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 1069. (e) Albinati, A.; Naegell, R.; Togni, A.; Venanzi, L. M. *Organometallics* **1983**, *2*, 9261. (f) Alcock, N. W.; Howarth, O. W.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1979**, 1160. (g) Deubzer, B.; Kaez, H. D. *J. Am. Chem. Soc.* **1968**, *90*, 3276.

[2] Casey, C. P.; Rutter, E. W.; Haller, K. J. *J. Am. Chem. Soc.* **1987**, *109*, 6886–6887.

[3] Casey, C. P.; Rutter, E. W.; Askham, F. R.; Nagashima, H. N.; Palermo, R. E. Paper Presented at the Sixth International Symposium on Homogeneous Catalysis, Vancouver, BC, Aug 1988.

[4] Yang, G. K.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 6500–6501.

[5] Crystallographic data: a = 9.784 (2) Å, b = 19.770 (5) Å, c = 12.205 (4) Å, β = 99.55 (2)°, V = 2328 (1) Å^3, Z = 2 in either space group $P2_1$ or $P2_1/m$.

[6] Carlton, L.; Lindsell, W. E.; McCullough, K. J.; Preston, P. N. *J. Chem. Soc., Dalton Trans.* **1984**, 1693.

[7] Casey, C. P.; Bullock, R. M.; Nief, F. *J. Am. Chem. Soc.* **1983**, *105*, 7574.

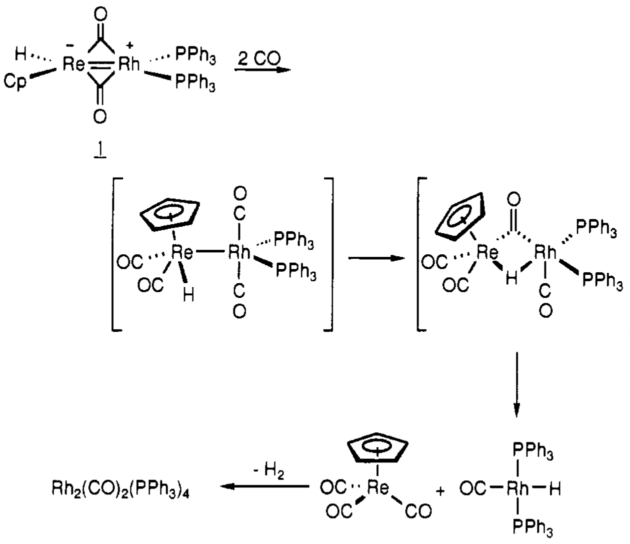
[8] Meakin, P.; Jesson, J. P.; Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 3240.

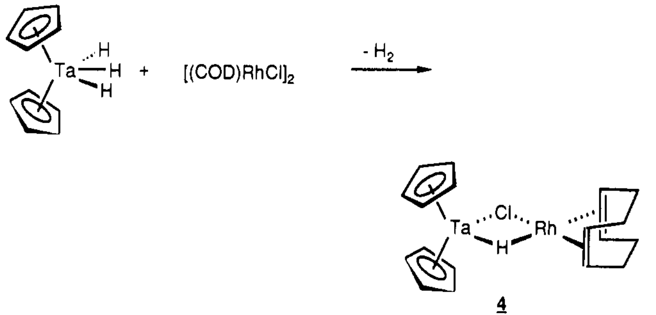
[9] Fischer, E. O.; Fellmann, W. *J. Organomet. Chem.* **1963**, *1*, 191.

[10] Evans, D.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 2660.

[11] Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.

[12] Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

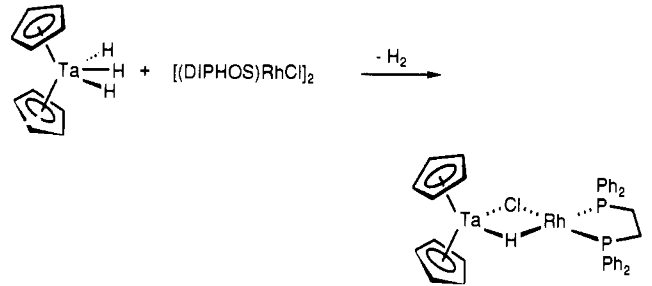




4

structure of **4** was established by spectroscopy and elemental analysis. The ^1H NMR spectrum of **4** in C_6D_6 provided evidence for a bridging hydride as a broad doublet at δ −15.96 (J_{RhH} = 26 Hz). The equivalent cyclopentadienyl ligands on tantalum appear as a finely split doublet at δ 4.71 ($^3J_{HH}$ = 0.5 Hz) due to the coupling to the bridging hydride. Similar long-range coupling between Cp and a hydride has been seen for $Cp_2Ta(CO)H$.[13] Both the ^1H and ^{13}C NMR spectra of **4** exhibit inequivalent sets of olefinic and methylene resonances for the inequivalent halves of the COD ligand.

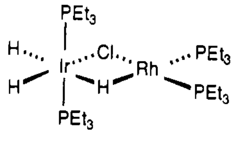
The reaction of Cp_2TaH_3 with $[(DIPHOS)RhCl]_2$[14] (DIPHOS = $Ph_2PCH_2CH_2PPh_2$) in benzene-d_6 at 48 °C was monitored by ^1H NMR spectroscopy. A new hydride-containing product, **5**, was observed along with formation of free H_2.[15] The structure of **5** was established spectroscopically. The ^1H NMR spectrum of **5** exhibits a multiplet at δ −12.61 (ddd, $J_{HP(trans)}$ = 61 Hz, J_{HRh} = 24, $J_{HP(cis)}$ = 15 Hz), which is consistent with a bridging hydride ligand coupled to rhodium and to cis and trans phosphorus atoms. The assignment of these coupling constants was made on the basis of ^{31}P NMR spectra with broad-band ^1H decoupling and with selective decoupling of the aromatic protons. In the $^{31}P\{^1H\}$ NMR spectrum of **5**, two doublets of doublets were seen at δ 79.0 (dd, J_{RhP} = 201 Hz, J_{PP} = 43 Hz) and δ 43.0 (dd, J_{RhP} = 175 Hz, J_{PP} = 43 Hz). When only the aromatic protons were decoupled, additional splitting due to the bridging hydride was evident. The phosphine at δ 79.0 showed a 15-Hz coupling to the bridging hydride and the phosphine at δ 43.0 showed a 61-Hz coupling to the bridging hydride. The resonance at δ 43.0 is assigned to the phosphine trans to the bridging hydride because of the much larger coupling to the bridging hydride.



5

In a preparative reaction, a benzene solution of Cp_2TaH_3 was stirred with solid $[(DIPHOS)RhCl]_2$ for 2 days at 48 °C. The resulting solution was filtered, and hexane was added to precipitate complex **5** as a dark brown, air-sensitive powder. ^1H NMR integration of the cyclopentadienyl region of the NMR spectrum showed that **5** was about 90% pure. The instability of **5** in ether and dichloromethane has frustrated our attempts to obtain purified **5**.

Venanzi has reported the synthesis and crystal structure of the related complex $[(PEt_3)_2Rh(\mu\text{-}H)(\mu\text{-}Cl)Ir(H)_2(PEt_3)_2]$ (**6**) from the reaction of $[(PEt_3)_2RhCl]_2$ with $(PEt_3)_2IrH_5$.[16] The bridging hydride of **6** appears as a multiplet in the ^1H NMR spectrum with rhodium and cis and trans phosphorus couplings. Another related complex is the rhodium–titanium μ-methylene complex **7**, reported by Grubbs[17] from the reaction of $[(COD)RhCl]_2$ with titanacyclobutanes. Compound **7** exhibits distinct resonances for the inequivalent halves of the COD ligand in the ^1H and ^{13}C NMR spectra due to the presence of bridging methylene and chloride ligands.



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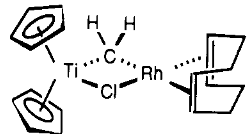
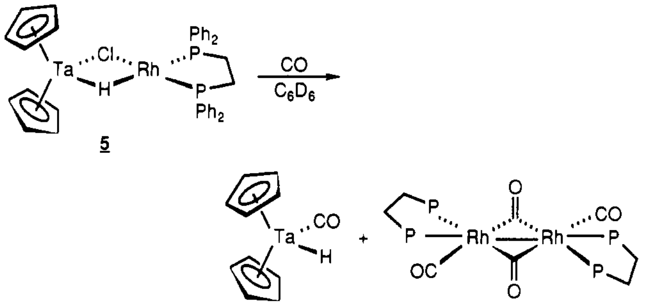


7

The reaction of complex **5** with CO was monitored by ^1H and ^{31}P NMR spectroscopy. Exposure of solutions of **5** in benzene-d_6 to 1 atm of CO resulted in formation of $Cp_2TaH(CO)$[13] and the known dimer $[(DIPHOS)Rh(CO)]_2(\mu\text{-}CO)_2$.[18]



Experimental Section

General Information. ^1H NMR spectra were recorded on a Bruker WP270 spectrometer. ^{13}C NMR spectra were recorded on a Bruker AM500 spectrometer operating at 125.76 MHz. ^{31}P NMR spectra were recorded on an AM500 spectrometer operating at 202.46 MHz and are referenced to external H_3PO_4. IR spectra were recorded on a Beckman 4230 infrared spectrometer calibrated with polystyrene film. C_6H_6, C_6D_6, THF, THF-d_8, and hexane were distilled from purple solutions of benzophenone ketyl. CH_2Cl_2 was distilled from CaH_2 under nitrogen. All solvents were stored in evacuated bulbs.

All air-sensitive materials were handled with use of standard high-vacuum manifold and inert-atmosphere glovebox techniques. $(Ph_3P)_3RhCl$,[19] $[(COD)RhCl]_2$,[12] $[(Ph_2PCH_2CH_2PPh_2)RhCl]_2$,[14] $K[CpRe(CO)_2H]$,[4] and Cp_2TaH_3[11] were prepared by literature methods.

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[13] Foust, D. F.; Rogers, R. D.; Rausch, M. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 5646.

[14] Albano, P.; Aresta, M.; Manassero, M. *Inorg. Chem.* **1980**, *19*, 1069.

[15] ^1H NMR spectra of compound **5** synthesized in a sealed NMR tube in C_6D_6 exhibited a singlet at δ 4.456, assigned to free H_2.

[16] Albinati, A.; Lehner, H.; Venanzi, L. M. *Inorg. Chem.* **1985**, *24*, 1483.

[17] Mackenzie, P. B.; Coots, R. J.; Grubbs, R. H. *Organometallics* **1989**, *8*, 8.

[18] James, B. R.; Mahajan, D.; Rettig, S. J.; Williams, G. M. *Organometallics* **1983**, *2*, 1452.

[19] Osborn, J. A.; Wilkinson, G. *Inorg. Synth.* **1967**, *10*, 67.

[Cp(H)Re(μ-CO)$_2$Rh(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)$_2$H] (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%). ^{1}H 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{^{1}H} 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{^{1}H} NMR (C_6D_6, 23 °C): δ 33.1 (d, J_{RhP} = 182 Hz). ^{31}P{^{1}H} 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$_3$P)$_3$RhH$_2$Cl with K[CpRe(CO)$_2$H]. $(Ph_3P)_3RhH_2Cl$ 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)$_2$H] (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)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%). ^{1}H NMR (C_6D_6): δ 4.83 (br m, 2 H, *H*C=CH), 4.71 (d, J = 0.46 Hz, 10 H, C_5H_5), 4.64 (br m, 2 H, HC=C*H*), 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, H*C*=CH), 72.67 (dd, J_{RhC} = 14 Hz, J_{CH} = 156 Hz, HC=*C*H), 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$_2$Ta(μ-H)(μ-Cl)Rh(Ph$_2$PCH$_2$CH$_2$PPh)] (5). A suspension of [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)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%). ^{1}H 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{^{1}H} 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 [(η^5-P$_5$)-FeCp*] (**1**). Recently,[3] the synthesis of naked P_5^- gives further support for the possible preparation of [(η^5-P$_5$)$_2$Fe] (**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.		stabilizn from interacn of e_1'' and P$_5$Fe LUMO[a]
	Fe–P$_5$	Fe–Cp	
(η^5-P$_5$)Fe	0.95[b]		
(η^1-P$_5$)Fe	0.85[c]		
(η^5-P$_5$)FeCp (**1**)	0.55[b]	0.65	1.72
(η^1-P$_5$)FeCp (**3**)	0.84[c]	0.70	1.1
(η^5-P$_5$)$_2$Fe (**2**)	−0.13[b]		−0.98
(η^1-P$_5$)(η^5-P$_5$)Fe (**6**)	0.25,[b] 0.78[c]		0.6
(η^1HP$_5$)$_2$Fe	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 [(η^1-P$_5$)FeCp] (**3**) appears in Figure 1. The levels are traced to show their parentage in the MOs of the ring and P$_5$Fe 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 (η^1-P$_5$)Fe fragment.

The HOMO of (η^1-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 (η^5-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 (η^5-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 (η^5-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 (η^5-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 (η^5-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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(1) Baird, N. C. *Can. J. Chem.* **1984**, *62*, 341.
(2) (a) Scherer, O. J.; Brück, T. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 59. (b) Scherer, O. J.; Brück, T.; Wolmershäuser, G. *Chem. Ber.* **1988**, *121*, 935.
(3) Baudler, M.; Akpapoglou, S.; Ouzounis, O.; Wasgestian, F.; Meinigke, B.; Budzikiewicz, H.; Münster, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 280.
(4) Elian, M.; Chem. M. M. L.; Mingos, D. P.; Hoffmann, R. *Inorg. Chem.* **1976**, *15*, 1148.
(5) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

0020-1669/90/1329-0879$02.50/0