$^{-}OC_6H_4NO_2$-*o*, 423; $[NP(OC_6H_4NO_2\text{-}m)_2]_3$ (III), 258 sh; $^{-}OC_6H_4NO_2$-*m*, 415; $[NP(OC_6H_4NO_2\text{-}p)_2]_3$ (IV), 264 (log ϵ 2.43); $[NP(OC_6H_4NO_2\text{-}p)_2]_4$, 265 (log ϵ 2.39); $^{-}OC_6H_4NO_2$-*p*, 405; $[NP(O_2C_{10}H_6\text{-}1,8)]_3$ (XII), 220, 225 sh, 269 sh, 280, 291 (log ϵ 4.37), 296 sh, 304 sh, 310, 318, 325; $[NP(O_2C_{10}H_6\text{-}1,8]_4$ (XIV), 220, 225 sh, 280, 291 (log ϵ 4.49), 296 sh, 305 sh, 310, 318, 325; and $[NP(O_2C_{12}H_8\text{-}2,2')]_4$ (XV), 243 (log ϵ 4.81), 270 sh, 278 sh. The spectra of V, X, XI, and XII have been recorded previously.[7,8]

The kinetic runs were monitored at the following wavelengths: $[NP(OC_6H_4NO_2\text{-}o)_2]_3$ (II), 423 mμ; $[NP(OC_6H_4NO_2\text{-}m)_2]_3$ (III), 415 mμ; $[NP(OC_6H_4NO_2\text{-}p)_2]_3$, 405 mμ; $[NP(O_2C_6H_4\text{-}1,2)]_3$ (X), 268 mμ; and $NP(O_2C_{10}H_6\text{-}1,2)]_3$ (XI), 276 mμ.

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Stereochemically Nonrigid Six-Coordinate Molecules. II. Preparations and Reactions of Tetrakis(organophosphorus) Metal Dihydride Complexes

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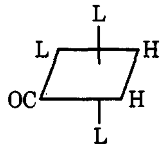
Abstract: A series of iron and ruthenium H_2ML_4 complexes were prepared with trivalent phosphorus (L) ligands. Synthesis of the iron complexes was greatly facilitated through a new and general procedure based on the reaction of bis(1,3,5,7-cyclooctatetraene)iron and a phosphorus(III) compound with hydrogen. The reaction chemistry of these coordinately saturated hydride complexes was explored. Reaction at the metal site required conditions where ligand dissociation was occurring at a reasonable rate. Consistent with this generalization, complexes possessing bulky ligands were found more reactive than those which have sterically less hindered ligands. Ostensibly, this reflects the greater propensity of the former class for ligand dissociation. Transesterification experiments using phosphites and methanol showed that metal-coordinated phosphites exchange with alcohol significantly slower than weakly coordinated or free phosphites.

Transition metal hydride complexes have attracted considerable interest during the past decade, especially in connection with catalytic processes[1] and structure elucidation.[2] We have recently communicated[3] on the stereochemical behavior of certain tetrakis(organophosphorus) metal dihydrides. These H_2FeL_4 complexes are stereochemically nonrigid on the nmr time scale and, because of $^1H-^{31}P$ couplings, are often amenable to detailed line-shape analyses yielding mechanistic information.[4] During these investigations, a substantial number of new iron and ruthenium complexes were prepared using synthetic methods of general utility. This paper describes the preparation and some reaction chemistry of metal dihydrides. A full discussion of the dynamic stereochemistry will be published in part III[5] of this series.

Structures of H_2ML_4 and H_2ML_3CO Complexes. Results of some nmr investigations of these hydride complexes and the structural implications have been reported;[3,4] the full analysis will be presented in part III.[5] Twelve of the fifteen H_2FeL_4 complexes exhibit evidence only for cis structures at −50° in toluene solution as discerned by analysis of the nmr spectra. Two complexes, $H_2Fe[P(C_6H_5)(OC_2H_5)_2]_4$ and $H_2Fe[P(C_6H_5)(OCH_3)_2]_4$, populate significant amounts of the cis and trans forms in solution. The cis/trans ratio is lowest in *n*-hexane (0.95) and highest in methylene chloride (6.52) for the former in the more common organic solvents. One complex, $H_2Fe\{o\text{-}C_6H_4[P(C_2H_5)_2]_2\}_2$, detectibly (nmr) populates only the trans structure at −50° in toluene, but exchange studies[5] showed that the cis form must be present in low concentration.[5] At higher temperatures, the limiting spectra of all iron compounds are quintets; relatively rapid intramolecular exchange is a characteristic feature of these molecules. This class of six-coordinate complexes is important because it provides the first unequivocal demonstration of intramolecular rearrangement in six-coordinate complexes.

The carbonyl complexes, H_2FeL_3CO [L = $P(C_6H_5)_2(CH_3)$, $P(C_6H_5)_2(C_2H_5)$], in toluene solution at −50° exhibit hydride spectra consistent with the cis structure, **1**.



1

Above −50°, the proton nmr spectra broaden and finally emerge as regular quartets, indicating averaging of phosphorus environments. These iron complexes are thus stereochemically nonrigid like the $H_2M(PX_3)_4$ molecules. The cis structure **1** was proposed by Keim,

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(1) C. A. Tolman in "Transition Metal Hydrides," Vol. 1, E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 6.

(2) J. P. Jesson, *ibid.*, Chapter 4.

(3) F. N. Tebbe, P. Meakin, J. P. Jesson, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **92**, 1068 (1970); P. Meakin, L. J. Guggenberger, J. P. Jesson, D. H. Gerlach, F. N. Tebbe, W. G. Peet, and E. L. Muetterties, *ibid.*, **92**, 3482 (1970).

(4) P. Meakin, E. L. Muetterties, F. N. Tebbe, and J. P. Jesson, *ibid.*, **93**, 4701 (1971).

(5) P. Meakin, E. L. Muetterties, and J. P. Jesson, *ibid.*, in press.

et al.,[6] for $H_2Ru[P(C_6H_5)_2(CH_3)]_3CO$. We found this ruthenium compound "rigid" on the nmr time scale from −50° to >100°.

Nine of the ten tetrakis(organophosphorus) ruthenium dihydrides exhibit nmr spectra which are consistent only with the cis ground state geometry. Only one compound, $H_2Ru[P(C_6H_5)(OC_2H_5)_2]_4$, is in equilibrium with the trans structure (~10%) at low temperatures (25–60°). At higher temperatures (60–150°) the spectra of all the ruthenium compounds broaden, but in no case was the fast exchange limit, a regular quintet, reached. These hydrides thermally decompose with the evolution of hydrogen or by ligand dissociation before the required fast exchange temperature is reached. The barriers to intramolecular rearrangement for the ruthenium complexes are significantly larger[5] than those of the iron analogs.

Preparation of H_2ML_4 Complexes. The preparations of six iron and two ruthenium dihydrides have appeared in the literature,[7–12] but no single satisfactory method has been reported which is sufficiently general to permit the synthesis of a number of similar H_2ML_4 complexes. We have a very simple, general route to H_2FeL_4 complexes in the reaction of bis(1,3,5,7-cyclooctatetraene)iron(0) $[Fe(C_8H_8)_2]$ with hydrogen and a trivalent phosphorus compound. Cyclooctatetraene is hydrogenated to cyclooctane, and the "vacant" coordination positions on the iron are filled by the phosphorus ligands and hydrogen atoms. There is no substantive separation problem for this reaction system. This method has been used successfully for the preparation of $H_2Fe[P(OC_2H_5)_3]_4$, $D_2Fe[P(OC_2H_5)_3]_4$, $H_2Fe[P(O\text{-}i\text{-}C_3H_7)_3]_4$, $H_2Fe[P(OCH_2)_3CC_2H_5]_4$, $H_2Fe[P(OC_6H_5)_3]_4$, $H_2Fe[P(O\text{-}o\text{-}C_7H_7)_3]_4$, $H_2Fe[P(C_6H_5)(OCH_3)_2]_4$, $H_2Fe\{o\text{-}C_6H_4\text{-}[P(C_2H_5)_2]_2\}_2$, and $H_2Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$.

Some H_2Fe[phosphine]$_4$ complexes were prepared more conveniently by room temperature hydridation (sodium borohydride in ethanol or lithium aluminum hydride in tetrahydrofuran) of iron(II) chloride–ligand mixtures. This method is particularly useful for phosphines with aromatic groups that are bulky; the resultant complexes are relatively thermally unstable and the high temperatures required for the $Fe(C_8H_8)_2$ reaction often lead to metal formation.

The synthesis of ruthenium complexes was generally more difficult. Keim, *et al.*,[6] have used hydrogen–hydrazine mixtures to prepare $H_2Ru[P(C_6H_5)_2(CH_3)]_4$. We have found that the most generally successful method involves sodium borohydride or lithium aluminum hydride reaction with the appropriate phosphinometal halide. Purification of many of these complexes proved extremely difficult even with the employment of column chromatography.

Reactions of H_2ML_4 Complexes. The iron and ruthenium H_2ML_4 complexes are coordinately saturated (18-electron complexes). Thus, the rate-determining step for reactions centered on the metal center was anticipated to be dissociation (1) of one of the trivalent phosphorus ligands to give a reactive 16-electron complex.[1]

$$H_2ML_4 \rightleftharpoons H_2ML_3 + L \qquad (1)$$

To assess this hypothesis, the relative reactivity of the H_2ML_4 complexes was investigated as a function of metal and ligand character. Most distinctive was the greater reactivity of the complexes based on phosphine ligands. We believe that the reason for this reactivity is the facility of ligand dissociation in the phosphine series. Electronically and sterically the phosphines and phosphites are distinct. We suggest that steric factors are important in this reactivity differential since the phosphites have smaller Tolman cone angles[13] than the bulky phosphines. Thus we found no evidence for the ligand exchange reaction (eq 2) within 72 hr at 25°. If

$$H_2M[P(OC_2H_5)_3]_4 + P(OCH_3)_3 \rightleftharpoons H_2M[P(OC_2H_5)_3]_3[P(OCH_3)_3] + P(OC_2H_5)_3 \qquad (2)$$

reaction 1 occurred to any extent, the less bulky trimethyl phosphite should have dominated in the reverse association process and free triethyl phosphite should have been detected. Under the same conditions $H_2M[P(C_6H_5)_2(CH_3)]_4$ and $P(OCH_3)_3$ showed substantial exchange; free phosphine and mixed ligand complexes were detected by nmr.

Additional evidence from nmr experiments support the above results. Detailed analysis of the pmr spectra of $H_2Fe[P(OC_2H_5)_3]_4$ from 25 to 130° in the absence and presence of triethyl phosphite indicate that if a dissociative process is operative it is slow on the nmr time scale. In contrast, the hydride spectra of the phosphine complex, $H_2Ru[P(C_6H_5)_2(CH_3)]_4$, at high temperatures (>130°) show H–P couplings are lost due to dissociation of phosphine. When the temperature was lowered the H–P couplings were restored proving the reversibility of reaction 1 for this compound. Thus ligand dissociation in this complex is very fast (~10^2 sec^{-1} mol^{-1}) above 130°. The irreversible instability of $H_2Ru[P(OC_2H_5)_3]_4$ and $H_2Fe[P(C_6H_5)_2(CH_3)]_4$ precluded establishing rates of dissociation by the nmr method.

The chemistry of the phosphine complexes proved to be consistent with the nmr data. In the phosphine complexes, a phosphine ligand can be readily displaced by other types of molecules. Carbon monoxide reacted with $H_2M[P(C_6H_5)_2(CH_3)]_4$ (M = Fe or Ru) under ambient conditions to give $H_2M[P(C_6H_5)_2(CH_3)]_3CO$, and benzonitrile reacted at 30–60° with the ruthenium complex to give $H_2Ru[P(C_6H_5)_2(CH_3)]_3NCC_6H_5$.[14] In contrast, the phosphite complexes were unreactive; $H_2M[P(OC_2H_5)_3]_4$ did not react with carbon monoxide at temperatures exceeding 100° and at pressures up to 100 atm.

Nitrogen can compete effectively for a coordination site in the iron–phosphine complexes but not in the ruthenium analogs. Two complexes, $H_2Fe[P(C_6H_5)(C_2H_5)_2]_3N_2$ and $H_2Fe[P(C_6H_5)(C_2H_5)_2]_4$, were obtained from the reaction of iron(II) chloride, excess phosphine, and sodium borohydride in ethanol under a nitrogen atmosphere. Only the tetrakisphosphine derivatives were obtained with ruthenium under the same

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[6] K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 7, 546 (1968).

[7] W. Kruse and R. H. Atalla, *Chem. Commun.*, 921 (1968).

[8] D. Titus, A. A. Orio, and H. B. Gray, *Inorg. Syn.*, to be submitted for publication.

[9] J. Chatt and R. G. Hayter, *J. Chem. Soc.*, 5507 (1961).

[10] H. F. Klein, *Angew. Chem., Int. Ed. Engl.*, **9**, 904 (1970).

[11] G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, **90**, 2278 (1968).

[12] T. Kruck and A. Prasch, *Z. Anorg. Allg. Chem.*, 371, 1 (1969).

[13] C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

[14] This complex has similar nmr spectral characteristics to $H_2Ru[P(C_6H_5)_2(CH_3)]_3CO$[6] and to $H_2Ru[P(C_6H_5)_3]_3NCC_6H_5$ which will be described by W. H. Knoth (private communication).

conditions with the phosphines, $P(C_6H_5)_2C_2H_5$ and $P(C_6H_5)(C_2H_5)_2$.

The iron complexes were generally more reactive than their ruthenium counterparts, *e.g.*, toward oxygen, producing phosphine oxides and phosphates for phosphine and phosphite complexes, respectively. Even mild heating of some $H_2Fe(phosphine)_4$ complexes caused decomposition to hydrogen gas and, in some cases, metal. Prolonged exposure to light also decomposed the compounds.[15]

The interaction of deuterium and metal dihydrides in benzene was examined in order to establish lability of metal hydride and of ligand hydrogen nuclei. It was found that the hydride atoms in $H_2Fe[P(O\text{-}i\text{-}C_3H_7)_3]_4$ exchanged appreciably with deuterium. A $D_2/HD/H_2$ ratio close to that expected for statistical exchange between D_2 and the metal hydride–hydrogen atoms was reached in 72 hr at 25°. In contrast, exchange was not significant under these conditions with the iron complexes based on triethyl phosphite, triphenyl phosphite, and dimethylphenyl phosphine.[16] At 80°, $H_2Fe[P(OC_2H_5)_3]_4$ was still largely inactive in the exchange reaction; $H_2Fe[P(OC_6H_5)_3]_4$, however, was active at 80° and introduced significantly *more* hydrogen into the vapor phase (24 hr) than could be accounted for by assuming complete statistical exchange of D_2 with hydride–hydrogen atoms.[17] Exchange experiments with C_6D_6–H_2 eliminated the solvent as a possible contributing factor since no HD or D_2 was detected in the vapor phase under identical conditions. Assuming that no more than two hydrogen atoms were liberated for every decomposed iron complex, the ligand hydrogen atoms must have exchanged with gaseous D_2. The manner of exchange could be similar to that proposed by Parshall[18] for the exchange of the ortho aromatic hydrogen atoms of $HClRu[P(OC_6H_5)_3]_4$ and D_2. A series of reversible reactions involving ortho-bonded species provides a satisfactory explanation of our results.

Carbon tetrachloride reacted at room temperature with all the complexes examined. Addition of 1 equiv of CCl_4 to a solution of $H_2Ru[P(C_6H_5)(CH_3)_2]_4$ resulted in the formation of the hydrido chloride, $HClRuL_4$, and $CHCl_3$. The hydrido chloride was identified by its hydride pmr spectrum which consists of a 1:4:6:4:1 quintet at τ 27.32. The presence of $CHCl_3$ was established by comparison of the chemical shift with that of an authentic sample.

Addition of CCl_4 to $H_2Ru[P(OC_2H_5)_3]_4$ and $H_2Fe[P(OC_2H_5)_3]_4$ yielded $Cl_2M[P(OC_2H_5)_3]_4$. The absence of a hydride resonance in the ir and pmr spectra and the spectroscopic comparison of the products with authentic samples provided characterization of this reaction.

Transesterification of Free and Coordinated Phosphites. Transesterification of free phosphites with alcohols occurred easily and in some cases was sufficiently rapid to effect equilibration within seconds or less.[19] Triethyl phosphite exchanged ethoxy for methoxy groups when exposed to CH_3OH. Several minutes after $P(OC_2H_5)_3$ and CH_3OH were mixed, the mixed phosphites, $P(OC_2H_5)_2(OCH_3)$ and $P(OC_2H_5)(OCH_3)_2$, in addition to $P(OC_2H_5)_3$ and $P(OCH_3)_3$, were detected by pmr. Triphenyl phosphite transesterified even faster; within seconds after mixing $P(OCH_3)_3$ was detected by odor. Pmr spectral studies showed that at 60° the exchange is rapid on the nmr time scale, *ca.* 10^2 sec^{-1} mol^{-1}.

Phosphites coordinated to iron and ruthenium showed no evidence of transesterification. Toluene solutions containing $H_2Fe[P(OC_6H_5)_3]_4$, $H_2Fe[P(OC_2H_5)_3]_4$, or $H_2Ru[P(OC_2H_5)_3]_4$, or $H_2Ru[P(OC_2H_5)_3]_4$ and methanol did not undergo exchange in 96 hr at ambient temperature. In complexes where the phosphites are loosely coordinated, transesterification is slow. The compound $Ni[P(O\text{-}o\text{-}C_7H_7)_3]_4$ in benzene solution dissociates to $Ni[P(O\text{-}o\text{-}C_7H_7)_3]_3$ and $P(O\text{-}o\text{-}C_7H_7)_3$.[20] It is possible to precipitate the pure tetrakis ligand complex from a hydrocarbon solution by addition of methanol.[21] However, prolonged exposure of solutions of the labile *o*-tolyl phosphite complex to methanol produced significant quantities of the mixed phosphite complexes.

Experimental Section

General Procedure. Because most hydride complexes react with atmospheric oxygen, reactions were run under rigorously oxygen-free conditions. Solid complexes and their solutions were exposed only to high-purity nitrogen or oil pump vacuum. Dry and thoroughly degassed solvents were used. The petroleum ether had a boiling point range of 38–53°. The yields of purified products were in the range of 30–60%.

$H_2Fe[P(OC_2H_5)_3]_4$. A mixture of 13 g (0.048 mol) of $FeCl_2 \cdot 4H_2O$ and 75 ml (excess) of $P(OC_2H_5)_3$ in absolute ethanol was refluxed for 30 min. The resulting, almost clear, yellow-green solution was cooled to −78° and 2.5 g (0.066 mol) of $NaBH_4$ was added. The temperature was allowed to rise slowly until evolution of hydrogen was vigorous. The mixture was warmed to room temperature and the solvent and excess ligand were removed *in vacuo*. The gummy residue was extracted with ten 50-ml portions of petroleum ether. The extract was vacuum evaporated to give a solid which was recrystallized from ethanol at −40°; ν_{Fe-H} 1925 cm^{-1}.

Anal. Calcd for $C_{24}H_{62}O_{12}P_4Fe$: C, 39.9; H, 8.65; P, 17.2; Fe, 7.73. Found: C, 39.9; H, 8.79; P, 17.4; Fe, 7.97.

$H_2Fe[P(C_6H_5)(OC_2H_5)_2]_4$. A mixture of 6.35 g (0.05 mol) of anhydrous $FeCl_2$ and 45 g (0.23 mol) of $P(C_6H_5)(OC_2H_5)_2$ in 200 ml of ethanol was refluxed for 30 min. While the solution was still hot, 1.4 g (0.037 mol) of $NaBH_4$ in 40 ml of ethanol was added dropwise. During the addition, the color changed from light green to dark yellow. The mixture was filtered and the filtrate cooled. Scratching the sides of the flask and cooling to −40° precipitated a yellow microcrystalline solid which was collected and washed with cold ethanol. Recrystallization from ethanol yielded a pure product;[3] ν_{Fe-H} 1810 (trans), 1965 (cis) cm^{-1}.

Anal. Calcd for $C_{40}H_{62}O_8P_4Fe$: C, 56.5; H, 7.34. Found: C, 56.2; H, 7.34.

$H_2Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2 \cdot 2C_7H_8$. A solution of 2.52 g (0.02 mol) of anhydrous $FeCl_2$ and 20 g (0.05 mol) of $(C_6H_5)_2PCH_2CH_2(C_6H_5)_2$ in tetrahydrofuran was stirred for 10 min at room temperature. Addition of 4 g (0.11 mol) of $NaBH_4$ resulted immediately in an intense purple-red coloration. The solution was heated to reflux and an additional 2 g (0.053 mol) of $NaBH_4$ was added, followed by slow addition of 20 ml of ethanol. After gas evolution ceased, the resultant chrome-yellow solution was refluxed for 10 min and filtered, and the volume of the filtrate was reduced by 80%. The yellow crystals which formed were col-

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(15) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968), have reported sunlight to degrade $H_2Fe[P(C_6H_5)_2(C_2H_5)]_3N_2$ reversibly to the *o*-carbon bonded species, $HFe[(C_6H_4P(C_6H_5)(C_2H_5)][P(C_6H_5)_2(C_2H_5)]_2N_2$, and H_2.

(16) $H_2Fe[P(C_6H_5)(CH_3)_2]_4$ partially decomposed during this time.

(17) $H_2Fe[P(O\text{-}i\text{-}C_3H_7)_3]_4$ partially decomposed during this time.

(18) G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(19) F. W. Hoffmann, R. J. Ess, and R. P. Usinger, Jr., *J. Amer. Chem. Soc.*, **78**, 5817 (1956), detected transesterification in $P(OR)_3 + R'OH$ mixture by heating the mixture to remove ROH reaction product.

(20) L. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).

(21) L. W. Gosser, private communication.

lected and recrystallized from toluene. Vacuum drying at 50° for 8 hr yielded 11.5 g of the solvated product; ν_{Fe-H} 1840 cm^{-1}.

Anal. Calcd for $C_{66}H_{64}P_4Fe$: C, 76.3; H, 6.40; Fe, 5.37; P, 11.9. Found: C, 76.0; H, 6.43; Fe, 5.37; P, 11.9.

$H_2Fe[P(C_6H_5)_2(CH_3)]_4$. A solution of 2.54 g (0.02 mol) of $FeCl_2$ in 150 ml of ethanol was treated with 17 g (0.085 mol) of $P(C_6H_5)_2(CH_3)$. The resulting mixture was stirred for 20 min and 1.5 g (0.039 mol) of $NaBH_4$ was added over 15 min. After 2 hr, an orange solid was collected by filtration and washed with cold ethanol. Orange crystals were obtained by recrystallization from toluene–ethanol; ν_{Fe-H} 1940, 1840 cm^{-1}.

Anal. Calcd for $C_{52}H_{54}P_4Fe$: C, 72.7; H, 6.34; P, 14.4. Found: C, 71.9; H, 6.54; P, 14.4.

$H_2Fe[P(C_6H_5)(CH_3)_2]_4$. A solution of 3.6 g (0.028 mol) of $FeCl_2$ in 150 ml of ethanol was treated with 16 g (0.12 mol) of $P(C_6H_5)(CH_3)_2$. After 10 min, 2 g (0.053 mol) of $NaBH_4$ was added slowly, and the mixture was stirred an additional 1.5 hr. The solvent was vacuum evaporated, and the residual orange semisolid was extracted with four 60-ml portions of petroleum ether. Reduction of the extract volume and of temperature to 0° gave orange crystals. The product was collected and dried *in vacuo;* ν_{Fe-H} 1960, 1940, 1870, 1850 cm^{-1}.

Anal. Calcd for $C_{32}H_{46}P_4Fe$: C, 62.4; H, 8.20; P, 20.2. Found: C, 62.4; H, 7.87; P, 20.7.

$H_2Fe[P(C_6H_5)(C_2H_5)_2]_4$. A mixture of 2.54 g (0.02 mol) of $FeCl_2$ and 13.5 g (0.08 mol) of $P(C_6H_5)(C_2H_5)_2$ in 150 ml of ethanol was stirred for 10 min; 2 g (0.053 mol) of $NaBH_4$ was added slowly, and the mixture was stirred for 1 hr. The solvent was removed and the orange semisolid extracted with $\sim$200 ml of petroleum ether. The solvent was evaporated from the extract, and the resultant residue was extracted with methanol. The extract was cooled to −40° to yield an orange solid which melted below room temperature. Attempts to purify this solid failed. The solid was a mixture of $H_2Fe[P(C_6H_5)(C_2H_5)_2]_4$ and $H_2Fe[P(C_6H_5)(C_2H_5)_2]_3N_2$ as shown by the ir and ^1H nmr[5] spectra; ν_{Fe-H} 1940 (sh), 1875, 1850 (sh) cm^{-1}; $\nu_{N\equiv N}$ 2040 cm^{-1}.

$H_2Fe[P(C_6H_5)(O\text{-}i\text{-}C_3H_7)_2]_4$. A mixture of 0.63 g (0.005 mol) of $FeCl_2$ and 5.0 g (0.026 mol) of $P(C_6H_5)(O\text{-}i\text{-}C_3H_7)_2$ in 100 ml of 2-propanol was refluxed for 3 hr; 4 g (0.11 mol) of $NaBH_4$ was added, and the refluxing was continued for 3 hr. During this time the color turned from yellow to green. The solids were removed by filtration. Solvent and excess ligand were removed from the filtrate by vacuum evaporation. The residual green oil was not further purified. The hydride was characterized by ir and ^1H nmr;[5] ν_{Fe-H} 1900 cm^{-1}.

$H_2Fe[P(C_6H_5)_2(C_2H_5)]_3N_2$.[15] Anhydrous $FeCl_2$ (2.54 g, 0.02 mol) and $P(C_6H_5)_2C_2H_5$ (18 g) were slurried in ethanol (150 ml) and stirred at room temperature for 15 min. $NaBH_4$ (2.0 g, 0.05 mol) was added, and the reaction mixture was stirred for 3 hr in the absence of light. The resulting yellow solids were separated by filtration and washed with cold ethanol (30 ml). Recrystallization was effected by dissolution in toluene, filtering, and adding ethanol and then cooling to −40°; ν_{Fe-H} 1960, 1860 cm^{-1}; $\nu_{N\equiv N}$ 2055 cm^{-1}.

Anal. Calcd for $C_{42}H_{47}N_2P_3Fe$: C, 69.2; H, 6.50; N, 3.85; P, 12.8. Found: C, 68.8; H, 6.44; N, 3.90; P, 12.8.

$Fe(C_8H_8)_2$. Carbonaro, *et al.*,[22a] reported that this compound can be obtained in $\sim$20% yield by the reaction of $FeCl_3$ and $i\text{-}C_3H_7MgCl$. Attempts to reproduce their yield were unsuccessful; only about 5% of the theoretical yield was obtained. The compound can, however, be prepared in 75% yield by an alternative procedure.[22b] A mixture of 36 g (0.10 mol) of tris(acetylacetonato)iron(III) and 70 ml (0.61 mol) of cyclooctatetraene (purified by filtering through a coarse fritted filter containing alumina) in 400 ml of anhydrous ether was cooled to −10°. A solution of 153 ml of 36% (0.44 mol) triethylaluminum in ether was added over 1.5 hr. The brown reaction mixture was allowed to warm to room temperature, stirred for 2 hr, and cooled to −78° for 1 day. Shiny black crystals were collected, washed two times with 80 ml of ether at −78°, and dried. The compound was purified by recrystallization from ether (or pentane). It should be noted that if during the addition of $Al(C_2H_5)_3$ the temperature is allowed to rise above $\sim$0°, tris(acetylacetonato)aluminum(III) forms and interferes with the purification of $Fe(C_8H_8)_2$.

Anal. Calcd for $C_{16}H_{16}Fe$: C, 72.8; H, 6.11; Fe, 21.1. Found: C, 72.4; H, 6.14; Fe, 21.3.

$D_2Fe[P(OC_2H_5)_3]_4$. This complex and the following eight tetrakis-ligand iron dihydrides (or dideuterides) were prepared using similar procedures. Reactions were carried out in stainless steel autoclaves. Hydrogen pressures above 100 atm did not increase the yields significantly.

A solution of 1.32 g (0.005 mol) of $Fe(C_8H_8)_2$ and 15 ml (0.096 mol) of $P(OC_2H_5)_3$ in 40 ml of toluene was pressured with 30 atm of deuterium, heated to 120°, and agitated for 12 hr. The tan solution was then filtered through Celite analytical filter aid, and the filtrate was evaporated to a solid. This residue was dissolved in $\sim$25 ml of ethanol. The solution was filtered and cooled to −40° for 1 day. The resulting white crystals were collected, washed with cold ethanol, and dried. The extent of deuteration determined by nmr[5] was $\sim$90%.

$H_2Fe[P(OCH_2)_3CC_2H_5]_4$. A mixture of 2.64 g (0.01 mol) of $Fe(C_8H_8)_2$ and 10 g (0.062 mol) of $P(OCH_2)_3CC_2H_5$ in 40 ml of toluene was pressured with 100 atm of H_2, agitated, and heated to 150° for 12 hr. The reaction product was filtered through Celite. The solvent was evaporated *in vacuo* from the filtrate. The residual yellow-brown oil solidified upon addition of petroleum ether and scratching the sides of the flask. The solid was extracted several times with petroleum ether in order to remove excess ligand. Recrystallization from ethanol–ether yielded a white crystalline solid; ν_{Fe-H} 1950 cm^{-1}.

Anal. Calcd for $C_{24}H_{46}O_{12}P_4Fe$: C, 40.8; H, 6.56; O, 27.2; P, 17.5. Found: C, 41.3; H, 6.90; O, 27.0; P, 16.5.

$H_2Fe[P(OC_6H_5)_3]_4$. A solution containing 1.32 g (0.005 mol) of $Fe(C_8H_8)_2$ and 10 ml (0.039 mol) of $P(OC_6H_5)_3$ in 50 ml of toluene was agitated for 12 hr at 70° and 1000 atm of H_2. The resulting dark mixture was filtered through Celite, and the filtrate was vacuum evaporated to a brown oil. The oil was extracted with several portions of petroleum ether which were combined and allowed to evaporate at room temperature to about 75% of the original volume. Yellow crystals were collected, washed with cold petroleum ether, and dried; ν_{Fe-H} 1870, 1900, 1940 cm^{-1}.

Anal. Calcd for $C_{72}H_{62}O_{12}P_4Fe$: C, 66.6; H, 4.81; O, 14.9; P, 9.54. Found: C, 66.8; H, 4.80; O, 14.7; P, 9.85.

$H_2Fe[P(O\text{-}i\text{-}C_3H_7)_3]_4$. A mixture of 2.64 g (0.01 mol) of $Fe(C_8H_8)_2$ and 20 ml (0.088 mol) of $P(O\text{-}i\text{-}C_3H_7)_3$ in 40 ml of toluene was agitated for 12 hr at 75° and 100 atm of H_2. The resulting solution was filtered through Celite. The filtrate was concentrated to an oil. A small amount of petroleum ether was added to the oil, followed by slow addition of methanol. Cooling to −10° for 3 hr yielded a white solid which was collected, washed with cold methanol, and recrystallized from toluene–ethanol; ν_{Fe-H} 1930 cm^{-1}.

Anal. Calcd for $C_{36}H_{86}O_{12}P_4Fe$: C, 48.7; H, 9.53; O, 21.6; P, 13.9. Found: C, 48.9; H, 9.84; O, 20.9; P, 14.3.

$H_2Fe[P(O\text{-}o\text{-}C_7H_7)_3]_4$. A mixture of 2.64 g (0.01 mol) of $Fe(C_8H_8)_2$ and 16 ml (0.05 mol) of $P(O\text{-}o\text{-}C_7H_7)_3$ in 60 ml of toluene was agitated for 12 hr at 70° and 1000 atm of H_2. The solution was filtered through Celite. The solvent was removed by vacuum evaporation. The residual dark oil was mixed with $\sim$50 ml of petroleum ether and cooled to −40° for several hours. The petroleum ether was then decanted from the dark oil. This procedure was repeated three more times until the oil solidified. The petroleum ether portions were combined and allowed to evaporate slowly at room temperature. The crystals which formed were collected and dried; ν_{Fe-H} 1920, 1940 cm^{-1}.

Anal. Calcd for $C_{84}H_{86}O_{12}P_4Fe$: C, 68.8; H, 5.91; O, 13.1; P, 8.44. Found: C, 69.0; H, 5.84; O, 12.9; P, 8.61.

$H_2Fe[P(C_6H_5)(OCH_3)_2]_4$. A mixture of 2.64 g (0.01 mol) of $Fe(C_8H_8)_2$ and 9 g (0.05 mol) of $P(C_6H_5)(OCH_3)_2$ in 40 ml of toluene was agitated for 12 hr at 80° and 100 atm of H_2. The resulting solution was filtered through Celite. The solvent was removed by vacuum evaporation. Addition of petroleum ether to the residue gave a tan solid which was recrystallized from methanol; ν_{Fe-H} 1810 cm^{-1}.

Anal. Calcd for $C_{32}H_{46}O_8P_4Fe$: C, 52.1; H, 6.28; O, 17.3. Found: C, 52.2; H, 6.28; O, 16.9.

$H_2Fe[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2$. A mixture of 2.6 g (0.01 mol) of $Fe(C_8H_8)_2$ and 4 g (0.027 mol) of $(CH_3)_2PCH_2CH_2P(CH_3)_2$ in 30 ml of toluene with 100 atm of H_2 was heated to 150° for 12 hr. Some decomposition to iron metal occurred during this time. The mixture was filtered through Celite, and the filtrate vacuum evaporated to a brown oil. After the oil was allowed to stand for 2 days, a yellow-brown solid formed. The supernatant liquid was

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(22) (a) A. Carbonaro, A. Greco, and G. Dallasta, *J. Organometal. Chem.*, **20**, 177 (1969); (b) D. H. Gerlach and R. A. Schunn, *Inorg. Syn.*, to be submitted for publication.

removed by decantation, and the solid was recrystallized from petroleum ether to yield light yellow cubes; ν_{Fe-H} 1775 cm^{-1}.

Anal. Calcd for $C_{12}H_{34}P_4Fe$: C, 40.2; H, 9.59. Found: C, 40.4; H, 9.52.

$H_2Fe(PF_3)_4$. A 10-ml stainless steel pressure vessel containing 3 g (0.011 mol) of $Fe(C_8H_8)_2$ and 9 g (0.10 mol) of PF_3 was pressured to 200 atm H_2 ($-78°$) and agitated at 160° for 15 hr. The volatile products were passed through a $-78°$ U trap; the fraction containing $Fe(PF_3)_5$ and cyclooctane was collected. The $Fe(PF_3)_5$ was purified by tenfold fractionation through a 0° U trap and transferred to a 500-ml quartz flask containing platinized asbestos. The flask was cooled to $-78°$, evacuated, supplied with 400 mm of H_2, and exposed to uv radiation for 12 hr. Every hour the flask was cooled to $-78°$, evacuated, and replenished with fresh H_2. The final product was vapor transferred from the vessel; ν_{Fe-H} 1940 cm^{-1} (lit.[11] 1935 cm^{-1}).

$H_2Fe[P(C_6H_5)_2CH_3]_3CO$. A mixture of 1 g (0.0017 mol) of $H_2Fe[P(C_6H_5)_2CH_3]_4$ in 30 ml of toluene was pressured with 30 atm of CO and heated to 50° for 6 hr. The yellow reaction solution was filtered, and the volume was reduced to 10 ml. Ethanol (40 ml) was added. After 2 days at $-40°$, yellow crystals formed which were collected and dried; ν_{Fe-H}, ν_{CO} 1820, 1830, 1880, 1940 cm^{-1}.

Anal. Calcd for $C_{40}H_{41}P_3OFe$: C, 70.0; H, 6.02; P, 13.5. Found: C, 70.2; H, 6.19; P, 13.4.

$H_2Fe[P(C_6H_5)_2(C_2H_5)]_3CO$. This previously reported compound[13] was prepared from $H_2Fe[P(C_6H_5)_2(C_2H_5)]_3N_2$ by a procedure similar to that described above for $H_2Fe[P(C_6H_5)_2(CH_3)]_3CO$; ν_{Fe-H}, ν_{CO} 1825, 1840, 1860, 1880, 1950 cm^{-1}.

Anal. Calcd for $C_{43}H_{47}P_3OFe$: C, 70.9; H, 6.50; P, 12.8. Found: C, 69.8; H, 6.68; P, 12.6.

$H_2Ru[P(OCH_3)_3]_4$. A mixture of 2.6 g (0.01 mol) of $RuCl_3 \cdot 3H_2O$ in 25 ml (excess) of $P(OCH_3)_3$ was stirred until the reaction subsided and the color turned red-brown. Sodium borohydride (2 g, 0.053 mol) was added and the mixture heated gently until the color turned off-white. Excess $P(OCH_3)_3$ was evaporated under vacuum. The residue was heated gently for 20 min in the presence of tetrahydrofuran, ethanol, and 3 g (0.079 mol) of $NaBH_4$. The volatile products were vacuum evaporated and the sticky residue was extracted with toluene. The toluene was evaporated from the extract, and the resulting solid was extracted with ~100 ml of petroleum ether. Reduction of the volume to ~30 ml and of the temperature to $-20°$ led to precipitation of a light yellow solid. The solid was recrystallized from methanol to yield white crystals; ν_{Ru-H} 1850 cm^{-1}.

Anal. Calcd for $C_{12}H_{38}P_4O_{12}Ru$: C, 24.1; H, 6.39; O, 32.0; P, 20.7. Found: C, 24.2; H, 6.26; O, 31.4; P, 20.7.

$H_2Ru[P(OC_2H_5)_3]_4$. A mixture of 2.6 g (0.01 mol) of $RuCl_3 \cdot 3H_2O$ and 25 ml (excess) of $P(OC_2H_5)_3$ was stirred for 15 min. The solution turned violet and evolved heat. After addition of 1 g (0.026 mol) of $NaBH_4$, the yellow solution was stirred for 5 min and filtered. The filtrate was cooled and the resulting yellow crystals of $Cl_2Ru[P(OC_2H_5)_3]_4$ were collected and dried. A mixture of 5 g (0.006 mol) of $Cl_2Ru[P(OC_2H_5)_3]_4$ and 2 ml (0.013 mol) of $P(OC_2H_5)_3$ in 75 ml of ethanol was gently heated in the presence of 3 g (0.079 mol) of $NaBH_4$ for 30 min. The solvent was then removed *in vacuo*. The solid residue was extracted several times with petroleum ether. The petroleum ether was vacuum removed, and the light yellow residue was recrystallized from ethanol to yield 2.6 g of white needles (51% of theory); ν_{Ru-H} 1880 cm^{-1}.

Anal. Calcd for $C_{24}H_{62}O_{12}P_4Ru$: C, 37.6; H, 8.14; O, 25.9; P, 16.1. Found: C, 37.8; H, 8.18; O, 24.8; P, 16.7.

$H_2Ru[P(O\text{-}i\text{-}C_3H_7)_3]_4$. A mixture of 2.6 g (0.01 mol) of $RuCl_3 \cdot 3H_2O$ and 35 ml (excess) of $P(O\text{-}i\text{-}C_3H_7)_3$ was stirred for 15 min. After addition of 2 g (0.053 mol) of $NaBH_4$, the resulting solution was warmed to reflux until it turned yellow. The excess phosphite was removed by vacuum evaporation, and the residue was refluxed in tetrahydrofuran–ethanol in the presence of 3 g (0.079 mol) of $NaBH_4$. Solvent was then vacuum evaporated. The residue was extracted with petroleum ether, and the petroleum ether extract was evaporated. Methanol was added to the residual oil. A solid formed which was collected and dried. The hydride pmr spectrum at room temperature was identical with that of $H_2Ru[P(OC_2H_5)_3]_4$; ν_{Ru-H} 1900 cm^{-1}.

$H_2Ru[P(C_6H_5)(OC_2H_5)_2]_4$. A mixture of 5.2 g (0.02 mol) of $RuCl_3 \cdot 3H_2O$ and 50 ml (excess) of $P(C_6H_5)(OC_2H_5)_2$ was gently heated until an exothermic reaction set in and a chrome-yellow coloration was evident. After addition of 250 ml of ethanol and 100 ml of tetrahydrofuran, the mixture was heated to reflux and 3 g (0.079 mol) of $NaBH_4$ was added over 10 min. Refluxing was continued for 30 min, during which the color lightened considerably. The mixture was filtered and the filtrate evaporated to a yellow oil. The addition of petroleum ether precipitated a white solid which was removed by filtration. The solvent was removed to give an oil which was heated to 90° (0.1 mm) to remove excess ligand. The oil was then chromatographed using a 24-in. silica gel column and petroleum ether as the eluent. A yellow fraction was collected and the solvent evaporated. The residual semisolid was recrystallized from methanol to yield off-white crystals; ν_{Ru-H} 1895, 1950 (sh) cm^{-1}.

Anal. Calcd for $C_{40}H_{62}P_4O_8Ru$: C, 53.6; H, 6.98. Found: C, 52.6; H, 6.91.

$H_2Ru[P(C_6H_5)(CH_3)_2]_4$. A mixture of 8 g (0.007 mol) of $RuCl_2[P(C_6H_5)(CH_3)_2]_3 \cdot 0.5H_2O$, 3 ml (0.02 mol) of $P(C_6H_5)(CH_3)_2$, and 2 g (0.053 mol) of $NaBH_4$ in 150 ml of ethanol was refluxed for 3 hr. The solvent was removed from the mixture, and the residue extracted with hexane. The extract was vacuum dried, and the residual semisolid was recrystallized from petroleum ether to yield yellow crystals; ν_{Ru-H} 1850 cm^{-1}.

Anal. Calcd for $C_{32}H_{46}P_4Ru$: C, 58.6; H, 7.07; P, 18.9. Found: C, 58.8; H, 6.96; P, 18.9.

Exchange Reactions between D_2 and H_2ML_4 Complexes. In a typical experiment 2×10^{-4} mol of complex, 2×10^{-4} mol of deuterium, and 5 ml of benzene were sealed in a 15-ml glass flask, and the mixture was agitated at room temperature for 3 days or at 80° for 1 day. Gas samples were analyzed mass spectrometrically: $H_2Fe[P(O\text{-}i\text{-}C_3H_7)_3]_4$, 25° (3 days), % D_2, 25.2; HD, 47.0; H_2, 29.8; $H_2Fe[P(OC_6H_5)_3]_4$, 80° (1 day), % D_2, 4.5; HD, 30.7; H_2, 64.7.

Reaction of CCl_4 with H_2ML_4 Complexes. The reactions were carried out at room temperature. Typically, a solution of 0.3 mmol of H_2ML_4 in 0.75 ml of toluene-d_8–tetramethylsilane in an nmr tube was mixed with 0.05 mmol of CCl_4. The reaction was allowed to proceed to completion, and the spectrum of the hydride and ligand protons recorded.

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