

The Chemistry of 2-Naphthyl Bis[bis(dimethylphosphino)ethane] Hydride Complexes of Fe, Ru, and Os. 1. Characterization and Reactions with H₂ and Lewis Base Ligands

C. A. Tolman,* S. D. Ittel,* A. D. English, and J. P. Jesson

Contribution No. 2501 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware
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Abstract: The preparation and spectroscopic characterization of 2-naphthyl bis[bis(dimethylphosphino)ethane] metal hydride complexes HMNp(dmpe)₂ (M = Fe, Ru, and Os) are described. Also described are their reactions with H₂ to give dihydrides and with CO, phosphorus ligands, olefins, disubstituted acetylenes, and azobenzene to give five-coordinate, zerovalent species. Anthracene forms an unusual tetrahapto diene-like complex with iron. Most of the reactions of HFeNp(dmpe)₂ are believed to proceed through the undetected intermediate Fe(dmpe)₂—an extremely electron-rich and reactive species; the half-life for reductive elimination of naphthalene to give the intermediate is about 35 min at 25 °C.

Introduction

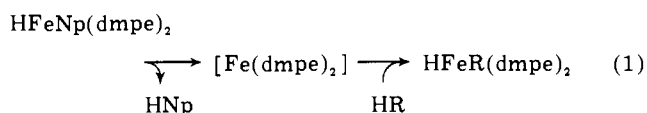
As part of our continuing program involving the chemistry of low-valent transition metal complexes with phosphorus ligands, complexes of zerovalent iron have been investigated. Earlier work in this area focused on zerovalent nickel. We reasoned that the greater steric crowding of an FeL₅ complex relative to a NiL₄ complex would favor ligand dissociation. Since ligand substitution and oxidative addition often proceed through coordinatively unsaturated 16-electron intermediates,¹ increased ligand dissociation should lead to enhanced reactivity. Additionally, because of the lower atomic number of iron, the 16-electron intermediate should be more electron rich and should therefore undergo more facile oxidative addition reactions.

The first complexes prepared were of the form FeL₅ [L = P(OMe)₃, P(OEt)₃, and P(O-*n*-Pr)₃],² and, contrary to expectation, were relatively inert to ligand dissociation.³ This result is analogous to the relative ease of dissociation of CO from Ni(CO)₄ compared to dissociation from Fe(CO)₅, suggesting that steric effects are of secondary importance in the dissociation of L from these FeL₅ species. The expected increase in basicity on going from Ni to Fe was, however, realized; this is most readily demonstrated by the protonation of the FeL₅ complexes by alcohols (pK_a ≈ 18) to give [FeL₅H]⁺. Protonation of NiL₄ complexes is effected only by the use of strong acids such as H₂SO₄ in methanol.⁴ Attempts to prepare FeL₅ or FeL₄ complexes of bulkier phosphites, such as P(O-*i*-Pr)₃ and P(OPh)₃, by techniques similar to those used to prepare the FeL₅ complexes of *n*-alkyl phosphites, were unsuccessful. Another attempted route of preparation, reaction of Fe(1,5-COD)₂⁵ with P(O-*i*-Pr)₃, P(OMe)₃, and P(OPh)₃, resulted in the isolation of Fe(η⁴-1,3-COD)L₃ complexes⁶ for the first two and of Fe[P(OPh)₃]₂[C₆H₄OP(OPh)₂]₂^{7a} for the aryl phosphite; the latter complex results from cleavage of two ortho C-H bonds of the triphenyl phosphite ligands, with the elimination of a molecule of hydrogen. Fe[P(OCH₂)₃CEt]₅ can, however, be prepared from Fe(1,5-COD)₂ and P(OCH₂)₃CEt.^{7b}

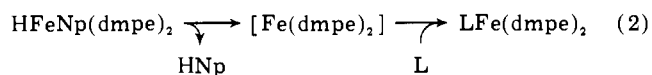
In an endeavor to increase both the basicity and the steric crowding of the complex, preparation of Fe(PMe₃)₅ was attempted. The isolated product, HFe(CH₂PMe₂)(PMe₃)₃,⁸ results from oxidative addition of one methyl C-H bond across the iron in the undetected species Fe(PMe₃)₄. The results did show that coordinatively unsaturated iron complexes are capable of cleaving C-H bonds under mild conditions.

A further possible route into the desired chemistry was suggested by the report of Chatt and Watson⁹ of the preparation of Fe(dmpe)₂ (dmpe = Me₂PCH₂CH₂PMe₂) by the sodium naphthylenide reduction of FeCl₂(dmpe)₂. We repeated this reaction as well as analogous reductions with RuCl₂(dmpe)₂¹⁰ and OsCl₂(dmpe)₂¹¹ to give the known *cis*-HMNp(dmpe)₂ complexes (Np = 2-naphthyl), whose single-crystal x-ray structures have been determined.¹¹

Two products were isolated from the FeCl₂(dmpe)₂ reduction. The first is analogous to the Ru and Os naphthyl hydrides. The second is a diphosphine bridged dimer, Fe₂(dmpe)₅, and is presumably the complex originally formulated as Fe(dmpe)₂⁹ based on its melting point, color, and reaction with I₂. Though Fe(dmpe)₂ was neither isolated nor observed spectroscopically in solution, HFeNp(dmpe)₂ readily loses naphthalene to form [Fe(dmpe)₂] as a highly reactive intermediate which undergoes a variety of novel reactions, including rapid cleavage of sp, sp², and sp³ C-H bonds at 25 °C (eq 1).



Reactions with Lewis base ligands (eq 2) give five-coordinate



zerovalent iron complexes with unusual spectroscopic properties, including extremely low ν_{CO} when L = CO, an unusually high field ¹H NMR shift of the ethylenic protons when L = C₂H₄, and a large decrease of ν_{C≡C} when L = PhC≡CPh. Other Fe(0) adducts include azobenzene symmetrically π bonded through its nitrogen-nitrogen double bond, and anthracene coordinated as a tetrahapto-1,3-diene in a complex having one of the four dmpe phosphorus atoms not coordinated to the iron atom.

This paper describes the spectroscopic characterization of Fe₂(dmpe)₅ and the HMNp(dmpe)₂ complexes and the reactions of the naphthyl hydrides with H₂ and Lewis base ligands; subsequent papers^{12,13} will describe C-H, C-O, and C-Cl bond cleavage. Though most of our work has been with M = Fe, we have explored some chemistry of the less reactive Ru and Os complexes for comparison. Preliminary reports of this work have appeared.¹⁴

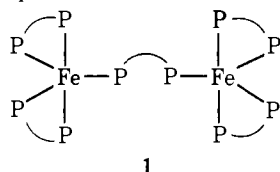
Table I. Selected Properties of Products Isolated from Sodium Naphthylenide Reductions of $MCl_2(dmpe)_2$ Complexes

Product	Color	Mp, °C	ν_{MH}^a	ν_{MD}^a	Ratio
$Fe_2(dmpe)_5$ (1)	Red-orange	194 ^b			
$HFeNp(dmpe)_2$ (2a) ^a	Gold	213–215	1725	1242 ^c	1.39
$HRuNp(dmpe)_2$ (2b)	Pale yellow	180–182 ^d	1780		
$HOsNp(dmpe)_2$ (2c)	White	126–132 ^e	1875		

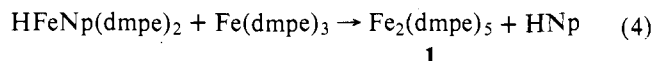
^a HNp = naphthylene. IR in Nujol mulls. ^b A mp of 205 °C was reported for $Fe(dmpe)_2$ in ref 9. ^c Product prepared using $C_{10}D_8$. ^d Lit. mp 182 °C (ref 10). ^e The ³¹P spectrum shows this to be a mixture of cis and trans isomers.

Results and Discussion

Characterization of Complexes from $MCl_2(dmpe)_2$ Reductions. Reductions of $MCl_2(dmpe)_2$ complexes ($M = Ru, Os$) by sodium naphthylenide in THF gave one compound in each case; with $M = Fe$, two products were formed. Selected physical properties of the compounds are given in Table I. The IR spectra of the three naphthyl hydride complexes are very similar, except for a broad band in the 1700–1900- cm^{-1} region assigned to ν_{MH} and confirmed, in the case of ν_{FeD} , by the expected isotopic shift. The red-orange iron complex, $Fe_2(dmpe)_5$, does not show hydride or naphthalenide bands in the IR (Np gives sharp bands near 735 and 815 cm^{-1}),⁹ nor are any resonances except those of dmpe found in the ¹H NMR spectrum. The complex is characterized as **1** by an AB_4 ³¹P{¹H}



NMR spectrum¹⁵ and the fact that it can be formed by adding 1 equiv of dmpe to 2 equiv of $HFeNp(dmpe)_2$. The reactions



can be followed with time by ³¹P{¹H} NMR. The initial adduct, $Fe(dmpe)_3$, has resonances at -60.4 (doublet, $J_{PP} = 10$ Hz),

-10.2 (doublet of quartets, $J_{PP} = 10, 20$ Hz), and $+49.8$ ppm (doublet, $J_{PP} = 20$ Hz). These resonances, in a 4:1:1 intensity ratio, are assigned to two bidentate dmpe molecules,¹⁶ and to the coordinated and uncoordinated phosphorus nuclei of a monodentate dmpe. The free end has a chemical shift very close to that of free dmpe ($+49.4$ ppm). As the reaction continues (eq 4), new resonances grow in at -60.4 (doublet, $J_{PP} = 10$ Hz) and -7.2 ppm (quintet, $J_{PP} = 10$ Hz), assigned respectively to the bidentate and bridging dmpe ligands of **1**. $Fe_2(dmpe)_5$ has a melting point (Table I) close to that reported by Chatt and Watson⁹ for $Fe(dmpe)_2$. It reacts rapidly with I_2 , as they reported, to give *trans*- $FeI_2(dmpe)_2$, which we identified by a ³¹P{¹H} NMR singlet at -57.8 ppm.

High-resolution mass spectra of the compounds in Table I gave $M(dmpe)_2^+$ ions [m/e 356 (Fe), 402 (Ru), or 492 (Os)] as the base peak in each case. A parent molecular ion was seen only in the case of the osmium complex and then only weakly [m/e 619 for $HOsNp(dmpe)_2^+$].

Both ³¹P{¹H} and ¹H NMR spectra showed that the ruthenium naphthyl hydride complex was entirely the cis isomer while the osmium compound contained some trans isomer. NMR data¹⁷ are given in Table II; the ³¹P{¹H} spectrum and the 220-MHz ¹H NMR spectrum of the ruthenium complex are shown in Figures 1 and 2. Bonding of the naphthyl group at C₂ was confirmed by analyzing the aromatic proton resonances. The assignment of the seven naphthyl hydrogens can be made on the basis of chemical shifts and coupling constants. Free naphthalene has two types of hydrogen, giving resonances (in C_6D_6) at δ 7.63 (α) and 7.25 (β). Doublets ($J_{HH} = 8$ Hz) at δ 7.81 and 7.76 in Figure 2 can be assigned to $H_{5,8}$,¹⁸ and triplets at δ 7.38 and 7.25 to $H_{6,7}$, on the basis that the ring more distant from the metal should have chemical shifts similar to those of free naphthylene. Low-field resonances at δ 8.35 and 8.24 are assigned to protons ortho to Ru, each coupled to a phosphorus nucleus with $J_{PH} = 4$ Hz. Phosphorus coupling was confirmed by selective decoupling of P_C .¹⁹ [H_3 gives a doublet ($J_{HH} = 8$ Hz) and H_1 a singlet.] Shifts to low field of aromatic protons ortho to metal substituents seem to be general, having also been observed in $[C_6H_5W(CO)_5]$ and $CH_3C(O)C_6H_4Mn(CO)_4$.²⁰ The couplings (8 Hz) of H_3 to H_4 and of H_5 and H_8 to H_6 and H_7 were confirmed by selective homonuclear decoupling experiments.

Selective decoupling of phosphorus while observing the ¹H spectrum shows that the large P–H coupling (90.5 Hz) in the hydride pattern is due to P_D while the three smaller couplings (24.5 Hz) with $P_A, P_B,$ and P_C are accidentally nearly equal

Table II. ³¹P and ¹H NMR Data^a for $HMNp(dmpe)_2$ Complexes

M	Trans isomer	³¹ P NMR										
		P_A	P_B	P_C	P_D	J_{AB}	J_{AC}	J_{AD}	J_{BC}	J_{BD}	J_{CD}	
Fe		-74.2	-73.7	-70.5	-59.8	-53.6	105	27	32	28	18	14
Ru		-45.3	-45.5	-40.1	-33.3	-27.4	281	13	25	13	13	13
Os ^c		-9.3	-7.9	-3.8	+5.0	+7.7	265	~5	~15	~10	~10	~10

M	Isomer	¹ H NMR		
		Hydride	dmpe Me	Aromatic
Fe	Cis	$-13.52 m^d$	d's: 1.52–0.73	H_4 : 7.25 d (8)
	Trans	$-19.56 qu$ (49)	1.35, 1.21 br	7.20 d (8)
Ru	Cis	$-8.54 dq$ (90.5, 24.5)	d's: 1.37–0.91	<i>e</i>
	Trans			
Os	Cis	$-9.21 dq$ (71, 21)	d's: to 0.70	<i>f</i>
	Trans	$-22.43 qu$ (16)	1.57, 1.35 br	

^a In THF- d_8 except for ¹H NMR on Ru and Os in C_6D_6 . Chemical shifts are in parts per million upfield from 85% H_3PO_4 or downfield from Me_4Si . Coupling constants (in parentheses) are in hertz. Abbreviations: d, doublet; q, quartet; qu, quintet; m, multiplet; br, broad. ^b A 1:1:1 triplet at -74.4 ($J_{PD} = 7.5$ Hz) in the complex prepared from $C_{10}D_8$. ^c The resolution was not sufficient to determine $J_{PP}(cis)$ to better than ± 3 Hz. ^d $J_{wings} = 212$ Hz. ^e H_3 , 8.34 dd (8, 3.5); H_1 , 8.24 d (4); $H_{5,8}$, 7.81, 7.76 d (8); H_4 , 7.50 d (8); $H_{6,7}$, 7.38, 7.25 t (7.5). ^f H_3 , 8.47 br d (8); H_1 , 8.38 br; $H_{5,8}$, 7.80, 7.77 d (8); H_4 , 7.47 d (8); $H_{6,7}$, 7.38, 7.26 t (7.5).

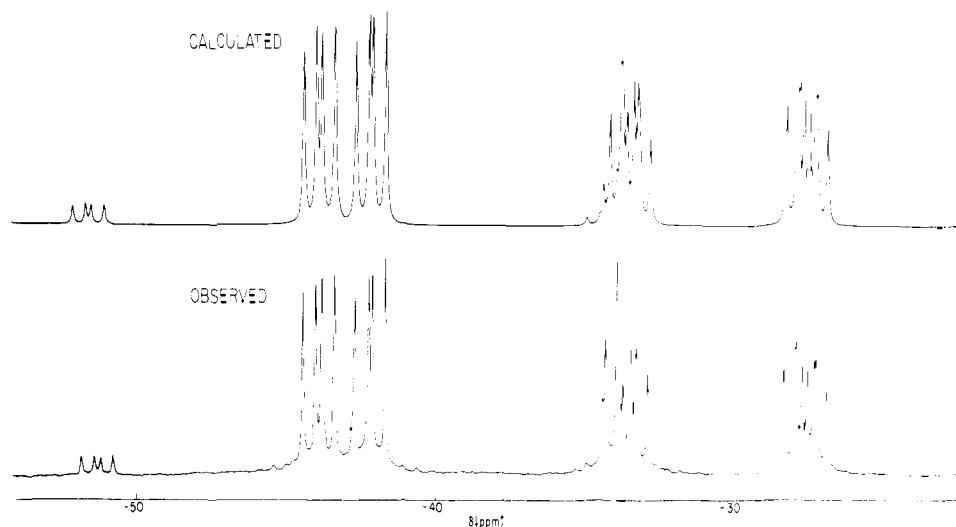


Figure 1. Calculated and observed $^{31}\text{P}\{^1\text{H}\}$ spectra of *cis*-HRuNp(dmpe) $_2$ in THF- d_8 .

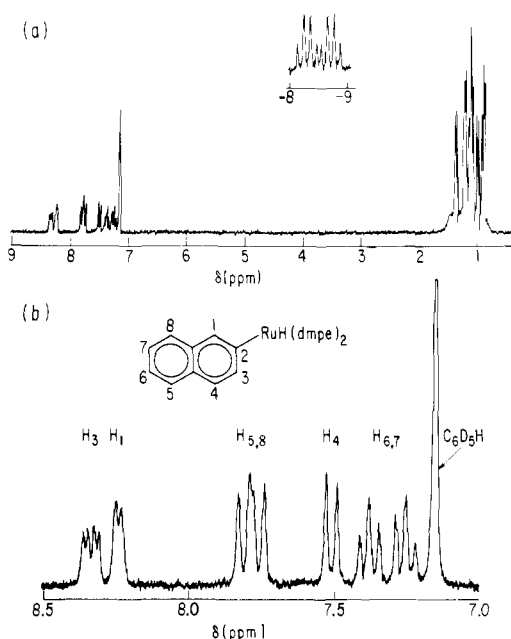
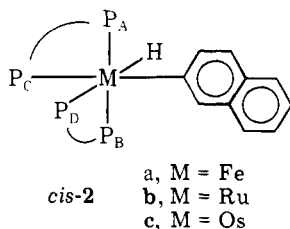


Figure 2. (a) The 220-MHz ^1H NMR spectrum of *cis*-HRuNp(dmpe) $_2$ in C_6D_6 . (b) Expansion of the aromatic region.

(24.5 Hz). Thus the NMR data for solutions of HRuNp(dmpe) $_2$ are consistent with the x-ray crystal structure 11 and permit an assignment of the ^{31}P spectrum as shown below in *cis*-2. 21 It can be seen that the ordering of ^{31}P chem-



ical shifts depends primarily on the ligand trans to the phosphorus nucleus, going to higher field in the sequence $\text{P} < \text{C} < \text{H}$.

NMR spectra of $\text{HONp}(\text{dmpe})_2$ were assigned by analogy to *cis*-2b. $\text{HFeNp}(\text{dmpe})_2$ was more difficult to characterize because with the exception of THF- d_8 it reacts rapidly with the most common NMR solvents (C_6D_6 , acetone- d_6 , tolu-

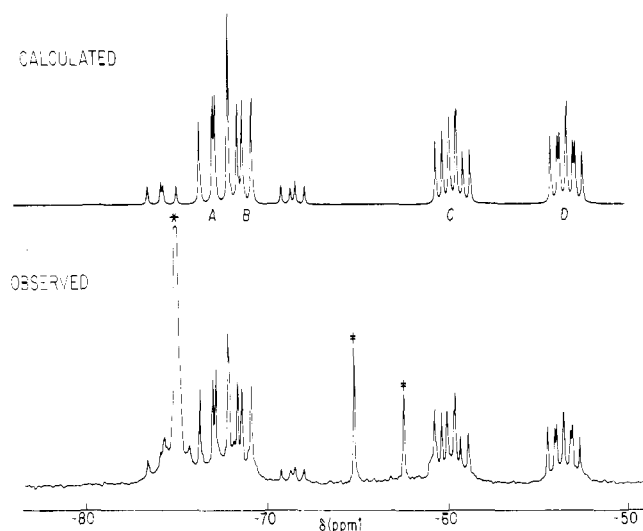
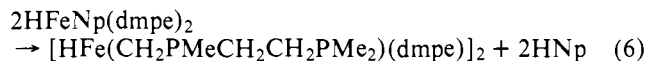


Figure 3. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of an equilibrium mixture of *cis*- and *trans*-HFeNp(dmpe) $_2$ in THF- d_8 : *, trans; †, impurities. The calculated spectrum is for the *cis* isomer.

ene- d_8 , CD_3CN , CDCl_3). 12,13 The complex slowly decomposes, even in THF, with liberation of naphthylene and precipitation of an off-white solid. The IR spectrum of the precipitate in Nujol shows a band at 1845 cm^{-1} assigned to a hydride, and bands characteristic of dmpe. Bands of 2-naphthyl and naphthylene are absent. The precipitate presumably forms by the reaction given in eq 6.



An x-ray study 22 of an analogous ruthenium complex, produced by pyrolysis of HRuNp(dmpe) $_2$, shows it to have structure 3. The off-white solid was too insoluble for NMR studies and has not been examined further.

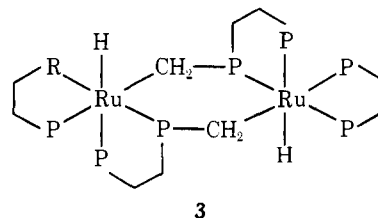
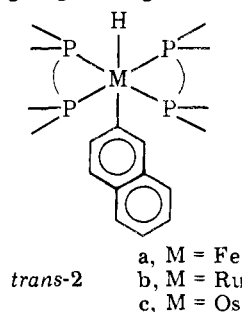


Table III. ^{31}P and ^1H NMR Data^a for $\text{H}_2\text{M}(\text{dmpe})_2$ and $\text{MCl}_2(\text{dmpe})_2$

Complex	^{31}P NMR			^1H NMR	
	P_A	P_B	J_{AB}	dmpe Me	Hydride
<i>cis</i> - $\text{H}_2\text{Fe}(\text{dmpe})_2$ (4a)	-76.0 t	-66.3 t	26.5	1.52, 1.22 br; 1.18, 1.07 d (6)	-14.06 m ^b
<i>cis</i> - $\text{H}_2\text{Ru}(\text{dmpe})_2$ (4b)	-49.6 t	-39.7 t	21	1.62, 1.24 br; 1.35, 1.06 d (6)	-9.56 dq ^c
<i>trans</i> - $\text{FeCl}_2(\text{dmpe})_2$	-58.8 s			1.95 m (14), ^d 1.35 br	
<i>trans</i> - $\text{FeI}_2(\text{dmpe})_2$	-57.8 s				
<i>trans</i> - $\text{RuCl}_2(\text{dmpe})_2$	-41.3 s			1.61 m (16), ^d 1.50 m	
<i>trans</i> - $\text{OsCl}_2(\text{dmpe})_2$	-4.7 s				
dmpe	+49.4 s			1.30 m (8), ^d 0.83 d (1.8)	

^a The solvent was C_6D_6 except for *cis*- $\text{H}_2\text{Fe}(\text{dmpe})_2$, where it was toluene- d_8 . Chemical shifts in parts per million positive upfield from 85% H_3PO_4 for ^{31}P and position downfield from Me_4Si for ^1H . Coupling constants in hertz. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^b The X part of a AA'BB'XX' multiplet. See ref 24. ^c J_{PH} (trans) = 76, J_{PH} (cis) = 24 Hz. ^d These are the dmpe $-\text{CH}_2-$ resonances. Frequencies in parentheses are the wing spacings of the multiplets.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $\text{HFeNp}(\text{dmpe})_2$ in THF- d_8 (Figure 3) shows the ABCD pattern expected for *cis*-**2a** and, in addition, a strong singlet assigned to *trans*-**2a**; if perdeut-



erionaphthylene is used in the reduction, this singlet is replaced by a 1:1:1 triplet ($J_{\text{PD}} = 7.5$ Hz).²³ The presence of a mixture of isomers is confirmed by the ^1H NMR spectrum (Figure 4), which shows a multiplet at $\delta -13.5$ assigned to *cis*-**2a** and a quintet at $\delta -19.5$ assigned to *trans*-**2a**. From the integrated intensities there is ~60% *trans* and ~40% *cis* isomer. The aromatic region is rather complex, since it shows resonances of naphthyl protons in both *cis*- and *trans*-**2a**, in addition to those of free naphthalene (formed by the reaction in eq 6). The pattern of resonances and relative intensities does, however, suggest that doublets ($J = 8$ Hz) at $\delta 7.25$ and 7.20 should be assigned to the H_4 protons of *trans*- and *cis*-**2a**, respectively. Note that the aliphatic region shows a series of doublets ($^2J_{\text{PH}} \sim 5-8$ Hz) in addition to two strong broader lines at $\delta 1.35$ and 1.27 . The doublets are due to the ligand methyl groups in *cis*-**2a**. (The eight methyl groups are inequivalent.) The broader singlets are assigned to the two types of ligand methyl groups in *trans*-**2a**. The aliphatic regions of the 220-MHz ^1H NMR spectra can be used to assign the stereochemistry of this and subsequent complexes. In favorable cases all eight doublets of *cis* complexes are resolved.

While $\text{HFeNp}(\text{dmpe})_2$ gives a facile equilibration of *cis* and *trans* isomers in solution (as judged by observation of their intensity ratio during various reactions), the *cis* Ru and Os complexes require several hours of heating at 65°C to reach isomeric equilibrium. In both cases the *cis* isomer is the more stable (94% *cis* in the case of ruthenium, 75% with osmium) in contrast to the result with iron (40% *cis*).

Reactions with H_2 and D_2 . Complexes **2a** and **2b** react with hydrogen to liberate naphthylene and produce the known dihydrides **4a**²⁴ and **4b**.¹⁰ The iron complex is formed by simply

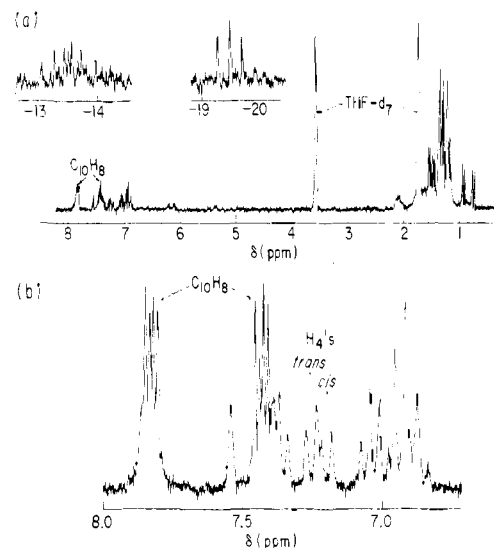
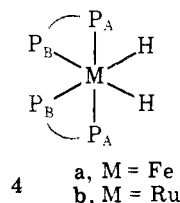


Figure 4. (a) The 220-MHz ^1H NMR spectrum of an equilibrium mixture of *cis*- and *trans*- $\text{HFeNp}(\text{dmpe})_2$ in THF- d_8 . (b) Expansion of the aromatic region.

stirring a toluene- d_8 ²⁵ solution of **2a** under 15 psig H_2 overnight at room temperature; the Ru complex was heated at 65°C . Exclusive *cis* geometries of the products were previously established²⁴ by the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Table III). The latter show clear A_2B_2 spin systems. Off-resonance decoupling experiments, in which the ^{31}P NMR spectra were observed while decoupling only the dmpe protons, show that P_A is more strongly coupled to the hydride proton in **4a**, while P_B is more strongly coupled in **4b**. This is consistent with the ^{31}P assignment indicated in structure **4** [J_{PH} (cis) > J_{PH} (trans) for Fe, and J_{PH} (CIS) < J_{PH} (trans) for Ru]. The assignment of **4** is also consistent with the rule that a P trans to H is at higher field than one trans to P in the same complex.

An interesting feature of the ^1H NMR spectra of the dihydrides is the presence of four ligand methyl resonances: two broad resonances (10 Hz wide) and two doublets with $J = 6$ Hz (see Figure 5). The broad resonances are assigned to protons of the methyl groups on P_A and the doublets to methyl groups on P_B . The broadening is a consequence of virtual coupling involving the strongly coupled *trans*-phosphorus nuclei.

Both **4a** and **4b** show broad bands in the infrared at about 1770 cm^{-1} (Nujol) assigned to ν_{MH} ; this band is missing from the IR spectrum of $\text{D}_2\text{Fe}(\text{dmpe})_2$, while its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows each of the components of P_A [an approximate 1:2:1 triplet in $\text{H}_2\text{Fe}(\text{dmpe})_2$] further split with $J_{\text{PD}} \sim 9$ Hz; deuterium coupling to P_B was not resolved. The ^1H NMR spectrum of $\text{D}_2\text{Fe}(\text{dmpe})_2$ is identical with that of

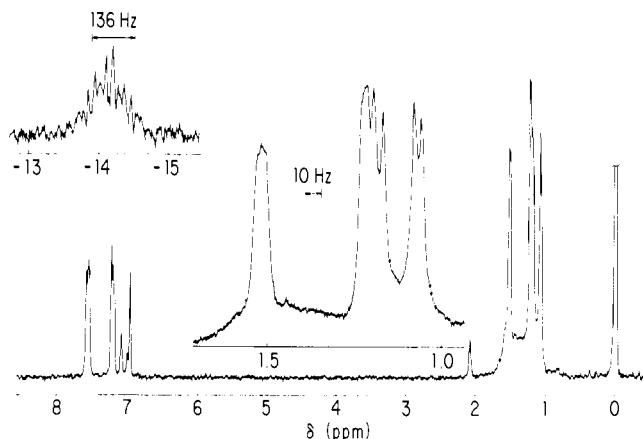
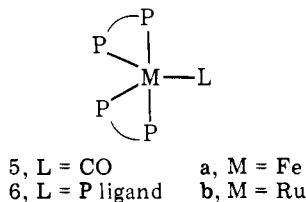


Figure 5. The 220-MHz ^1H NMR spectrum of $\text{H}_2\text{Fe}(\text{dmpe})_2$ in toluene- d_8 . Displaced C_{10}H_8 may be seen in the aromatic region.

$\text{H}_2\text{Fe}(\text{dmpe})_2$, except for the absence of the high-field hydride resonance. This shows that both protons in the dihydride come from H_2 .²⁶ Mass spectra showed $\text{Fe}(\text{dmpe})_2^+$ (m/e 356) as the highest mass.

Reactions with CO. Complex **2a** reacts completely with 15 psig CO in a few hours at room temperature to give $(\text{CO})\text{-Fe}(\text{dmpe})_2$ (**5a**). The complex is characterized by its high-



resolution mass spectrum (m/e 384.0772 vs. 384.0753 calcd), and $^3\text{P}\{^1\text{H}\}$ NMR spectrum (a singlet even at -78°C consistent with rapid intramolecular exchange).²⁷ A very strong IR band at 1812 cm^{-1} (in C_6D_6) is at unusually low frequency for terminal carbonyl [compare 1938 cm^{-1} in $\text{trans}-[(\text{CO})\text{-FeCl}(\text{dmpe})_2]^+$,²⁸ 1908 cm^{-1} in $(\text{CO})\text{Ni}(\text{PEt}_3)_3$,²⁹ and 1864 cm^{-1} in $(\text{CO})\text{W}(\pi\text{-C}_5\text{H}_5)_2$]³⁰ implying a very high electron density on the iron. On standing under CO, higher frequency bands (1878 and 1915 cm^{-1}) gradually grow in and are tentatively assigned to $(\text{CO})_3\text{Fe}(\text{dmpe})$.³¹

Complex **2b** was heated under CO overnight at 60°C to give complete conversion to **5b**. The IR band at 1830 cm^{-1} (in C_6D_6) implies a reduced electron density on the fragment $\text{Ru}(\text{dmpe})_2$ relative to $\text{Fe}(\text{dmpe})_2$.³² Complex **2c** showed no new band in the $1800\text{--}1900\text{-cm}^{-1}$ region even when the solution was heated under 15 psig CO for 18 h at 60°C , followed by 60 h at 75°C . At that point the osmium hydride band was gone but a band assignable to the carbonyl stretch in $(\text{CO})\text{-Os}(\text{dmpe})_2$ was not observed; the product was not characterized.

The kinetics of reaction of **2a** with CO in THF were examined to find the effects of changing CO pressure (1–3 atm) and the concentration of added naphthylene (0–0.3 M). The rate is essentially independent of both variables, consistent with rate-determining loss of HNp in eq 2, followed by rapid capture of $[\text{Fe}(\text{dmpe})_2]$ by CO. The rate constant of $0.020 \pm 0.004\text{ min}^{-1}$ implies a half-life of about 35 min for reductive elimination of naphthylene from $\text{HFeNp}(\text{dmpe})_2$ at 25°C .

Reactions with Phosphorus Ligands. Complex **2a** also reacts in a few hours at 25°C with various phosphorus ligands to form stereochemically nonrigid complexes of type **6**, which show AB_4 $^3\text{P}\{^1\text{H}\}$ NMR spectra. Table IV shows that the resonance

Table IV. ^3P NMR Data^a for $\text{LM}(\text{dmpe})_2$ Complexes

Complex	δ dmpe ^b	δ_L	J_{PP}
$(\text{CO})\text{Fe}(\text{dmpe})_2$ (5a)	-63.7 s		
$(\text{PF}_3)\text{Fe}(\text{dmpe})_2$ ^c	-65.5 d	-133.8 qqu^d	11
$\text{P}(\text{OCH}_2)_3\text{CETe}(\text{dmpe})_2$ ^c	-65.4 br	-135.8 br	<i>e</i>
$\text{P}(\text{OPh})_3\text{Fe}(\text{dmpe})_2$	-64.7 d	-137.6 qu	5
$\text{P}(\text{O-}o\text{-tolyl})_3\text{Fe}(\text{dmpe})_2$	-64.7 d	-134.7 qu	6.5
$\text{P}(\text{OMe})_3\text{Fe}(\text{dmpe})_2$	-62.6 d	-184.0 qu	6
$\text{Fe}_2(\text{dmpe})_5$ (1)	-60.4 d	-7.2 qu	10
$\text{Fe}(\text{dmpe})_3$	-60.4 d	-10.2 m , $+49.8\text{ d}^f$	10, 20 ^f
$\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{PMe}_2\text{Fe}(\text{dmpe})_2$	-60.1 d	-10.2 m , -34.2 d^g	11, 27
$\text{PEt}_3\text{Fe}(\text{dmpe})_2$	-58.7 d	-36.9 qu	5
$(\text{CO})\text{Ru}(\text{dmpe})_2$ (5b)	-39.0 s		
$\text{P}(\text{OMe})_3\text{Ru}(\text{dmpe})_2$ ^h	-44.9 d	-115.0 qu	39
$\text{Ru}_2(\text{dmpe})_5$	-40.6 d	$+3.9\text{ qu}$	12
$\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{PMe}_2$		$+48.5\text{ d}$, -34.6 d^g	37

^a In C_6D_6 unless noted otherwise. Negative chemical shifts are downfield from 85% H_3PO_4 . Coupling constants are in hertz. Abbreviations: s, singlet; d, doublet; q, quartet; qu, quintet; m, multiplet; br, broad. ^b Chemical shift of chelating dmpe. ^c In toluene. ^d Fluorine gave a quartet with $J_{\text{PF}} = 1256\text{ Hz}$. ^e Coupling not resolved. ^f The high-field resonance, assigned to the uncoordinated end of one dmpe, is coupled to the coordinated end by 20 Hz. ^g Assigned to the $\text{Me}_2\text{P}(\text{O})$ end. ^h This was gradually converted on prolonged heating to a second isomer: -38.9 d , -181.5 qu , $J_{\text{AB}} = 35\text{ Hz}$.

of the coordinated dmpe moves to high field as the phosphorus ligand L becomes more electron donating. L can be quite bulky, for example $\text{P}(\text{O-}o\text{-tolyl})_3$, with a ligand cone angle of 141° .³³ This can be contrasted with the attempted preparation of $\text{Fe}(\text{PMe}_3)_5$; apparently five PMe_3 ligands are too crowded,³⁴ and the resulting $\text{Fe}(\text{PMe}_3)_4$ undergoes oxidative addition of the methyl C–H to give the isolated species, $\text{HFe}(\text{CH}_2\text{PMe}_2)(\text{PMe}_3)_3$. Reaction of PPh_3 (cone angle 145°) with **2a** does not give a complex of type **6** but rather $\text{HFe}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{dmpe})_2$, formed by cleavage of one of the aromatic C–H bonds.¹³

The ruthenium complex **2b** also reacts with phosphorus ligands, but requires more forcing conditions. The half-life for the reaction of $\text{P}(\text{OMe})_3$, followed by $^3\text{P}\{^1\text{H}\}$ NMR, is about 5 h at 65°C . With prolonged heating, $\text{P}(\text{OMe})_3\text{Ru}(\text{dmpe})_2$ is slowly converted to a more stable complex with a new AB_4 ^3P NMR pattern, possibly $\text{trans-HRuCH}_2\text{P}(\text{O})(\text{OMe})_2(\text{dmpe})_2$. (This formulation is supported by a weak hydride multiplet at $\delta -11.86$.) PPh_3 and dmpe also react with **2b** on heating, but the reactions were complex and were not fully characterized.

Reactions with Olefins. Ethylene reacts with **2a** to form a complex³⁵ with very broad features in its ^1H or $^3\text{P}\{^1\text{H}\}$ NMR spectra at 25°C . Sharp spectra can be obtained at other temperatures; Figure 6 shows spectra near the limits of slow (-25°C) and fast (80°C) exchange. The assignment of the quintet at $\delta 0.59$ in the fast exchange spectrum to the coordinated ethylene in $(\text{C}_2\text{H}_4)\text{Fe}(\text{dmpe})_2$ is consistent with the integration. The quintet structure arises from the apparent equivalence on the NMR time scale of the four phosphorus nuclei ($J_{\text{PH}} = 4.1\text{ Hz}$). The quintet collapses to a singlet with ^3P noise decoupling. The retention of P–H coupling at 80°C shows that the dynamic process is intra- rather than intermolecular. Cooling to -25°C freezes out the motion to give four types of ligand methyl resonances (as expected for a static C_2 structure), and two types of olefinic hydrogen. The resonances at $\delta 0.44$ and 0.80 are the A and B parts of an $\text{AA}'\text{BB}'$ (nearly A_2B_2) pattern ($J_{\text{AB}} = 8.2\text{ Hz}$), additionally coupled to the phosphorus nuclei ($J_{\text{PH}} = 4.2\text{ Hz}$). The origin of the inequivalence of H_A and H_B can be seen by reference to structure **7**.

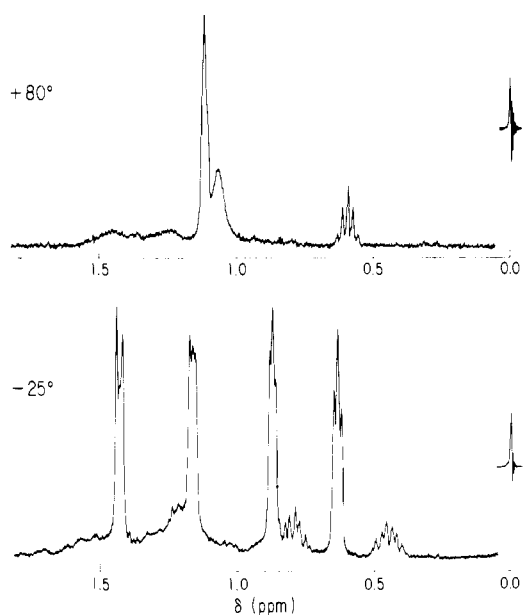
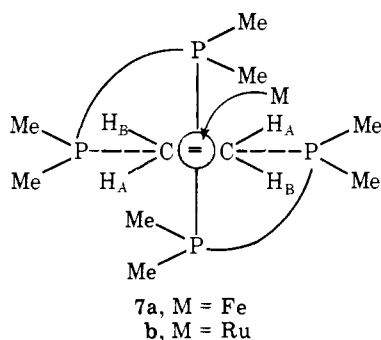


Figure 6. The 220-MHz ^1H NMR spectra of $(\text{C}_2\text{H}_4)\text{Fe}(\text{dmpe})_2$ in toluene- d_8 at 80 and $-25\text{ }^\circ\text{C}$.



It should be noted that the exchange process involves a 90° rotation of the olefin; 180° rotation does not exchange the four phosphorus nuclei.

The δ 0.59 resonance (at $80\text{ }^\circ\text{C}$) of complex **7a** is the highest field shift reported to date for a transition metal ethylene complex,³⁶ again consistent with a very high electron density on the metal. The resonance in the Ru complex **7b** is to lower field (δ 0.77 at $80\text{ }^\circ\text{C}$). The barrier to intramolecular exchange is higher for **7b** than for **7a**; four types of ligand methyl appear at $25\text{ }^\circ\text{C}$ and the fast exchange limiting spectrum is not achieved by $80\text{ }^\circ\text{C}$. Higher barriers to rotation in (olefin)-Ru(CO)₄ than in (olefin)Fe(CO)₄ (olefin = ethyl acrylate or diethyl fumarate) have been reported by Takats and co-workers.³⁷

Other types of olefin complexes can also be prepared from

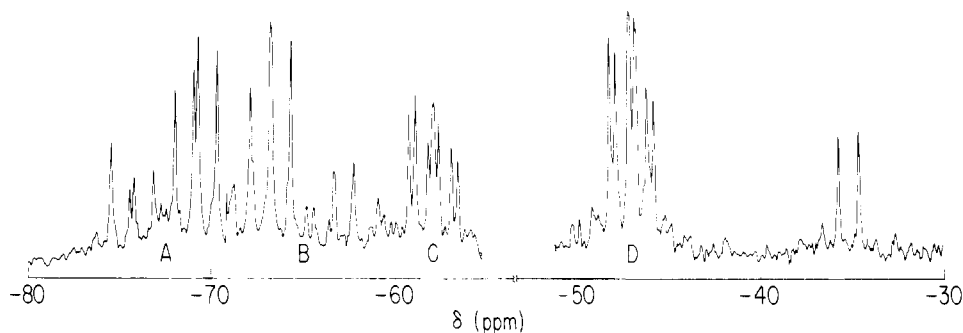
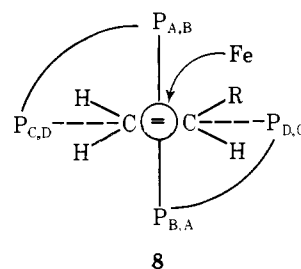


Figure 7. The $^{31}\text{P}\{^1\text{H}\}$ spectrum of $(\text{styrene})\text{Fe}(\text{dmpe})_2$ in toluene- d_8 at $-50\text{ }^\circ\text{C}$. The right-hand portion has a higher vertical expansion (1.5 \times) than the left. The doublet ($J_{\text{PP}} = 37$) at -35.8 is due to the $\text{Me}_2\text{P}(\text{O})$ end of a $\text{Me}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{PMe}_2$ impurity; the unoxidized end at $+48.5$ is not shown.

2a. While *cis*-2-butene does not displace naphthylene, propylene and 1-butene do form $(\text{olefin})\text{Fe}(\text{dmpe})_2$ complexes. Their low-temperature limit ^1H NMR spectra show eight types of ligand methyl and their high-temperature spectra show four, in accord with structure **8**. There was no evidence for olefin isomerization in the solution containing 1-butene. This is in contrast to the facile isomerization observed by Schroeder and Wrighton³⁸ in a photocatalyzed reaction using $\text{Fe}(\text{CO})_5$, and supports their idea that a CO must be lost from (1-butene)- $\text{Fe}(\text{CO})_4$ before an oxidative addition to give a π -allyl hydride can occur. In the present case, the two dmpe ligands and the olefin gave a coordinatively saturated system.³⁹

Styrene gives an olefin complex instead of cleaving a C-H bond. The ortho, meta, and para protons in the complex appear as well-resolved resonances in a 2:2:1 ratio at δ 7.53 d (8), 7.16 t (8), and 6.96 t (8).⁴⁰ In accord with the formulation as an olefin complex of Fe(0), the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the expected stereochemical nonrigidity—a feature not observed for Fe(II) complexes. Figure 7 shows the low-temperature limit ^{31}P NMR spectrum. The major resonances form an ABCD pattern, as expected for structure **8**. At $80\text{ }^\circ\text{C}$ the



spectrum simplifies to an A_2B_2 pattern, with spectral parameters similar to those of $(\text{C}_2\text{H}_4)\text{Fe}(\text{dmpe})_2$ at low temperatures (Table V).

The activated olefins, methyl acrylate and acrylonitrile, also give olefin complexes, the former nearly stereochemically rigid at $25\text{ }^\circ\text{C}$ and the latter completely so. The ordering of rotational barriers $\text{R} = \text{CH}_3 < \text{H} < \text{COOMe} < \text{CN}$ is in qualitative agreement with the expected strengths of the olefin-metal bonds,⁴¹ on the basis of equilibrium⁴² and calorimetric⁴³ studies on Ni(0) complexes. Methacrylonitrile gives a stereochemically nonrigid olefin complex; the much lower barrier to intramolecular exchange relative to the acrylonitrile is consistent with weakening of the metal-olefin bond by replacing an α hydrogen with a methyl group. The CN stretching frequency of 2155 cm^{-1} (in C_6D_6) is, however, very similar to that in the acrylonitrile complex. Observation of separate sharp bound and free methacrylonitrile CH_3 resonances at δ 1.57 and 1.18 in the ^1H NMR spectrum shows that intermolecular exchange is slow.

Comparison of IR stretching frequencies (Table VI) shows the increased π back-bonding of metal fragments in the se-

Table V. ^{31}P NMR Data^a for Selected Olefin, Acetylene, and Azobenzene Complexes

Compd	P _A	P _B	P _C	P _D	J _{AB}	J _{AC}	J _{AD}	J _{BC}	J _{BD}	J _{CD}	Temp, °C
(C ₂ H ₄)Fe(dmpe) ₂ (7a)	-73.1 t	-58.3 t			47						-25
(C ₂ H ₃ Ph)Fe(dmpe) ₂ (8)	-64.7 t	-55.2 t			42						80
(PhCCPh)Fe(dmpe) ₂ (11)	-68.8 t	-58.9 t			37						25
(PhNNPh)Fe(dmpe) ₂ (12)	-63.3 t	-56.0 t			34						25
(C ₂ H ₄)Ru(dmpe) ₂ (7b)	-42.8 t	-36.1 t			30						-25

^a In toluene-*d*₈ for temperatures listed as other than 25 °C; 25 °C spectra are in C₆D₆.

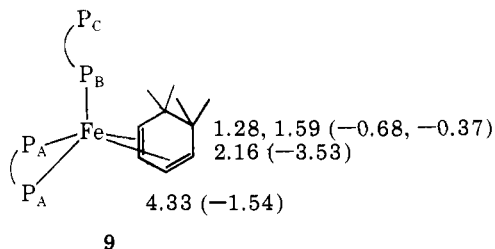
quence Fe(CO)₄ < Ni[P(O-*o*-tolyl)₃]₃ < Ru(dmpe)₂ ≲ Fe(dmpe)₂. Note that the ligands on iron can markedly affect its back-bonding ability.

Fumaritrile gives a complex, with bands at 2178 and 2142 cm⁻¹, which gradually isomerizes on standing to one with bands at 2195 and 2063 cm⁻¹. The former is tentatively assigned to an olefin complex. The low CN stretching frequency in the latter suggests a cyanovinyl Fe(II) cyanide complex.

The reaction of TCNE with **2a** occurs immediately upon mixing, in contrast to the much slower reactions of other olefins, and suggests a different mechanism. It is likely that, as a first step, a one-electron oxidation occurs to give TCNE^{-•} and HFeNp(dmpe)₂⁺, followed by rapid loss of HNp from the latter. The ESR spectrum of TCNE^{-•} has been observed in this reaction.⁴⁴ TCNE^{-•} has also been observed in the reaction of TCNE with *cis*-Mo(CO)₂(dmpe)₂.⁴⁵ Green radical cations Fe(CO)₃L₂⁺ have been produced by reversible one-electron oxidations of Fe(CO)₃L₂.⁴⁶ The dark green tetrahydrofuran solution displays bands at 2185, 2145, and 2080 cm⁻¹ which may be attributable to TCNE^{-•}. We cannot rule out structures similar to those observed by Connor⁴⁷ in *cis*-[C₂(CN)₃-Mo(CO)₂(dmpe)₂]CN (2210 w, 2170 m, 2160 m, 2082 vs cm⁻¹), in the reaction of TCNE with *cis*-Mo(CO)₂(dmpe)₂, or by Rettig in the N-bonded π-C₅H₅VBr·TCNE (2211 w, 2192 s, 2152 s, 2128 m cm⁻¹).⁴⁸

Reactions with Butadiene, 1,3-Cyclohexadiene, and Anthracene. 1,3-Butadiene forms a dihapto olefin complex analogous to the complex of 1-butene. Figure 8 shows the protons of the uncoordinated end of the diene,⁴⁹ along with free butadiene in solution. The mean coordination chemical shift of 1.0 ppm can be compared with the much larger 4.6 ppm of the coordinated olefinic hydrogens in (C₂H₄)Fe(dmpe)₂. Only H_B (the proton closest to Fe) shows a resolved P-H coupling (1.7 Hz). Formation of a dihapto complex might at first appear surprising, in view of the well-known stability of tetrahapto 1,3-diene complexes of Fe(0). The second C-C double bond appears unable to overcome the chelating effect of the bidentate dmpe. Heating at 80 °C in an attempt to chelate the butadiene causes thermal decomposition of the complex. The analogous (η²-butadiene)Fe(CO)₄ is known.^{50a}

A tetrahapto 1,3-diene complex is, however, formed in the reaction of 1,3-cyclohexadiene with **2a**. The NMR data are in accord with structure **9**, which shows chemical shifts and

**9**

coordination chemical shifts ($\Delta\delta$) in parentheses. A square pyramidal coordination is assumed by analogy with the x-ray structure of (1,3-butadiene)Fe(CO)₃.^{50b} The proton chemical shifts in (1,3-cyclohexadiene)Fe(CO)₃ for comparison with

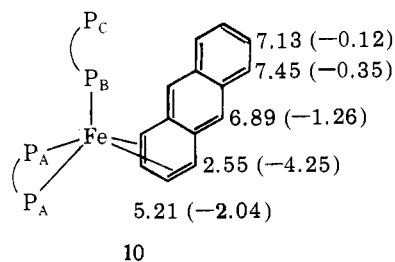
Table VI. Selected IR Stretching Frequencies^a (cm⁻¹) of ν_{CO} or ν_{CN} in Olefin Complexes

Complex	ν_{CO} or ν_{CN}	Solvent
(C ₂ H ₃ COOMe)Ni[P(O- <i>o</i> -tolyl) ₃] ₂	1714	CH ₂ Cl ₂
(C ₂ H ₃ COOMe)Fe(dmpe) ₂	1669 w, 1648 m	Nujol
(C ₂ H ₃ CN)Fe(CO) ₄	2210 ^b	
(C ₂ H ₃ CN)Ni[P(O- <i>o</i> -tolyl) ₃] ₂	2194	CH ₂ Cl ₂
(C ₂ H ₃ CN)Ru(dmpe) ₂	2159	THF
(C ₂ H ₃ CN)Fe(dmpe) ₂	2156	THF
(<i>trans</i> -NCC ₂ H ₂ CN)Ni[P(O- <i>o</i> -tolyl) ₃] ₂	2210	CH ₂ Cl ₂
(<i>trans</i> -NCC ₂ H ₂ CN)Fe(dmpe) ₂	2178, 2142 2195, 2063 ^c	THF

^a Values for nickel complexes are from ref 42. ^b S. F. A. Kettle and L. E. Orgel, *Chem. Ind. (London)*, 49 (1960). ^c These bands, attributed to a cyanovinyl cyanide isomer, grew in more slowly than the first two, which are attributed to a C=C bonded isomer.

9 are δ 5.22, 3.14, and 1.63 (2:2:4 ratio).^{50c} The larger negatives $\Delta\delta$'s in **9** are consistent with better electron donation by phosphine than by CO. Three types of phosphorus nuclei are shown by the ^{31}P NMR spectrum, with resonances in a 2:1:1 ratio at -63.8, -38.3, and +49.3 ppm ($J_{\text{BC}} = 22$ Hz).

Though most arenes react with **2a** by cleavage of sp² C-H bonds,¹³ anthracene is exceptional in giving the tetrahapto Fe(0) complex **10**. The ^1H NMR spectrum shows five reso-

**10**

nances of equal intensity. Those at δ 7.13 and 7.45 have the characteristic 1:1:1 quartet pattern ($J = 3.1$ Hz) of the outer ring protons of free anthracene and the smallest $\Delta\delta$. They are assigned to the most distant protons in **10**. The resonance at δ 6.89 is a singlet with intermediate $\Delta\delta$ and is identified with the central protons. The resonances at highest field (δ 5.21 and 2.55) have the most negative values of $\Delta\delta$, suggesting their proximity to Fe; both appear as broad bands (13 Hz wide) because of unresolved P-H coupling. Structure **10** is supported by the ^{31}P NMR spectrum, with resonances in a 2:1:1 ratio at -63.4, -26.7, and +49.0 ppm ($J_{\text{BC}} = 20$ Hz). Compound **10** has an unusual deep red color, presumably because of the extended π system. In contrast to the behavior of **2a** with anthracene, the Ru complex **2b** gives the more usual C-H bond cleavage product.¹³

Reactions with Disubstituted Acetylenes and Azobenzene. Diphenylacetylene forms a stereochemically rigid complex **11** whose $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows an A₂B₂ pattern even at 25 °C. The infrared spectrum shows a band assigned to the

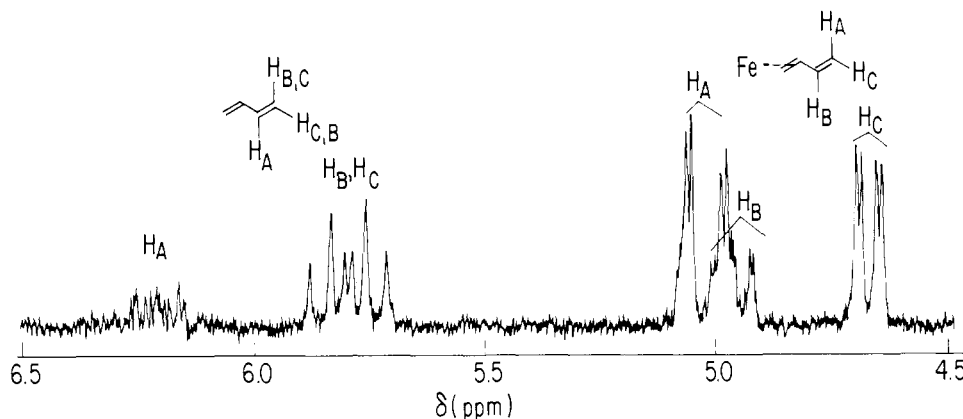
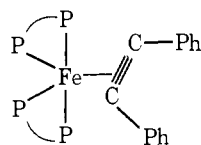


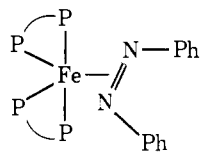
Figure 8. A portion of the 220-MHz ^1H NMR spectrum of $(\text{C}_4\text{H}_6)\text{Fe}(\text{dmpe})_2$ in toluene- d_8 , showing free butadiene and the free end of butadiene in the complex. For the latter $J_{\text{AB}} = 16.5$, $J_{\text{AC}} = 2.5$, $J_{\text{BC}} = 9.5$, $J_{\text{BP}} = 1.7$ Hz.



11

carbon-carbon bond stretch at 1720 cm^{-1} , some 502 cm^{-1} lower than in the free acetylene, an exceptionally large shift to lower frequency.⁵¹ A complex analogous to **11** does not form with di(*tert*-butyl)acetylene, presumably for steric reasons. Monosubstituted acetylenes (and acetylene itself) react with **2a** with cleavage of the sp C-H bond.¹²

Azobenzene forms a stereochemically rigid complex **12**. The



12

structure is indicated by the A_2B_2 ^{31}P NMR pattern (Table V), and by the presence of four ligand methyl resonances (δ 1.52, 1.09, 0.60, and 0.55) in the ^1H NMR spectrum. Stronger π bonding of azobenzene and of diphenylacetylene than of unactivated olefins is expected on the basis of results on $\text{Ni}(0)$.⁴³ Though **12** is not very soluble in C_6D_6 , its IR spectrum shows a medium band at 1240 cm^{-1} not present in the spectrum of azobenzene. This is tentatively assigned to one of the three stretching vibrations of the three-membered FeN_2 ring. $(\text{PhN}_2\text{Ph})\text{Ni}[\text{P}(o\text{-tolyl})_3]_2$ shows an analogous band at 1245 cm^{-1} .⁵² A symmetrical N-bonded structure for the Ni complex has been established by an x-ray crystal structure.⁵³

Experimental Section

$^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded in the FT mode using 10-mm tubes on a Bruker HFX-90 spectrometer with a Digilab FTS/NMR-3 data system. The deuterium in the C_6D_6 or toluene- d_8 solvent was used to provide an internal lock. ^{31}P chemical shifts are in parts per million (positive upfield) from external 85% H_3PO_4 .

^1H NMR spectra were normally recorded in CW mode in 5-mm tubes on a Varian HRS-1X-VFT 220/300 spectrometer. Weak hydride signals were enhanced by signal averaging with a Varian SS100 data system. A Varian XL-100 spectrometer was also used, particularly in heteronuclear $^1\text{H}\{^{31}\text{P}\}$ and homonuclear decoupling experiments. ^1H chemical shifts δ are in parts per million (positive downfield) from internal tetramethylsilane (Me_4Si).

Infrared spectra were recorded using a 0.1-mm NaCl Barnes Engineering microcell in a Perkin-Elmer 221 spectrometer, and calibrated with CO gas (2143 cm^{-1}). High-resolution mass spectra (HRMS) were recorded on a CEC 21-110B mass spectrometer with

a heated direct introduction source, and calibrated with perfluorokerosene. Chemical purities of reaction products were ascertained by spectroscopic techniques; analyses were not obtained.

All manipulations were carried out in a dry nitrogen atmosphere. dmpe ,⁵⁷ $\text{FeCl}_2(\text{dmpe})_2$,⁵⁸ $\text{HRuNp}(\text{dmpe})_2$,¹⁰ and $\text{HONp}(\text{dmpe})_2$ ¹¹ were prepared by literature techniques. All ligands other than dmpe are commercial samples and were used as received. Tetrahydrofuran was distilled from sodium/benzophenone under argon; other solvents were dried over molecular sieves and purged with nitrogen.

Preparation of $\text{HFeNp}(\text{dmpe})_2$. Under an inert atmosphere, *trans*- $\text{FeCl}_2(\text{dmpe})_2$ (6 g, 14.1 mmol) was dissolved in THF. The green solution was stirred while a THF solution of the dark green sodium naphthalenide (28.2 mmol) was added dropwise. The dark green color was discharged after each drop. The color of the solution changed from green to orange and then started to darken. When addition was complete, the solution was taken to dryness under vacuum. Repeated pentane extraction of the solids followed by reduction of the filtrate resulted in a yellow-orange powder which was collected by vacuum filtration. The product was washed with cold pentane and dried *in vacuo*, yield up to 40% (see next preparation).

Preparation of $[\text{Fe}(\text{dmpe})_2]_2\text{-}\mu\text{-dmpe}$. The filtrate from the preceding section contains a mixture of $\text{Fe}_2(\text{dmpe})_5$, $\text{HFeNp}(\text{dmpe})_2$, and naphthalene. It was treated with dmpe (2 mL) and stirred for at least 1 h. It was then stripped to dryness and the naphthalene removed by sublimation. The residue was extracted with pentane, filtered through a small quantity of alumina, and reduced in volume. Cooling resulted in formation of a red-orange product which was collected by vacuum filtration and dried under vacuum, yield up to 40% (based on the starting complex in the previous preparation). Total isolated yield for the two products was as high as 73%.

Preparation of $\text{DFe}(\text{C}_{10}\text{D}_7)(\text{dmpe})_2$. This compound was prepared using the same procedure as for the nondeuterated complex, using $\text{FeCl}_2(\text{dmpe})_2$ (1.00 g, 2.34 mmol) and C_{10}D_8 (0.64 g, 4.68 mmol). Workup was the same. The ^1H NMR spectrum had no hydride or aromatic resonances; the dmpe resonances were the same as in the nondeuterated complex.

Reactions

Typically 0.1 mmol of $\text{HMNp}(\text{dmpe})_2$ in a small test tube was treated with 0.15 mmol of reactant in 0.8 mL of C_6D_6 . Reactions with gases were normally carried out in a thick-walled 4×1 in. glass tube connected by an O-ring seal to a pressure gauge and needle valve. After most of the N_2 was removed with a pump, the tube was charged with gas to a pressure of 15 psig, while the solution was stirred with a small magnetic stirring bar coated with Teflon fluorocarbon resin. In the case of 1-butene, a serum cap was wired to a test tube containing the Fe complex in toluene- d_8 . After the tube was frozen in liquid N_2 and evacuated via a hypodermic syringe needle, 7.5 mL (0.3 mmol) of 1-butene gas was added with a syringe. The tube was warmed to room temperature, shaken, and then allowed to stand. To prevent loss of butene, the solution was chilled to $-30\text{ }^\circ\text{C}$ before transferring to a chilled 5-mm tube.

Table VII. Rates of Reaction of HFeNp(dmpe)₂ with CO in THF at 25.0 °C

[HFeNp(dmpe) ₂] ₀		[HNp] added.		<i>k</i> , min ⁻¹
M	<i>P</i> _{CO} , atm	M		
0.04	1.0	0.0		0.016
0.02	1.0	0.0		0.020
0.02	1.0	0.1		0.014
0.02	1.0	0.3		0.027
0.02	2.0	0.0		0.020
0.02	2.0	0.1		0.020
0.02	3.0	0.3		0.027
0.02	3.0	0.3		0.016
				0.020 ± 0.004

Reactions were usually allowed to proceed overnight at room temperature (Fe), 60 °C (Ru), or 75 °C (Os). Solutions containing Fe usually gave a little solid precipitate on standing and were filtered before running ¹H NMR spectra. For ³¹P NMR spectra the same solutions were washed into 10-mm tubes with 1 mL of fresh solvent. IR spectra were run on these solutions or after stripping the NMR solvent and redissolving part of the residue in THF or mulling it in Nujol. These residues were also used for mass spectra.

Kinetics of Reaction of CO with HFeNp(dmpe)₂. Reactions were carried out in magnetically stirred 25-mL reactors. A jacketed glass reactor for low-pressure runs was maintained at 25.0 °C by circulating water from a Forma constant temperature bath. A steel reactor for runs at 3 atm was immersed in a constant temperature oil bath. The reactors were loaded in a Vacuum Atmospheres drybox under N₂ with HFeNp(dmpe)₂ and HNp (if present). The reactor was removed from the drybox, evacuated, and filled with CO to a final pressure of 1.0, 2.0, or 3.0 atm. At *t* = 0, deoxygenated THF was added by syringe through a side arm septum. Small samples (25 μL) of solution were removed by syringe from time to time and injected into a N₂-flushed Barnes Engineering 0.1-mm NaCl microcell. IR spectra were quickly recorded over the range 2000–1600 cm⁻¹, and calibrated with polystyrene (1601 cm⁻¹). Rate constants were taken from semilogarithmic plots of *A*_∞(1824) – *A*(1824), which were linear over 3 half-lives. The results are summarized in Table VII.

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Molybdenum Enzyme Model Studies. Synthesis and Structure of the Oxo-Bridged Binuclear Complex, μ -Oxo-bis[oxo(2,2'-methyliminodiethanethiolato)molybdenum(V)], $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$

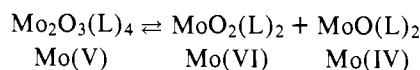
Ying-Yen P. Tsao,^{1a} Charles J. Fritchie, Jr.,* ^{1a} and Henri A. Levy^{1b}

Contribution from the Percival Stern Chemical Laboratories, Tulane University, New Orleans, Louisiana 70118, and the Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830. Received November 21, 1977

Abstract: The complex μ -oxo-bis[oxo(2,2'-methyliminodiethanethiolato)molybdenum(V)], $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$, has been synthesized and its crystal structure has been determined from three-dimensional x-ray diffractometer data. The crystals are monoclinic, space group $P2_1/c$, with four molecules in a cell having parameters $a = 14.849$ (2), $b = 7.956$ (2), $c = 15.861$ (2) Å, $\beta = 90.97$ (2)°, and $Z = 4$. Full-matrix least-squares refinement using 1488 observed and 54 unobserved intensities (Mo $K\alpha$ radiation) has yielded a conventional R factor of 0.049. The asymmetric unit consists of halves of two independent molecules of $\text{Mo}_2\text{O}_3[\text{NCH}_3(\text{C}_2\text{H}_4\text{S})_2]_2$ located on crystallographic centers of symmetry. Disorder of the three carbons around each nitrogen atom, representing alternate conformations of the chelate rings, has been found. The configuration of the molecule is that of two distorted trigonal bipyramids centrosymmetrically connected through the central, bridging oxygen. The terminal oxygen and two sulfur atoms of each half molecule form a trigonal plane, and the nitrogen atom is trans to the bridging oxygen atom. The average Mo-O(terminal), Mo-O(bridge), Mo-N, and Mo-S bond distances are 1.667 (8), 1.858 (1), 2.233 (10), and 2.346 (3) Å, respectively. This is the first known five-coordinate complex of the $\text{Mo}_2\text{O}_3^{4+}$ unit with a ligand containing sulfur.

Although molybdoenzymes have been widely studied, the detailed catalytic mechanisms and three-dimensional structures around their active sites are still not well understood because of their complexity. Research on the coordination chemistry of molybdenum-sulfur complexes has been stimulated by evidence that redox reactions which are catalyzed by molybdoenzymes occur at sites where the molybdenum is coordinated by one or more sulfur atoms.^{2a} A basic group, presumably a nitrogen atom, but possibly oxygen, is proposed to coordinate to the molybdenum in xanthine oxidase.² Recent x-ray absorption edge spectra of the molybdenum-iron component of nitrogenase and of some model compounds imply the presence of Mo(V) coordinated with at least one cysteine sulfur ligand.^{3,36} However, the existing Mo(V) complexes containing cysteine or its ester are di- μ -oxo or di- μ -sulfido dimers⁴⁻⁷ with short Mo-Mo distances (~ 2.56 and ~ 2.81 Å, respectively) which suggest a direct metal-metal bond.^{8,9} The existence of this direct metal-metal interaction is unlikely in enzyme systems;^{2a} there is in fact no evidence that enzyme active sites contain more than one molybdenum atom, although all the known model complexes are binuclear.

Several μ -oxo dimers¹⁰⁻¹³ which contain the $\text{Mo}_2\text{O}_3^{4+}$ unit have been postulated as possible models because of the following disproportionation^{14,15} reaction:



where $\text{L} = (\text{RO})_2\text{PS}_2^-$, and R_2NCS_2^- . However, these ligands do not closely resemble cysteine. This led us to synthesize and study a series of Mo complexes containing aminothiols tridentate and tetradentate ligands which have an S:N mole ratio of

2 or 3. Here we first report the synthesis and structure of a five-coordinate $\text{Mo}_2\text{O}_3\text{L}_2$ complex which contains Mo(V) in a configuration not previously observed.

Experimental Section

Synthesis. 2,2'-(Methylimino)diethanethiol, $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{SH})_2$, was synthesized by using the known procedure.¹⁶ Under nitrogen atmosphere the following reactions were carried out: 2 mL of acetic acid was added to 0.716 g (2.96 mmol) of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ dissolved in 15 mL of water. This solution was added slowly to a solution of 0.5 mL (3.48 mmol) of $\text{CH}_3\text{N}(\text{C}_2\text{H}_4\text{SH})_2$ in 10 mL of ethanol. Impure product in about 50% yield precipitated as a deep brown powder within a few minutes. The yellow filtrate deposited small additional amounts of analytically pure product over a few days. The solid was dissolved in a minimum amount of dimethyl sulfoxide. After 4 days of liquid diffusion of absolute ethanol into this solution, deep brown prismatic crystals were obtained. Anal. Calcd for $\text{C}_{10}\text{H}_{22}\text{Mo}_2\text{N}_2\text{O}_3\text{S}_4$: C, 22.31; H, 4.12; N, 5.20. Found: C, 22.35; H, 4.20; N, 5.09.

The complex is moderately air stable as the solid; it is insoluble except sparingly and with slow decomposition in dimethyl sulfoxide, dimethylformamide, and hexamethylphosphoramide. IR bands (KBr) at 945 (s) and 746 cm^{-1} (m) are attributed to $\nu_{\text{Mo}=\text{O}}$ and $\nu_{\text{Mo}-\text{O}-\text{Mo}}$, respectively.

Collection and Reduction of the X-Ray Data. On the basis of Weissenberg photographs, the crystals were assigned to the monoclinic system. The observed systematic absences are $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, which suggest that the space group is $P2_1/c$. A specimen with dimensions of $0.12 \times 0.21 \times 0.09$ mm along a , b , and c , respectively, was mounted in a glass capillary with the b axis approximately along the ϕ axis of the goniometer. A computer-controlled Picker x-ray diffractometer equipped with a scintillation-counter detector was used with filtered, Mo $K\alpha$ radiation to obtain intensity data and for measurement of angles for precise determination of the unit-cell dimensions. The cell parameters obtained by the least-squares