# Comparison of the Molecular Structures and Solution Stereodynamics of (diene)Fe(CO)₂L Complexes (L = CO, PPh₃, P(OMe)₃, PMe₃, NMe₃, Pyridine, CNMe)

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Several (diene)Fe(CO)₂L complexes (**1b**–**g**) of methyl 5-formyl-2,4-pentadienoate have been structurally characterized in solution and the solid state. Crystal structures of **1e,f** (L = NMe₃, PMe₃) allow a direct stereochemical comparison of NMe₃ and PMe₃ ligands in otherwise isostructural compounds. In solution, complex **1d** (L = pyridine) undergoes differential rates of axial/basal and basal/basal exchange which are not observed with the phosphite or isonitrile complexes (**1c,g**). A theoretical interpretation of this phenomenon is presented. Crystal structure data: **1d**, monoclinic, space group $P2_1/n$, $a = 8.417(1)$ Å, $b = 9.147(2)$ Å, $c = 19.235(3)$ Å, $\beta = 98.84(2)°$, $Z = 4$, $R_w = 0.041$ for 191 parameters using 2575 observed reflections; **1e**, monoclinic, space group $P2_1/n$, $a = 15.167(4)$ Å, $b = 8.048(3)$ Å, $c = 26.334(9)$ Å, $Z = 8$, $R_w = 0.082$ for 344 parameters using 2691 observed reflections; **1f**, triclinic, space group $P\bar{1}$, $a = 7.984(1)$ Å, $b = 12.439(2)$ Å, $c = 16.249(3)$ Å, $\alpha = 110.85(2)°$, $\beta = 90.48(2)°$, $\gamma = 101.13(2)°$, $Z = 4$, $R_w = 0.062$ for 341 parameters using 2468 observed reflections.

## Introduction

Cyclic and acyclic (diene)Fe(CO)₃ complexes continue to attract attention as intermediates, particularly for asymmetric synthesis.[1] The ease of preparation of the related (diene)Fe(CO)₂L derivatives also makes these complexes attractive candidates due to their enhanced or altered reactivity relative to the tricarbonyl.[2] Hence, structural and stereodynamic studies have mainly been confined to the tricarbonyls and their phosphine- and phosphite-substituted derivatives.[3] We wish to report here our results on the series **1a**–**g**; complex **1f** represents the first example of a (diene)Fe(CO)₂L complex containing an aliphati N-donor[4] and in comparison with **1e** provides a direct comparison between isostructural PMe₃ and NMe₃ complexes. Complex **1d** reveals a hitherto unobserved facet of the fluxionality in the (diene)Fe(CO)₂L series.

## Results and Discussion

**(a) Synthesis.** Complexes **1b**–**g** were prepared by reaction of the tricarbonyl **1a** with L in the presence of
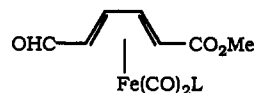


L = CO (**1a**), PPh₃ (**1b**), P(OMe)₃ (**1c**), pyridine (**1d**), PMe₃ (**1e**), NMe₃ (**1f**), CNMe (**1g**)

Me₃NO. In all cases except **1g**, a minor component identified as **1f** was formed; reaction of **1a** with Me₃NO in the presence of an excess of NMe₃ provided **1f** in good yield. Though implicated as an intermediate in many reactons of this type,[5] **1f** represents the first isolation of such an aliphatic N-donor complex. The presence of two terminal electron-withdrawing groups seems essential;[6] we have not isolated such intermediates in the cases of

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(2) For recent examples, see: (a) Pearson, A. J.; Burello, M. P. *Organometallics* **1992**, *11*, 448. (b) Pearson, A. J. *J. Chem. Soc., Chem. Commun.* **1991**, 392. (c) Pearson, A. J.; Chang, K. *J. Chem. Soc., Chem. Commun.* **1991**, 394. (d) Howell, J. A. S.; Squibb, A. D.; Goldschmidt, Z.; Gottlieb, H. E.; Almadhoun, A.; Goldberg, I. *Organometallics* **1990**, *9*, 80. (e) Pearson, A. J.; Lai, Y. S.; Srinavasan, K. *Aust. J. Chem.* **1992**, *45*, 109.

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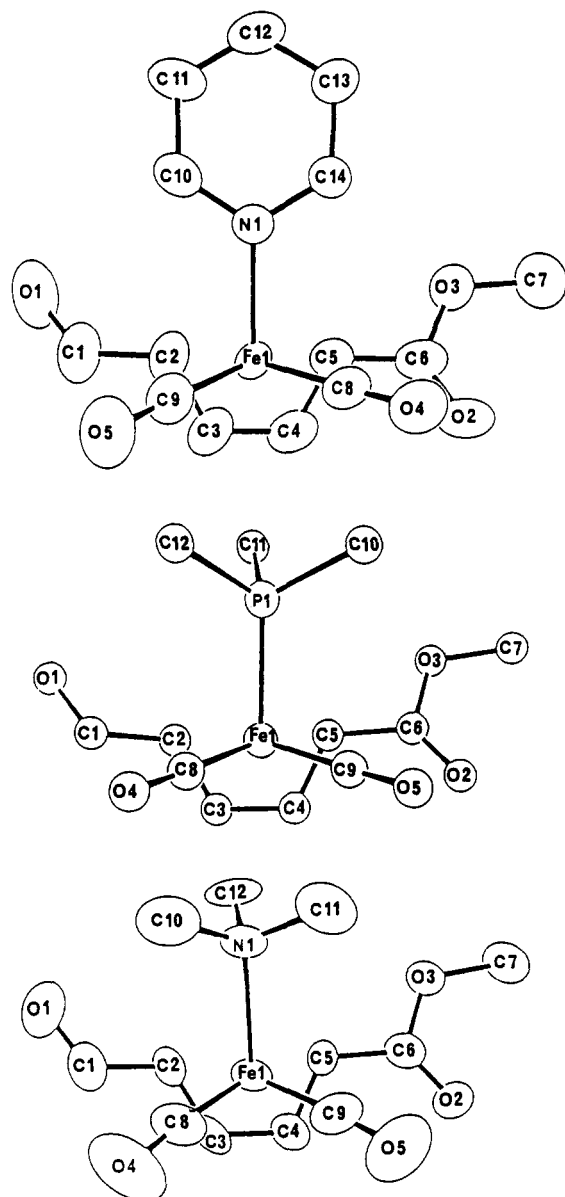
**Figure 1.** Molecular structures of (top) 1d, (middle) 1e, and (bottom) 1f.

**Table I. Important Structural Data for 1a–d,f (Distances in Å and Angles in deg)**

|  | 1a | 1f | 1e | 1d |
|---|---|---|---|---|
| Fe–L | 1.82 | 2.102(6) | 2.209(2) | 2.029(2) |
| Fe–C8/C9 (av) | 1.79 | 1.76(1) | 1.753(8) | 1.771(3) |
| Fe–C2/C5 (av) | 2.13 | 2.119(8) | 2.113(7) | 2.138(3) |
| Fe–C3/C4 (av) | 2.05 | 2.030(8) | 2.034(8) | 2.052(3) |
| Fe–Z[a] | 1.68 | 1.66 | 1.67 | 1.68 |
| C8–Fe–C9 | 89 | 86.9(5) | 88.2(4) | 89.8(1) |
| L–Fe–C8/C9 (av) | 98 | 100.3(4) | 98.5(4) | 99.1(1) |
| P1–P2[b] | 25 | 19 | 27 | 20 |
| P1–P3 | 18 | 24 | 27 | 14 |
| C2–C3–C4–C5 | 0.8 | 1.6 | 2.0 | 1.2 |
| C1–C2–C3–C4 | 12 | 16 | 16 | 16 |
| C3–C4–C5–C6 | 9 | 10 | 15 | 11 |
| C–N–C |  | 108.0(8) |  |  |
|  |  | 106.8(8) |  |  |
|  |  | 106.0(9) |  |  |
| C–P–C |  |  | 105.0(7) |  |
|  |  |  | 97.9(6) |  |
|  |  |  | 101.1(7) |  |

[a] Z = centroid of C2–C5. [b] P1 = plane of C2–C5, P2 = plane of C1–O1–H, P3 = plane of C6–O2–O3.

**Scheme I**



unsubstituted or monosubstituted complexes or in the cases of alkyl-substituted derivatives.

**(b) Solid-State Structures of 1d–f.** The molecular structures of 1d–f are shown in Figure 1, and important bond lengths and angles are given in Table I, together with those of the tricarbonyl 1a. Structures are typical of the distorted-square-pyramidal geometry common to (diene)Fe(CO)₃ complexes; in all cases, the substituting ligand occupies the axial position. Common structural features include a bending of the formyl and carbomethoxy substituents toward the iron by an average of 15 and 11°, respectively. The formyl and carbomethoxy planes are twisted relative to the diene plane by an average of 23 and 21°, respectively, thus placing O1 and O3 closer to the

metal. The pyridine ligand presents a face-on configuration to the diene plane. In a view down the L–Fe bond of 1e,f a single methyl bisects the diene bite angle, while the other two methyls approximately eclipse the two basal carbonyls. The molecular framework of 1d is essentially identical with that reported previously for (diethyl muconate)Fe(CO)₂(pyrazine).[6b] The shortened Fe–N bond length in 1d compared to that in 1f is consistent with the reduced covalent radius of sp²-hybridized nitrogen. The C–N–C angle in 1f is contracted by about 4° relative to that in the free ligand (110.9°),[7] while the C–P–C angle for 1e is expanded by about 3° relative to that in the free ligand (98.8°).[7] The Fe–L bond in 1f is shortened by only about 5% relative to that in 1e, much less than the decrease in covalent radii between nitrogen and phosphorus.

Complexes 1e,f provide an opportunity for assessment of the steric characteristics of PMe₃ and NMe₃ in complexes which are otherwise isostructural. Though cone angles are widely used as a qualitative measure of steric effects for phosphines and phosphites,[8] until recently[9] little information was available on the steric effects of the analogous amines. Analysis[10] of several recent structures

(4) Aliphatic N-donor Fe(CO)₄L complexes of limited stability have been reported: (a) Birencwaig, F.; Shamai, H.; Shvo, Y. *Tetrahedron Lett.* **1979**, 2947. (b) Elzinga, J.; Hogeveen, H. *J. Chem. Soc., Chem. Commun.* **1977**, 705.

(5) For a mechanistic discussion, see: Shen, J. K.; Gao, Y. C.; Shi, Q. Z.; Rheingold, A. L.; Basolo, F. *Inorg. Chem.* **1991**, *30*, 1868 and references therein.

(6) Heterocyclic N-donor (diethyl muconate)Fe(CO)₂L complexes have been prepared: (a) de Paoli, M. A.; Makita, M. *J. Organomet. Chem.* **1981**, *216*, 79. (b) de Paoli, M. A.; Lechat, J. R.; Inumaru, A. T. *J. Organomet. Chem.* **1987**, *320*, 91.

(7) Beagley, B.; Medwid, A. R. *J. Mol. Struct.* **1977**, *38*, 229.

(8) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.

(9) Seligson, A.; Trogler, W. C. *J. Am. Chem. Soc.* **1991**, *113*, 2520.

(10) Cone angles were measured using CHEM-X,[11] and a value of 2.0 Å was used for the van der Waals radius of the methyl group.

(11) CHEM-X, designed and distributed by Oxford Molecular Design, Oxford, England.

## Table II. NMR Data

| L | T (°C) | ¹³C[a] position | ¹³C[a] shift | ¹H[b,c] position | ¹H[b,c] shift | ³¹P[c] shift |
|---|---|---|---|---|---|---|
| PPh₃ | −60 | 2,5 | 60.4 | 1 | 9.08 [5.5] | 60.9 |
| | | | 49.4 (5) | 2 | 0.15 (8.0) | |
| | | | | 3 | 5.20 | |
| | | 3,4 | 88.1 | 4 | 5.75 | |
| | | | 84.6 | 5 | 0.48 (7.5) | |
| | | 1 | 197.2 | 7 | 3.18 | |
| | | 6 | 172.8 | PPh₃ | 7.0–7.8 | |
| | | 7 | 50.7 | | | |
| | | CO | 210.7 (8) | | | |
| | | | 209.7 (8) | | | |
| | | PPh₃ | 127–134 | | | |
| P(OMe)₃ | −50 | 2,5 | 55.3 (7) | 1 | 9.19 [5.1] | 178.1 |
| | | | 46.4 (7) | 2 | 0.98 | |
| | | | | 3 | 5.27 | |
| | | 3,4 | 86.9 | 4 | 5.60 | |
| | | | 83.5 | 5 | 1.02 | |
| | | 1 | 197.4 | 7 | 3.37 | |
| | | 6 | 172.8 | P(OMe)₃ | 3.25 (11.5) | |
| | | 7 | 51.0 | | | |
| | | CO | 208.2 (24) | | | |
| | | | 208.9 (24) | | | |
| | | P(OMe)₃ | 52.0 (4) | | | |
| PMe₃ | −40 | 2,5 | 57.0 (4) | 1 | 8.92 [7.3] | 17.1 |
| | | | 46.0 (7) | 2 | 0.53 | |
| | | 3,4 | 86.3 | 3 | 4.90 | |
| | | | 84.5 | 4 | 5.51 | |
| | | 1 | 197.5 | 5 | 0.60 | |
| | | 6 | 172.9 | 7 | 3.34 | |
| | | 7 | 50.8 | PMe₃ | 1.05 (9.3) | |
| | | CO | 210.1 (11) | | | |
| | | | 210.0 (11) | | | |
| | | PMe₃ | 17.8 (31) | | | |
| NMe₃ | −20 | 2,5 | 61.4 | 1 | 9.22 [7.3] | |
| | | | 51.4 | 2 | 1.42 | |
| | | 3,4 | 88.4 | 3 | 4.35 | |
| | | | 86.2 | 4 | 5.05 | |
| | | 1 | 198.3 | 5 | 1.44 | |
| | | 6 | 173.9 | 7 | 3.42 | |
| | | 7 | 50.3 | NMe₃ | 2.07 | |
| | | CO | 208.7 | | | |
| | | | 208.3 | | | |
| | | NMe₃ | 60.1 | | | |
| CO | −40 | 2,5 | 55.5 | 1 | 8.89 [3.0] | |
| | | | 48.1 | 2 | 0.94 | |
| | | 3,4 | 88.3 | 3 | 5.10 | |
| | | | 85.1 | 4 | 5.37 | |
| | | 1 | 195.9 | 5 | 0.62 | |
| | | 6 | 171.9 | 7 | 3.26 | |
| | | 7 | 52.2 | | | |
| | | CO | 211.2 | | | |
| | | | 205.3 | | | |
| | | | 205.2 | | | |

| L | T (°C) | ¹³C[a] position | ¹³C[a] shift | ¹H[b,c] position | ¹H[b,c] shift | ³¹P[c] shift |
|---|---|---|---|---|---|---|
| pyridine isomer A | −25 | 2,5 | 60.5 | 1 | 9.31 [7.4] | |
| | | | 49.9 | 2,5 | 1.8–1.9 | |
| | | 3,4 | 88.6 | 3 | 5.45 | |
| | | | 87.0 | 4 | 5.59 | |
| | | 1 | 198.4 | 7 | 3.70 | |
| | | 6 | 173.7 | py | 8.52 (α) | |
| | | 7 | 51.5 | | 7.80 (γ) | |
| | | CO | 208.4 | | 7.34 (β) | |
| | | | 209.1 | | | |
| | | py | 156.9 (α) | | | |
| | | | 137.6 (γ) | | | |
| | | | 125.6 (β) | | | |
| isomers B/B′ | | 2,5 | 55.7, 47.6 | 1 | 8.98 [4.4], 8.96 [br] | |
| | | | 39.8, 30.2 | 2,5 | −0.14, −0.04; 1.56, 1.66 | |
| | | 3,4 | 97.6, 95.0 | 3 | 6.00, 5.94 | |
| | | | 85.4, 82.2 | | | |
| | | 1 | 198.9, 197.6 | 4 | 6.56, 6.40 | |
| | | 6 | 175.0, 172.5 | 7 | 3.22, 3.54 | |
| | | 7 | 51.2, 51.5 | py | 8.33, 8.46 (α) | |
| | | CO | 217.7, 218.0 | | 7.61 (γ) | |
| | | | 215.3, 215.4 | | 7.10 (β) | |
| | | py | 156.1, 156.4 (α) | | | |
| | | | 137.3, 137.5 (γ) | | | |
| | | | 124.8, 124.9 (β) | | | |
| MeNC isomers A/B/B′ | −20 | 2,5 | 56.4, 56.7, 57.6 | 1 | 9.31 [3.4] | |
| | | | 43.7, 48.0, 48.4 | | 9.19 [4.5] | |
| | | 3,4 | 88.4, 88.7, 90.8 | | 9.15 [6.0] | |
| | | | 85.3, 85.7, 87.8 | 2,5 | 0.8–1.4 (m) | |
| | | 1 | 199.3, 199.4, 199.7 | 3,4 | 5.6–5.9 (m) | |
| | | 6 | 175.2, 175.3, 175.8 | 7 | 3.64, 3.62, 3.61 | |
| | | 7 | 53.1, 55.6, 55.9 | MeNC | 3.60, 3.31, 3.26 | |
| | | CO | 217.9, 218.0 (axial) | | | |
| | | | 212.5, 212.4 (basal) | | | |
| | | | 211.4, 211.2 (basal) | | | |
| | | MeNC | 32.6, 32.8, 33.0 | | | |

[a] Shifts in ppm from TMS; CD₂Cl₂ solvent; J(P–C) in parentheses. [b] Shifts in ppm from TMS; C₆D₆ solvent, except 1d in CD₂Cl₂ and 1g in CDCl₃; J(P–H) in parentheses and J(1,2) in brackets. Other coupling constants are in the ranges J(2,3) ≈ J(4,5) = 8–9 Hz and J(3,4) ≈ 5–8 Hz. [c] All spectra at room temperature except those of 1d and 1g (−20 °C).

of PMe₃ complexes,[12] which include all first-row elements except Mn and include mono-, bis-, and tris-substituted complexes, reveal a wide range of M–PMe₃ bond lengths

(2.17–2.56 Å) which, when normalized to the standard M–P bond length of 2.28 Å,[8] yield a quite constant value for the PMe₃ cone angle of 124–128°; the observed value for 1e is 125°. The smaller quoted literature value for PMe₃ of 118° is based on rotation of the methyl groups to give C₃ᵥ symmetry[8b] rather than an assignment of a van der Waals radius to the methyl group.[10]

Structurally characterized NMe₃ complexes are fewer

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(13) (a) Millington, K. R.; Wade, S. R.; Willey, G. R.; Drew, M. G. B. Inorg. Chim. Acta 1984, 89, 185. (b) Greene, P. T.; Orioli, P. L. J. Chem. Soc. A 1969, 1621. (c) Fowles, G. W. A.; Greene, P. T. J. Chem. Soc., Chem. Commun. 1967, 971. (d) Russ, B. J.; Wood, J. S. J. Chem. Soc., Chem. Commun. 1966, 745.
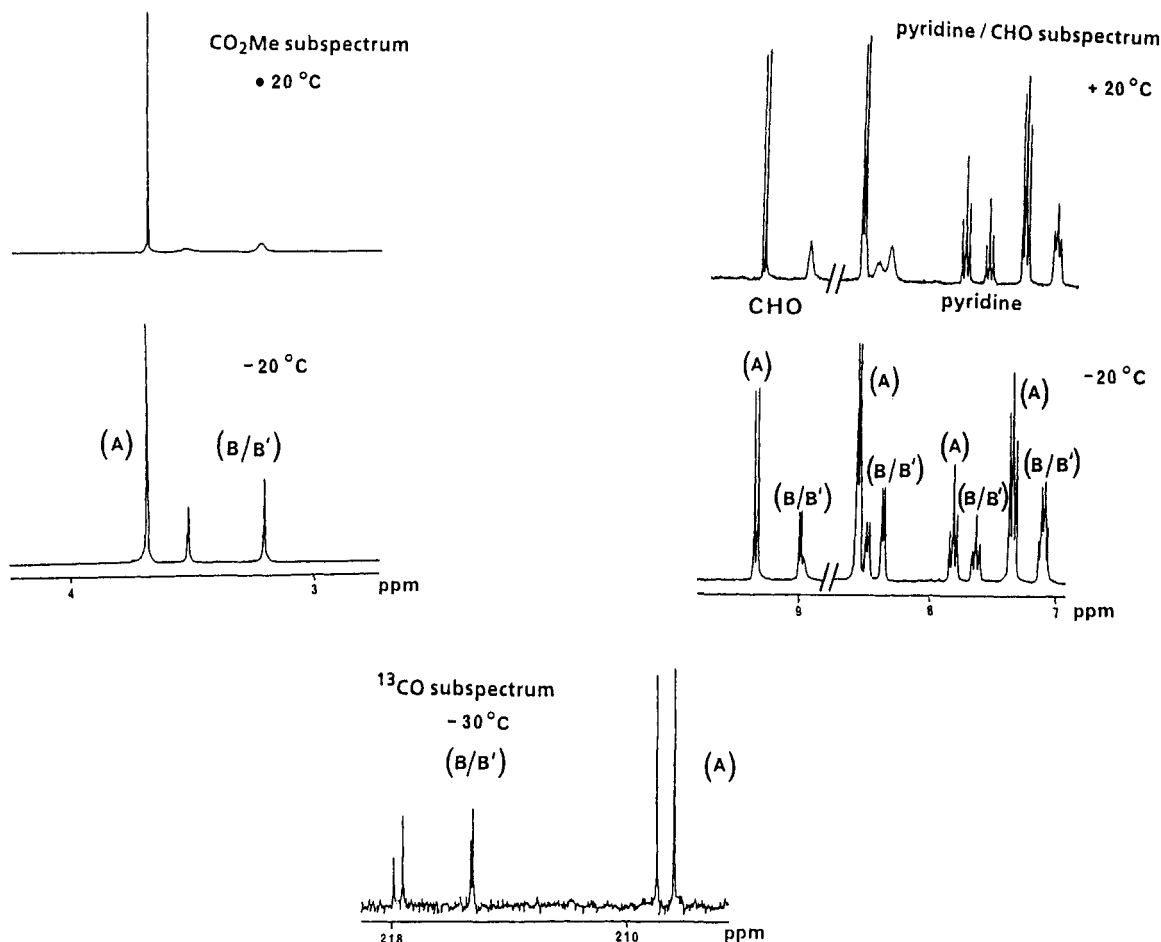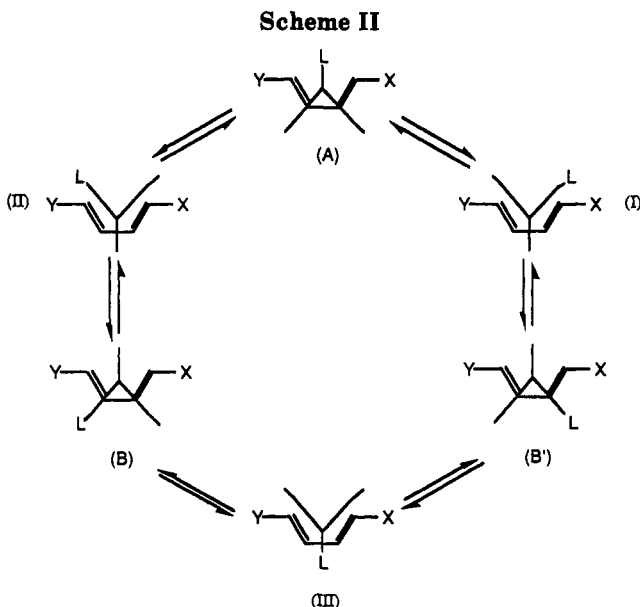
**Figure 2.** NMR spectra for **1d** in $CD_2Cl_2$.

**Scheme II**



in number[13] but reveal Fe–N distances of 2.20–2.28 Å and a cone angle for $NMe_3$ of 135° when M–N distances are normalized to 2.2 Å.[9] The value for **1f** is close to the value of 132° calculated from equilibrium constant measurements.[9] The increased cone angle for $NMe_3$ is clearly the result of decreased C–N distances and increased C–N–C angles relative to $PMe_3$.

**(c) Solution Structure and Fluxionality.** Rotation of the diene relative to the $ML_3$ fragment is a well-established phenomenon in $(diene)Fe(CO)_3$[14] and (diene)-

$Fe(CO)_2L$ complexes[3] which has also been analyzed theoretically.[15]

The fluxional process may be represented in Scheme I. For a complex possessing no mirror plane (X ≠ Y), A, B, and B′ represent chemically distinct conformational isomers in which two noninterconverting sets of CO ligands ($b^1/b^3/a^2$ and $b^2/a^1/b^4$) undergo exchange. The appearance of the averaged $^{13}CO$ spectrum will depend on the identities and relative populations of the conformers, but exchange does not completely average the CO resonances, and two resonances would therefore be expected in the high-temperature limiting spectrum. Calculations on $(butadiene)Fe(CO)_2PH_3$ suggest a slight preference of 11 kJ mol$^{-1}$ for occupation of the basal site by $PH_3$,[15c] but isomer stabilities are quite dependent on diene substituent; in particular, for trans terminal disubstitution, as in the complexes described herein, diene–ligand interactions are greatly reduced in isomer A for ligands of large cone angle.

NMR spectra of **1b,e,f** are temperature-independent in the range +25 to –60 °C, indicating that only the axial isomer is populated in solution.[16] Particularly for **1f**, this is most likely due to the steric argument outlined above. In contrast, the single room-temperature $^{31}P$ resonance of **1c** at 178.1 ppm is resolved into three at –40 °C (179.1,

(14) Howell, J. A. S. In *Advances in Dynamic Stereochemistry*; Gielen, M. F., Ed.; Freund: London, 1985; pp 111–205.

(15) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Albright, T. A.; Hoffmann, R. *Chem. Ber.* **1978**, *111*, 1591. (c) Calhorda, M. J.; Vichi, E. J. S. *Organometallics* **1990**, *9*, 1060.

(16) Below –60 °C, a fluxional process involving rotation about the C–CHO bond may be observed; this will be discussed in a separate publication. Doubling of the infrared bands observed for some of these complexes is a result of this conformational equilibrium.
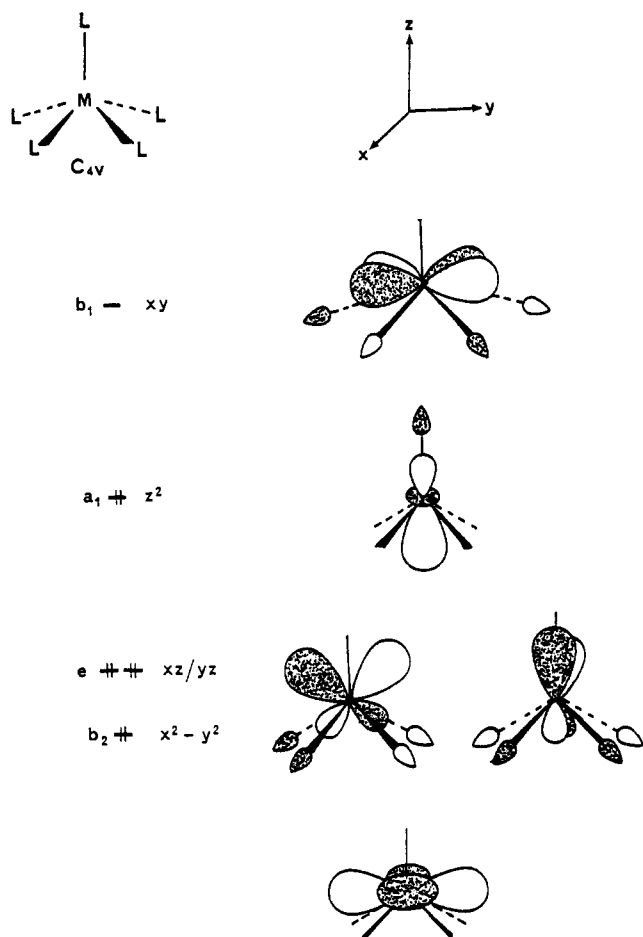
**Figure 3.** Orbital splitting pattern for a square pyramid.

177.6, 175.4 ppm) in the ratio 43:2:1. The minor resonances are assigned to the B/B' basal isomer pair.

Of most interest, however, are the spectra of **1d** at -20 °C, which show more substantial population of the B/B' pair. This is most evident in the pyridine/aldehyde and CO$_2$Me subspectra and i n the $^{13}$CO subspectrum (Figure 2). The isomer ratio determined from the CO$_2$Me subspectrum is 4.3:1:1.2. The major isomer is assigned as A on the basis of the $^{13}$CO subspectrum.

When the temperature is raised to +25 °C, *only* exchange between the B/B' pair is observed; resonances assignable to A undergo no reversible temperature broadening on warming to +40 °C. On the basis of line widths of the broadened resonances in the CO$_2$Me subspectrum at 293 K, a barrier to B/B' exchange of $\Delta G^{\ddagger}_{293} = 65$ kJ mol$^{-1}$ may be calculated.[17] Lack of line broadening of the resonance assigned to A precludes any estimate of the barrier to A/B or A/B' exchange. Isomer A and the B/B' pair are not chemically separable; only a single compound is isolated from careful preparative TLC, and dissolution of crystalline **1d** consistently reproduces the spectrum at thermodynamic equilibrium.

Observation of such a differential barrier to isomer exchange in a (diene)Fe(CO)$_2$L complex is unprecedented and implies a substantially lower energy for the transition state III in B/B' exchange as compared to transition states I and II, which result in A/B and A/B' exchange in Scheme II. These observations are, however, consistent with a

(17) Calculated using the relationship $k_{293} = \pi$(excess line width): Gunther, H. *NMR Spectroscopy*; Wiley: Chichester, England, 1980; p 243. The observed excess line width for the CO$_2$Me resonances of the B/B' pair of **1d** at 293 K is 6 Hz.
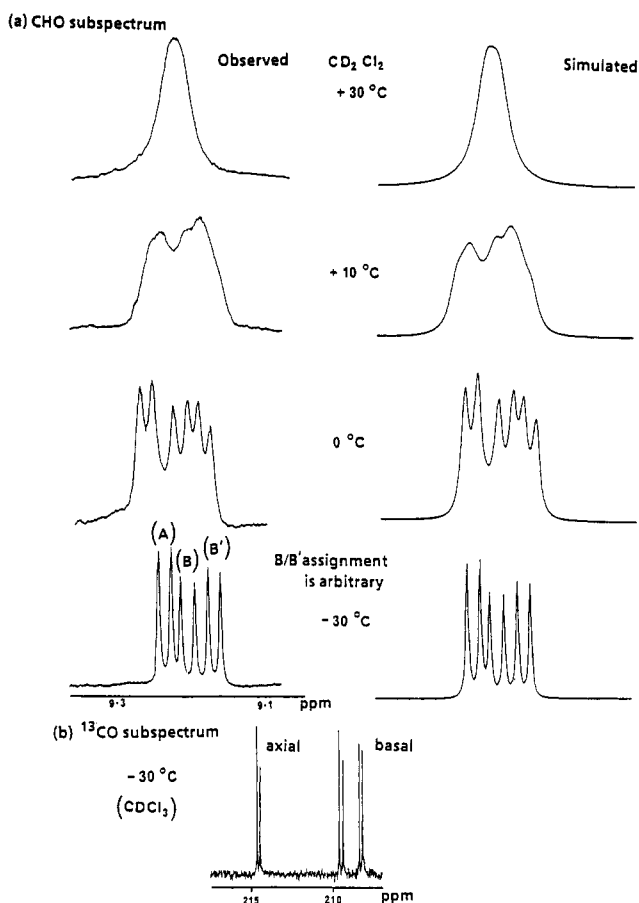


**Figure 4.** Variable-temperature NMR spectra for **1g**.

qualitative molecular orbital description of ground and transition states in the diene rotation process.

Shown in Figure 3 is the d-orbital splitting pattern for a $C_{4v}$ square-pyramidal ML$_5$ complex. Of particular relevance is the hybridization of the a$_1$ ($z^2$) orbital away from the apical group. The a$_1$ orbital is primarily d$_{z^2}$ antibonding to the apical lone pair; however, some metal s and metal p$_z$ mix in a bonding way to the apical lone pair. The hybridization (the mixing of metal s and p$_z$) serves to increase the density of $z^2$ in a region surrounding the basal ligands.

The butadiene ligand can be viewed as occupying two cis basal sites in a square pyramid, and the two filled $\pi_1$ and $\pi_2$ molecular orbitals serve as two σ-donor functions. There is also the empty orbital $\pi_3$, which lies low in energy, particularly so where the terminal diene substituents are π-acceptors, as is the case here. This empty orbital will interact with, and stabilize, the filled $z^2$ combination. This stabilizing interaction for the ground-state staggered conformation when L = CO is shown by **2**. The coefficients



**2**
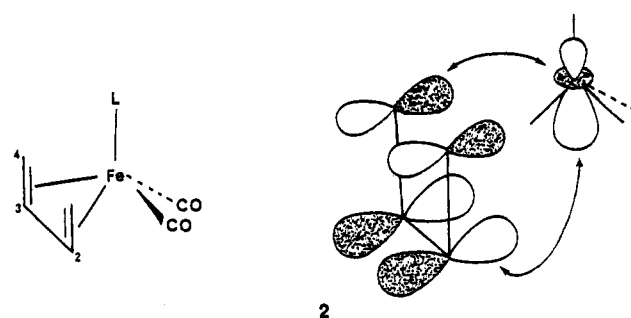
in $\pi_3$ at C$_2$ and C$_3$ are much larger than those at C$_1$ and C$_4$. The hybridization of $z^2$ creates a larger overlap with

**Table III. Rate and Equilibrium Constant Data for Exchange in 1g[a]**

| $T$ (K) | $k_{B\to B'}$ (s$^{-1}$) | $k_{B\to A} = k_{B'\to A}$ (s$^{-1}$) | $\Delta G^*_{B\to B'}$ (kJ mol$^{-1}$) | $\Delta G^*_{B\to A} = \Delta G^*_{B'\to A}$ (kJ mol$^{-1}$) | $K_1$ | $K_2$ |
|---|---|---|---|---|---|---|
| 253 | 0.4 | 0.8 | 63.5 | 62.0 | 0.84 | 0.75 |
| 267 | 1.4 | 2.8 | 64.3 | 62.8 | 0.82 | 0.76 |
| 273 | 2.8 | 5.0 | 64.2 | 63.0 | 0.77 | 0.77 |
| 278 | 3.7 | 7.7 | 64.8 | 63.2 | 0.78 | 0.77 |
| 283 | 6.7 | 13.4 | 64.7 | 63.0 | 0.77 | 0.78 |
| 288 | 10.5 | 21.0 | 64.7 | 63.1 | 0.75 | 0.78 |
| 293 | 18.0 | 36.0 | 64.6 | 62.9 | 0.74 | 0.79 |
| 303 | 45.0 | 90.0 | 64.6 | 62.9 | 0.73 | 0.79 |

[a] Rate constants are defined in Scheme I; $k_{B'\to A}$ was always taken equal to $k_{B\to A}$. The ratio $k_{B'\to A}/k_{B\to B'}$ was fitted independently up to 278 K and then set to 2.0. Equilibrium constants ($K_1 = k_{A\to B'}/k_{B'\to A}$, $K_2 = k_{A\to B}/k_{B\to A}$, $K_3 = k_{B'\to B}/k_{B\to B'}$) were fitted in the range 253–278 K and extrapolated above. $K_3$ is equal to 1.00 in all cases.

**Table IV. Fractional Atomic Coordinates for 1d**

| atom | x | y | z |
|---|---|---|---|
| Fe1 | 0.24068(4) | 0.21254(3) | 0.39891(2) |
| N1 | 0.3132(2) | 0.4243(2) | 0.4027(1) |
| O1 | -0.1648(3) | 0.4243(4) | 0.4051(2) |
| O2 | 0.4722(3) | 0.0172(2) | 0.2772(1) |
| O3 | 0.4798(3) | 0.2484(2) | 0.2389(1) |
| O4 | 0.5582(2) | 0.0858(2) | 0.4419(1) |
| O5 | 0.1661(3) | 0.1636(3) | 0.5404(1) |
| C1 | -0.1095(4) | 0.3015(4) | 0.4008(2) |
| C2 | -0.0028(3) | 0.2567(3) | 0.3531(1) |
| C3 | 0.0401(4) | 0.1066(3) | 0.3502(2) |
| C4 | 0.1705(4) | 0.0675(3) | 0.3182(1) |
| C5 | 0.2586(3) | 0.1788(3) | 0.2906(1) |
| C6 | 0.4111(4) | 0.1358(3) | 0.2689(1) |
| C7 | 0.6320(4) | 0.2190(4) | 0.2165(2) |
| C8 | 0.4328(3) | 0.1341(2) | 0.4256(1) |
| C9 | 0.1951(3) | 0.1879(3) | 0.4850(1) |
| C10 | 0.2236(3) | 0.5330(3) | 0.4226(2) |
| C11 | 0.2683(4) | 0.6789(3) | 0.4212(2) |
| C12 | 0.4112(4) | 0.7143(2) | 0.4014(2) |
| C13 | 0.5025(4) | 0.6065(3) | 0.3810(2) |
| C14 | 0.4508(3) | 0.4637(3) | 0.3825(2) |

**Table V. Fractional Atomic Coordinates for 1e**

| atom | x | y | z |
|---|---|---|---|
| Fe1 | 0.68500(7) | 0.75883(11) | 0.09043(4) |
| P1 | 0.7016(1) | 1.0087(2) | 0.1262(1) |
| O1 | 0.6208(4) | 1.0475(9) | -0.0355(2) |
| O2 | 0.5886(5) | 0.5293(7) | 0.1827(2) |
| O3 | 0.5248(4) | 0.7784(7) | 0.1870(2) |
| O4 | 0.8431(5) | 0.7598(14) | 0.0461(3) |
| O5 | 0.7965(5) | 0.5783(11) | 0.1787(3) |
| C2 | 0.5932(5) | 0.8298(9) | 0.0189(3) |
| C3 | 0.5971(6) | 0.6572(10) | 0.0279(3) |
| C4 | 0.5788(6) | 0.5957(9) | 0.0727(3) |
| C5 | 0.5594(5) | 0.7118(8) | 0.1089(3) |
| C1 | 0.6337(5) | 0.9074(10) | -0.0200(3) |
| C6 | 0.5607(5) | 0.6587(8) | 0.1626(3) |
| C7 | 0.5213(8) | 0.7379(11) | 0.2408(4) |
| C8 | 0.7799(6) | 0.7576(15) | 0.0631(4) |
| C9 | 0.7498(6) | 0.6491(11) | 0.1438(3) |
| C10 | 0.7331(11) | 1.0159(15) | 0.1971(4) |
| C11 | 0.6011(8) | 1.1403(10) | 0.1159(5) |
| C12 | 0.7804(12) | 1.1453(15) | 0.1058(7) |
| Fe2 | 0.16893(7) | 0.73138(12) | 0.12014(4) |
| P2 | 0.1053(1) | 0.4817(2) | 0.1184(1) |
| O101 | 0.3548(6) | 0.4273(g) | 0.0875(3) |
| O102 | 0.1165(5) | 0.9444(7) | 0.2327(3) |
| O103 | 0.1140(4) | 0.6798(6) | 0.2562(2) |
| O104 | 0.0115(5) | 0.9459(11) | 0.1120(4) |
| O105 | 0.1419(8) | 0.7746(15) | 0.0079(3) |
| C102 | 0.3050(5) | 0.6404(9) | 0.1359(3) |
| C103 | 0.2994(5) | 0.8160(10) | 0.1416(3) |
| C104 | 0.2514(5) | 0.8740(9) | 0.1771(3) |
| C105 | 0.2078(5) | 0.7465(8) | 0.2021(3) |
| C101 | 0.3339(6) | 0.5690(12) | 0.0910(3) |
| C106 | 0.1427(5) | 0.8075(8) | 0.2310(3) |
| C107 | 0.0461(9) | 0.7220(12) | 0.2849(6) |
| C108 | 0.0731(6) | 0.8520(10) | 0.1161(4) |
| C109 | 0.1551(7) | 0.7565(13) | 0.0522(4) |
| C110 | 0.1576(7) | 0.3395(11) | 0.1690(4) |
| C111 | -0.0104(6) | 0.4820(13) | 0.1251(6) |
| C112 | 0.0993(11) | 0.3575(15) | 0.0607(4) |

the atomic p orbitals on $C_2$ and $C_3$. This interaction is very strong; in a sense, this could be represented as the alternative localized bonding description in **3**. Using a (butadiene)$^{2-}$ formulation and constructing Fe–C $\sigma$-bonds to $C_1$ and $C_4$ creates a 16e ML$_5$ complex which has one empty orbital analogous to $z^2$; this orbital overlaps with the filled $\pi$-bond between $C_2$ and $C_3$ to saturate the complex.



**3**
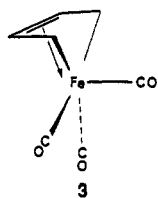
On rotation to the eclipsed transition state, overlap between $\pi_3$ and $a_1$ is diminished (see **4**) since there is less electron density in the torus of $a_1$. Thus, the staggered



**4**
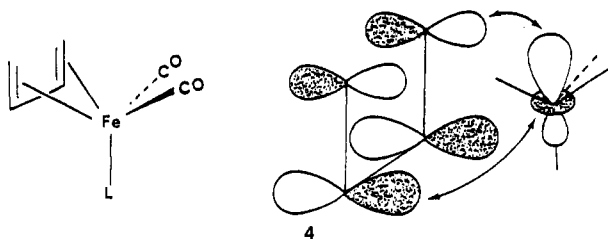
rather than eclipsed ground-state structure is preferred. The important point is that increasing the amount of hybridization (mixing of s and p$_z$) will increase the overlap difference; hence, increasing the hybridization will increase

the energy difference between these two structures. Where L = NMe$_3$ or pyridine, the nitrogen-based lone pair lies at a lower energy and overlaps less than the 2$\sigma$ orbital of CO or the lone pair of a phosphine. In other words, it is a poorer $\sigma$-donor for zerovalent iron. Thus, there will be less hybridization than when a CO or phosphine $\sigma$-donor occupies the apical position. This is energetically unfavorable for the staggered minimum but favorable for the eclipsed maximum when one rotates about the butadiene–Fe axis. The relative energies of B, B', I, and II will not be much altered from that of the L = CO parent system. Thus, rotation of A to either I or II exchanges apical nitrogen for apical CO and is increased in energy relative to rotation of B or B' to III in which apical CO is replaced by apical nitrogen (disregarding steric factors). For CO/L ligand pairs which are closer in $\sigma$-donor characteristics, intermediates I–III will lie closer in energy. This is in fact observed for **1c**, where equivalent collapse of the three ^{31}P resonances is observed, though the small population of the basal isomer pair precludes line-shape analysis.

**Table VI. Fractional Atomic Coordinates for 1f**

| atom | x | y | z |
|---|---|---|---|
| Fe1 | 0.16171(14) | 0.77872(9) | 0.06119(7) |
| N1 | 0.3740(9) | 0.7230(6) | −0.0032(5) |
| O1 | 0.5450(12) | 0.9734(7) | 0.2352(5) |
| O2 | −0.1306(8) | 0.7816(7) | −0.1151(4) |
| O3 | 0.1217(8) | 0.8395(7) | −0.1601(4) |
| O4 | 0.1389(13) | 0.6711(8) | 0.1945(6) |
| O5 | −0.1157(10) | 0.5838(7) | −0.0351(6) |
| C1 | 0.3893(17) | 0.9510(8) | 0.2251(6) |
| C2 | 0.2911(12) | 0.9468(7) | 0.1475(5) |
| C3 | 0.1125(13) | 0.9316(8) | 0.1461(6) |
| C(4) | 0.0159(12) | 0.8974(7) | 0.0648(5) |
| C5 | 0.1108(10) | 0.8839(7) | −0.0105(5) |
| C6 | 0.0183(12) | 0.8298(7) | −0.0983(5) |
| C7 | 0.0452(14) | 0.7908(11) | −0.2498(6) |
| C8 | 0.1545(13) | 0.7149(8) | 0.1427(7) |
| C9 | −0.0022(12) | 0.6597(9) | 0.0008(7) |
| C10 | 0.4698(16) | 0.6735(12) | 0.0474(9) |
| C11 | 0.3218(16) | 0.6289(10) | −0.0907(7) |
| C12 | 0.4943(13) | 0.8192(10) | −0.0180(7) |
| Fe2 | 0.35184(13) | 0.26533(9) | 0.58896(7) |
| N101 | 0.1424(8) | 0.3283(5) | 0.5609(4) |
| O101 | −0.0247(10) | 0.0423(6) | 0.6436(4) |
| O102 | 0.6415(8) | 0.2765(6) | 0.4140(4) |
| O103 | 0.3908(7) | 0.2132(5) | 0.3309(3) |
| O104 | 0.3685(12) | 0.3594(7) | 0.7815(4) |
| O(105) | 0.6307(10) | 0.4640(6) | 0.6091(5) |
| C(101) | 0.1273(14) | 0.0774(8) | 0.6488(5) |
| C102 | 0.2245(11) | 0.0895(6) | 0.5749(5) |
| C103 | 0.4067(11) | 0.1103(6) | 0.5844(5) |
| C104 | 0.4994(11) | 0.1489(7) | 0.5236(5) |
| C105 | 0.3999(10) | 0.1654(6) | 0.4559(5) |
| C106 | 0.4928(11) | 0.2239(7) | 0.4007(5) |
| C107 | 0.4688(12) | 0.2589(8) | 0.2682(6) |
| C108 | 0.3555(12) | 0.3224(7) | 0.7056(6) |
| C109 | 0.5188(12) | 0.3875(8) | 0.5977(6) |
| C110 | 0.0809(31) | 0.4061(20) | 0.6417(15) |
| C111 | 0.1900(25) | 0.4018(17) | 0.5041(12) |
| C112 | 0.0030(26) | 0.2336(18) | 0.5039(13) |
| C10a | 0.0727(36) | 0.2916(24) | 0.4680(18) |
| C11a | −0.0233(43) | 0.2882(30) | 0.5990(22) |
| C12a | 0.1717(44) | 0.4574(29) | 0.5968(22) |

**Table VII. Crystallographic Data**

| | 1d | 1e | 1f |
|---|---|---|---|
| cryst habit | monoclinic | monoclinic | triclinic |
| space group | $P2_1/n$ | $P2_1/n$ | $P\bar{1}$ |
| a (Å) | 8.417(1) | 15.167(4) | 7.984(1) |
| b (Å) | 9.147(2) | 8.048(3) | 12.439(2) |
| c (Å) | 19.235(3) | 26.334(9) | 16.249(3) |
| α (deg) | | | 110.85(2) |
| β (deg) | 98.84(2) | 103.98(3) | 90.48(2) |
| γ (deg) | | | 101.13(2) |
| Z | 4 | 8 | 4 |
| V (Å³) | 1463 | 3119 | 1474 |
| μ (cm⁻¹) | 27.63 | 26.82 | 9.74 |
| range (deg) | 2 < 2θ < 52 | 4 < 2θ < 60 | 2 < 2θ < 52 |
| no. of rflns with $I > 3\sigma(I)$ | 2575 | 3691 | 2468 |
| no. of variable params | 191 | 344 | 341 |
| max shift/esd | <0.001 | <0.001 | <0.001 |
| max excursion (e/Å³) | 0.32 | 0.47 | 0.40 |
| min excursion (e/Å³) | −0.13 | −0.40 | −0.20 |
| R | 0.038 | 0.076 | 0.056 |
| Rw | 0.041 | 0.082 | 0.062 |

More convincing are the spectra of the isonitrile complex **1g**. The reduced steric demand of the isonitrile provides an almost equivalent population of all three conformers, most clearly indicated by the low-temperature $^{13}CO$ subspectrum (Figure 4). Conformer exchange is best monitored using the three doublet aldehyde $^1H$ resonances. By analogy with **1d**, the more intense high-field resonance is assigned to A; assignment of the lower field resonances to B and B' is arbitrary. The resonance assigned to A uniquely exhibits a downfield shift with temperature and is selectively broadened relative to the B and B' resonances.

Though the line-shape analysis (Table III) is in theory a three-parameter problem, the line shapes of the two high-field doublets can be reproduced exactly using only two parameters ($k_{B\rightarrow A} = k_{B'\rightarrow A}$).

The results indicate a slightly lower barrier for exchange of resonance A with the B/B' pair as compared to the barrier for exchange between B and B'. While the barriers for B/B' exchange in **1d** and **1g** are comparable ($\Delta G^\ddagger_{273}$ = 65 and 64 kJ mol⁻¹, respectively), the barrier for A/(B/B') exchange in **1d** significantly exceeds that for **1g** ($\Delta G^\ddagger_{273}$ = 63 kJ mol⁻¹).

## Experimental Section

NMR spectra were recorded on a JEOL GSX 270 spectrometer using the in-built copper/constantan thermocouple. Reactions were conducted under $N_2$ using freshly distilled solvents. Line-shape analysis was performed using the EXCHANGE program (R. E. D. McClung, University of Alberta).

(a) **Synthesis. (i) 1b–e,g.** Me₃NO·2H₂O (300 mg, 2.7 mmol) was added to a solution of **1a** (200 mg, 0.7 mmol) and PPh₃ (183 mg, 0.7 mmol) in acetone (25 mL). The mixture was stirred at 42 °C until infrared monitoring indicated disappearance of starting material (10 min). Diethyl ether (30 mL) was added and the solvent removed after filtration through Celite. The residue was purified by chromatography on grade IV alumina (10% ethyl acetate and 90% 40–60 °C petroleum ether) and crystallized from 60–80 °C petroleum ether (450 mg, 37% yield); mp 113–114 °C. Anal. Calcd: C, 64.2; H, 4.73. Found: C, 64.5; H, 4.69. Infrared (hexane): 1999, 1947 cm⁻¹. Complexes **1c,d,g** were prepared similarly. Complex **1e** was prepared similarly using a 1.0 M solution of PMe₃ in toluene.

**1c**: 61% yield; mp 104–105 °C. Anal. Calcd: C, 38.3; H, 4.52. Found: C, 38.6; H, 4.60. Infrared (hexane): 2019, 1963 cm⁻¹ (broad).

**1d**: 68% yield; mp 96–97 °C. Anal. Calcd: C, 50.8; H, 3.93; N, 4.23. Found: C, 50.9; H, 3.95; N, 4.23. Infrared (hexane): 2011, 2005, 1949, 1945 cm⁻¹.

**1e**: 33% yield; mp 69–70 °C. Anal. Calcd: C, 43.9; H, 5.18. Found: C, 43.9; H, 5.19. Infrared (hexane): 2015, 2007, 1957, 1951 cm⁻¹.

**1g**: 80% yield; orange oil; M⁺ at m/e 292.9987 (calculated and found). Infrared (hexane): 2175 (CN), 2027, 1983 cm⁻¹.

(ii) **1f.** Me₃NO·2H₂O (380 mg, 3.4 mmol) was added to an ice-cooled solution of **1a** (250 mg, 0.9 mmol) and Me₃N (0.2 mL, 1.8 mmol) in acetone (30 mL). The mixture was warmed to 42 °C and stirred until infrared sampling indicated disappearance of the starting material. Diethyl ether (30 mL) was added and the solvent removed after filtration through Celite. The residue was purified by preparative TLC using 20% ethyl acetate/80% 40–60 °C petroleum ether as eluant and recrystallized from 60–80 °C petroleum ether containing a trace of Me₃N (220 mg, 78% yield); mp 81–82 °C. Anal. Calcd: C, 46.3; H, 5.47; N, 4.51. Found: C, 46.5; H, 5.67; N, 4.42. Infrared (hexane): 2007, 1999, 1947, 1943 cm⁻¹.

(b) **X-ray Crystallography.** Crystallographic data are given in Table VII. Data were collected on an Enraf-Nonius CAD4F diffractometer using Mo Kα radiation (λ = 0.710 69 Å). The structures were solved by direct methods (SHELX86)[18] and refined by full-matrix least squares (SHELX76).[19] Data were corrected for Lorentz and polarization effects but not for absorption. For **1d,e** the hydrogen atoms were included in calculated positions with fixed thermal parameters; non-hydrogen atoms were refined anisotropically. For **1e** and **1f** there are two molecules per asymmetric unit with no chemically significant differences; the NMe₃ group is disordered in one of the molecules

(18) Sheldrick, G. M. SHELX86, A Computer Program for Crystal Structure Determination; University of Göttingen: Göttingen, Germany, 1986.

(19) Sheldrick, G. M. SHELX76, A Computer Program for Crystal Structure Determination; University of Cambridge: Cambridge, England, 1976.

only. Hydrogen atoms were attached in calculated positions with fixed thermal parameters (except for disordered carbons); non-hydrogen atoms were refined anisotropically (except for disordered carbons). The atomic scattering factors for non-hydrogen and hydrogen atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature.[20-22] Atomic coordinates are given in Tables IV-VII.

(20) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321.

(21) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(22) Cromer, D. T.; Liberman, D. J. *J. Chem. Phys.* **1970**, *53*, 1891.

**Supplementary Material Available:** Listings of bond distances and angles, crystal data and refinement details, positional parameters for the hydrogen atoms, and anisotropic thermal parameters for the non-hydrogen atoms and additional views of the structures for **1d–f** (28 pages). Ordering information is given on any current masthead page.

OM920796D