A Search for π/σ Equilibria in Chiral Rhenium Imine Complexes of the Formula $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(N(H)=C(CF_3)X)]^+TfO^-$: Investigation of Electronic Effects upon the Binding Mode

Gene A. Stark and J. A. Gladysz*

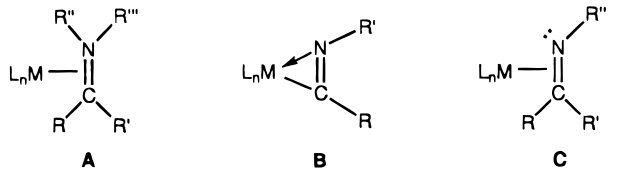
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

Received March 20, 1996[⊗]

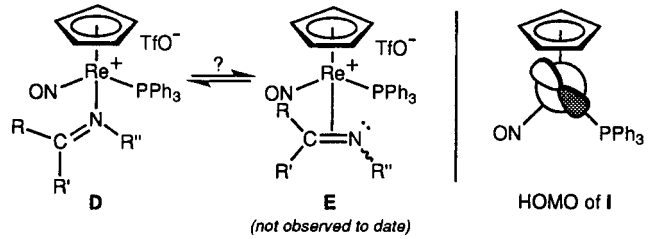
Reaction of the amido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}H_2)$ (**2**) and hexafluoroacetone gives the methyleneamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}{=}C(CF_3)_2)$ (**3**, 58%). Addition of TfOH to **3** yields the σ-imine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H){=}C(CF_3)_2)]^+TfO^-$ (**4**, 96%). Similar reactions of **2** with trifluoroacetaldehyde and then TfOH give the σ-imine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H){=}C(CF_3)H)]^+TfO^-$ (**5**, 78%) and sometimes small amounts of the corresponding π-trifluoroacetaldehyde complex. Reaction of **5** and $t\text{-}BuO^-K^+$ gives the methyleneamido complex $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\ddot{N}{=}C(CF_3)H)$ (**6**, 82%). The IR and NMR properties of **3**−**6** are studied in detail. The ^{13}C NMR spectra show C=N signals (157−142 ppm) diagnostic of σ-binding modes. No evidence is observed for π isomers of **4** or **5**. Analogous $O{=}C(CF_3)X$ complexes give exclusively π isomers, and rationales are discussed. Reactions of **3** or **6** with MeOTf and heteroatom electrophiles are also described.

Several classes of transition metal complexes have been described in which a C=N linkage is bound in an η^2 manner. For example, numerous π adducts of *iminium* ions (**A**, Chart 1) have been characterized.[1] Iminoacyl complexes in which both carbon and nitrogen ligate to the metal are also abundant (**B**).[2] However, π complexes of imines (**C**) seem to be rarer.[3] With most transition metal fragments, σ isomers appear to be strongly favored thermodynamically.[4] Indeed, we have prepared a variety of imine complexes of the chiral, 16-valence-electron rhenium Lewis acid $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)]^+$ (**I**)[5,6] and have to date only observed the σ-binding mode (**D**, Scheme 1).

Chart 1. Possible η^2-Binding Modes of Ligands with C=N Linkages



Scheme 1. π/σ Equilibria in Imine Complexes of the Chiral Rhenium Lewis Acid **I**



We have conducted an extensive study of π/σ equilibria in aldehyde and ketone complexes of **I**.[7−10] In particular, there is a profound electronic effect upon the binding mode, with electron-withdrawing substituents favoring π-isomers. For example, pentafluorobenzaldehyde, benzaldehyde, and *p*-methoxybenzaldehyde ligands give >96:<4, 84:16, and 15:85 π/σ mixtures in CH_2Cl_2 at room temperature, as assayed from measurements of IR ν_{NO} bands.[7] The π ligands are weaker σ

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1996.

(1) Representative examples: (a) Barefield, E. K.; Carrier, A. M.; Sepelak, D. J.; Van Derveer, D. G. *Organometallics* **1985**, *4*, 1395 and references therein. (b) Hasegawa, T.; Kwan, K. S.; Taube, H. *Inorg. Chem.* **1992**, *31*, 1598. (c) Brunner, H.; Wachter, J.; Schmidbauer, J.; Sheldrick, G. M.; Jones, P. G. *Organometallics* **1986**, *5*, 2212. (d) Matsumoto, M.; Nakatsu, K.; Tani, K.; Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1974**, *96*, 6777.

(2) Reviews and literature since 1993: (a) Durfee, L. D.; Rothwell, I. P. *Chem. Rev.* **1988**, *88*, 1059. (b) Galakhov, M. V.; Gómez, M.; Jiménez, G.; Pellinghelli, M. A.; Royo, P.; Tiripicchio, A. *Organometallics* **1994**, *13*, 1564. (c) Legzdins, P.; Rettig, S. J.; Ross, K. J. *Organometallics* **1994**, *13*, 569. (d) Hagadorn, J. R.; Arnold, J. *Organometallics* **1994**, *13*, 4670.

(3) (a) Galakhov, M. V.; Gómez, M.; Jiménez, G.; Royo, P.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1995**, *14*, 1901. (b) Coles, N.; Harris, M. C. J.; Whitby, R. J.; Blagg, J. *Organometallics* **1994**, *13*, 190. (c) Clark, J. R.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1233. (d) Durfee, L. D.; Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1990**, *9*, 75. (e) Buchwald, S. L.; Watson, B. T.; Wannamaker, M. W.; Dewan, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 4486. (f) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651. (g) Chiu, K. W.; Jones, R. A.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1981**, 2088. (h) Hoberg, H.; Götz, V.; Krüger, C.; Tsay, Y. H. *J. Organomet. Chem.* **1979**, *169*, 209. (i) Empsall, H. D.; Green, M.; Shakshooki, S. K.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 3472.

(4) Calligaris, M.; Randaccio, L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gilliard, R. D., McCleverty, J. A., Eds.; Pergamon: New York, 1987; Chapter 20.1.

(5) (a) Knight, D. A.; Dewey, M. A.; Stark, G. A.; Bennett, B. K.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 4523. (b) Cantrell, W. R., Jr.; Richter-Addo, G. B.; Gladysz, J. A. *J. Organomet. Chem.* **1994**, *472*, 195.

(6) For imine complexes derived from additions to isoquinoline, quinoline, indolyl, and related complexes of **I**, see: (a) Richter-Addo, G. B.; Knight, D. A.; Dewey, M. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 11863. (b) Stark, G. A.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 4523. (c) Johnson, T. J.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 3182. (d) Johnson, T. J.; Alvey, L. J.; Brady, M.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Chem.−Eur. J.* **1995**, *1*, 292.

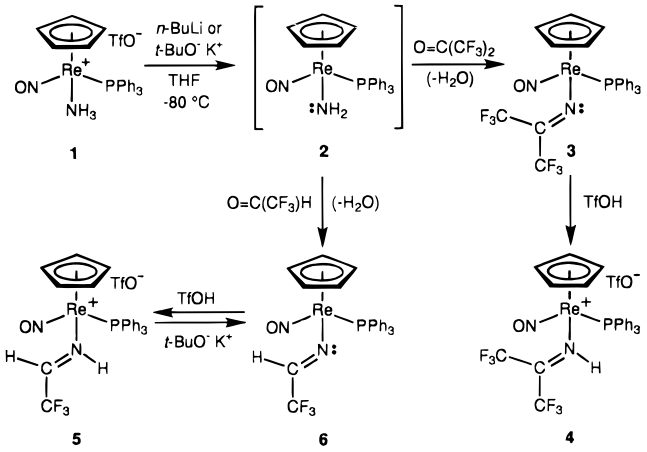
(7) Quirós Méndez, N.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 2323.

(8) Klein, D. P.; Dalton, D. M.; Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7.

(9) Wang, Y.; Agbossou, F.; Dalton, D. M.; Liu, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2699.

S0020-1669(96)00302-3 CCC: $12.00

Scheme 2. Syntheses of Imine and Methyleneamido Complexes of **I**



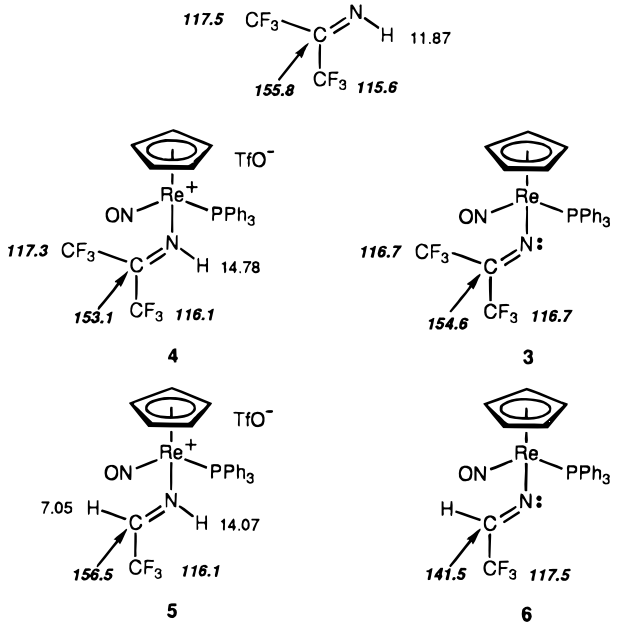
donors and stronger π acceptors than the σ ligands, resulting in ν_{NO} values that are ca. 40 cm^{-1} higher. Simple ketones such as acetone or acetophenone give, within IR detection limits (<4%), only σ isomers.[10b] In contrast, 1,3-difluoroacetone and 1,3-dichloroacetone give only π isomers.[8] In most cases, NMR properties also indicate the dominant isomer. However, since π/σ isomerization is usually rapid on the NMR time scale, even at −95 °C, equilibrium ratios are more difficult to quantify.

We wondered whether similar electronic effects upon π/σ equilibria could be demonstrated for imine complexes of **I**. In particular, electron-withdrawing C═N substituents might allow the detection of the heretofore unobserved π-binding mode (**E**, Scheme 1). Importantly, π/σ isomerizations of imine ligands have been proposed to play key roles in rhodium-catalyzed hydrogenation reactions.[11] However, to our knowledge such equilibria have never been directly observed. Hence, we decided to attempt the preparation of complexes of **I** and highly fluorinated imines, as described below.

Results

As illustrated in Scheme 2, the cationic ammonia complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(NH_3)]^+TfO^-$ (**1**)[12,13] has previously been shown to react with alkoxide or alkyllithium bases in THF at −80 °C to generate the neutral amido complex $(\eta^5\text{-}C_5H_5)$-Re(NO)(PPh$_3$)(N̈H$_2$) (**2**).[14] Subsequent additions of aldehydes or ketones (O═CRR′) give, upon workup, cationic *N*-protioimine complexes $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H)═CRR')]^+$ TfO^-.[5a] Accordingly, **2** was similarly treated with hexafluoroacetone (Scheme 2). However, workup gave the neutral hexafluorinated methyleneamido complex $(\eta^5\text{-}C_5H_5)$Re(NO)-

Chart 2. Comparison of ^{13}C (Bold and Italicized) and ^1H (Plain Text) NMR Chemical Shifts of Fluorinated Imine Derivatives (ppm, $CDCl_3$)



(PPh$_3$)(N̈═C(CF$_3$)$_2$) (**3**) in 58% yield. Apparently, the electron-withdrawing trifluoromethyl C═N substituents reduce the basicity of the ligating nitrogen, suppressing the protonation observed in the other condensations.

The fluorinated methyleneamido complex **3** was characterized by microanalysis and IR and NMR (^1H, ^{13}C, ^{31}P, ^{19}F) spectroscopy, as summarized in the Experimental Section. Several nonfluorinated methyleneamido adducts of **I** have been isolated previously.[5a] Complex **3** gave a higher IR ν_{NO} value (1648−1649 vs 1624−1637 cm^{-1}), consistent with diminished Lewis basicity and/or enhanced π acidity of the N═C(CF$_3$)$_2$ moiety, and a slightly upfield ^{31}P NMR signal (19.6 vs 20.8−21.6 ppm). As depicted in Chart 2, the $^{13}C\{^{19}F\}$ NMR spectrum of **3** showed a C═N signal at 154.6 ppm, also upfield from nonfluorinated adducts (155.3−159.1 ppm). Only one ^{13}C and ^{19}F NMR signal was observed for the *cis* and *trans* trifluoromethyl groups (116.7 and 109.7 ppm). The *C*═N substituents of other methyleneamido complexes of **I** undergo rapid *cis*/*trans* exchange, as detailed previously ($\Delta G^{\ddagger}$(181.4 K) = 8.9 kcal/mol for *p*-tolyl).[5a]

We sought to convert **3** to a cationic imine complex. However, **3** and MeOTf did not react after 3 days in CD_2Cl_2 at room temperature, as assayed by ^1H and ^{31}P NMR. Interestingly, the corresponding N═CHPh complex and MeOTf reacted rapidly at −50 °C.[5a] Next, **3** and TfOH were combined in $CDCl_3$ or ether (Scheme 2). NMR spectra showed the quantitative formation of a new species. Preparative experiments gave the cationic σ *N*-protio ketimine complex $[(\eta^5\text{-}C_5H_5)Re(NO)$-$(PPh_3)(\eta^1\text{-}N(H)═C(CF_3)_2)]^+TfO^-$ (**4**) in 96% yield. Complex **4** was characterized analogously to **3**. The ^1H NMR spectrum exhibited a downfield NH signal (δ 14.78).

A σ-binding mode was assigned to the imine ligand in **4** on the basis of ^{13}C NMR data. Importantly, π-aldehyde and -ketone complexes of **I** give C═O resonances that are markedly upfield from those of the free ligands.[7−9,10a,e] An identical trend has been established for nickel π-imine complexes.[3h] In contrast, σ-aldehyde, -ketone, and -imine complexes of **I** give C═O or C═N resonances close to those of the free ligands.[5a,7,9,10b,c] Thus, an authentic sample of hexafluoroiso-

(10) Other papers in which aldehyde or ketone complexes of **I** are characterized: (a) Garner, C. M.; Quirós Méndez, N.; Kowalczyk, J. J.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5146. (b) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198. (c) Dalton, D. M.; Gladysz, J. A. *J. Chem. Soc., Dalton Trans.* **1991**, 2741. (d) Klein, D. P.; Quirós Méndez, N.; Seyler, J. W.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1993**, *450*, 157. (e) Wang, Y.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1994**, *13*, 2164. (f) Boone, B. J.; Klein, D. P.; Seyler, J. W.; Quirós Méndez, N.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 2411.

(11) Becalski, A. G.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kang, G. J.; Rettig, S. J. *Inorg. Chem.* **1991**, *30*, 5002 and references therein.

(12) Dewey, M. A.; Knight, D. A.; Klein, D. P.; Arif, A. M.; Gladysz, J. A. *Inorg. Chem.* **1991**, *30*, 4995.

(13) TfO = CF_3SO_3.

(14) Dewey, M. A.; Knight, D. A.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1992**, *125*, 815.

propylideneamine ($HN{=}C(CF_3)_2$) was prepared.[15] A $^{13}C\{^{19}F\}$ NMR spectrum showed a C=N signal very near that of **4** (155.8 vs 153.1 ppm; Chart 2).

A CH_2Cl_2 solution of **4** showed only one IR ν_{NO} band, consistent with the presence of a single isomer. As noted with **3**, the ν_{NO} value was higher than those of nonfluorinated analogs (1723 vs 1671−1684 cm^{-1}), and the ^{31}P NMR signal was upfield (12.2 vs 17.0−21.7 ppm). However, the differences were more pronounced, giving absorptions quite similar to those of π-aldehyde or -ketone complexes of **I**.[7−9,10a,e] As with other σ-imine complexes of **I**,[5] an IR $\nu_{C=N}$ band could not be located. In contrast to **3**, separate ^{13}C and ^{19}F NMR signals were observed for the *cis* and *trans* trifluoromethyl *C*=N substituents. The ^{13}C NMR assignments in Chart 2 are based upon the larger $^3J_{CH}$ value for the trifluoromethyl group *trans* to the NH proton (14.1 vs 8.6 Hz).[16] When ^{19}F spectra were recorded at 100 °C (CD_3CO_2D), the trifluoromethyl signals shifted slightly and broadened but did not coalesce.

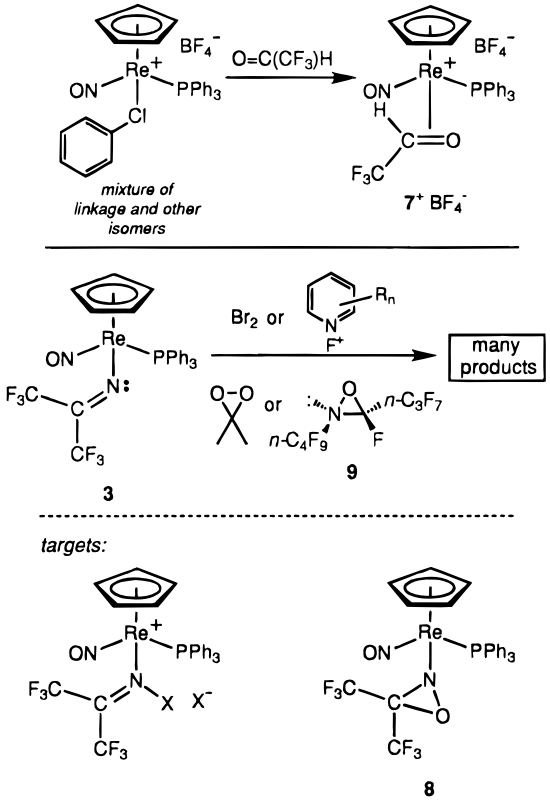
Several rationales were considered for the absence of any detectable amount of a π isomer of ketimine complex **4**. We sought to probe for possible steric factors by preparing a similar aldimine complex, which would have smaller *C*=N substituents. Thus, the amido complex **2** and trifluoroacetaldehyde[17] were combined as in the analogous reaction with hexafluoroacetone (Scheme 2). Then TfOH was added. Workup gave the *N*-protio trifluoroacetaldimine complex $[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(\eta^1\text{-}N(H){=}C(CF_3)H)]^+TfO^-$ (**5**) in 78% yield.

Complex **5** was characterized analogously to **4**, as summarized in the Experimental Section. Interestingly, no literature references to free trifluoroacetaldimine ($HN{=}C(CF_3)H$) were found with a CAS-ONLINE search. A $^{13}C\{^1H\}$ NMR spectrum of **5** exhibited a fluorine-coupled C=N signal at 156.5 ppm, diagnostic of a σ isomer. A ^1H NMR spectrum showed a *H*C=NH signal (δ 7.05, ddq) that was coupled to hydrogen, phosphorus, and fluorine. The $^3J_{HH}$ value (18.7 Hz) was similar to that of the nonfluorinated *N*-protio acetaldimine analog characterized earlier (22.8 Hz)[5a] and was in the range of *trans* couplings. A CH_2Cl_2 solution showed one IR ν_{NO} band, with a frequency somewhat greater than that of the nonfluorinated analog (1703 vs 1678 cm^{-1}).[5a]

All samples of **5** contained ca. 2% of an inseparable minor species, as evidenced by doubled cyclopentadienyl ^1H and ^{13}C NMR (δ 5.75/5.56, 94.1/93.5 ppm), ^{31}P NMR (19.6/14.7 ppm), and ^{19}F NMR (108.3/107.8 ppm) signals. This was provisionally assigned as a *Z* or *cis* C=N geometric isomer, as opposed to a π-linkage isomer. However, potentially diagnostic HC=NH ^1H NMR signals were not located. As an additional probe, CH_2Cl_2 solutions of **5** and *t*-BuO^-K^+ were combined in an NMR tube at −80 °C. A ^{31}P NMR spectrum (−20 °C) showed complete conversion to a new complex (25.7 ppm). Workup of a preparative reaction gave the methyleneamido complex ($\eta^5\text{-}C_5H_5$)Re(NO)(PPh_3)(N̈=$C(CF_3)H$) (**6**) as a spectroscopically pure orange powder in 82% yield. Complex **6** displayed IR and NMR properties similar to those of **3** (Experimental Section). When **6** and TfOH were combined in CH_2Cl_2 in a NMR tube at room temperature, **5** was regenerated as a 98:2 mixture of isomers.

In the course of repeating the synthesis of **5**, variable quantities of two additional species were sometimes observed (up to 20%, but typically 3−5%). On the basis of several hints,

Scheme 3. Other Reactions Involving **I**



these were suspected to be Re,C configurational diastereomers of the π-trifluoroacetaldehyde complex ($\eta^5\text{-}C_5H_5$)Re(NO)(PPh_3)(η^2-O=$C(CF_3)H$)]$^+TfO^-$ ($\mathbf{7}^+TfO^-$). Thus, the tetrafluoroborate salt $\mathbf{7}^+BF_4^-$ was prepared from the substitution-labile chlorobenzene complex of **I**[18] as shown in Scheme 3. Similar procedures have been described for other aldehyde complexes earlier.[10e,18] Unexpectedly, $\mathbf{7}^+BF_4^-$ was very sparingly soluble in most solvents, and NMR spectra could only be obtained in CD_3NO_2. An authentic sample of $\mathbf{7}^+TfO^-$ was then prepared by metathesis (excess $Bu_4N^+TfO^-$, acetone). The NMR chemical shifts of this much more soluble salt matched those of the reaction byproduct. Also, the IR ν_{NO} values of $\mathbf{7}^+X^-$ (1762−1769 cm^{-1}) were much higher than those of any of the compounds described above.[10f,19]

In order to further test the accessibility of π-imine complexes of **I**, thermal and chemical isomerizations of the σ complexes were attempted. First, a $CDCl_3$ solution of **5** was kept at room temperature for 7 days. The sample remained unchanged, as assayed by NMR. A second $CDCl_3$ solution was then kept at 60 °C for 18 h. Small amounts of a new species formed (16.6 ppm, <2%). A $CDCl_3$ solution of **4** was kept at room temperature for 6 days. The sample darkened, and a ^1H NMR spectrum showed a 64:3:11:6:2:14 mixture of **4** and five new species (δ 5.76, 6.18, 5.89, 5.49 (**3**), 5.40, 5.28). Next, CH_2Cl_2 solutions of **5** were treated with 10 mol % of the weak bases triethylamine and DBU. The ^{31}P NMR signals of the two isomers broadened, but the area ratios (98:2) were unaffected and no new peaks appeared.

(15) Middleton, W. J.; Krespan, C. G. *J. Org. Chem.* **1965**, *30*, 1398.
(16) Analogous trends are well-known for alkenes: Kingsbury, C. A.; Draney, D.; Sopchik, A.; Rissler, W.; Durham, D. *J. Org. Chem.* **1976**, *41*, 3863.
(17) Husted, D. R.; Ahlbrecht A. H. *J. Am. Chem. Soc.* **1952**, *74*, 5422.
(18) Kowalczyk, J. J.; Agbossou, S. K.; Gladysz, J. A. *J. Organomet. Chem.* **1990**, *397*, 333.
(19) Samples of $\mathbf{7}^+X^-$ were isolated as 95:5 mixtures of Re,C configurational diastereomers that differ in the O=C enantioface bound to **I**. We have conducted detailed analyses of such equilibria for other aldehyde complexes of **I**[10f] and sought to determine if 95:5 represented an equilibrium value. Thus, a CD_3NO_2 solution of $\mathbf{7}^+BF_4^-$ was kept at room temperature, and ^{31}P NMR spectra were periodically recorded: 1 day, 97:3; 3 days, 99:1; 6 days, 99:1.

Finally, we wondered whether complexes of **I** and imines of even greater π acidity might give detectable amounts of π isomers. Thus, adducts with *three* electron-withdrawing C═N substituents were sought. However, reactions of **3** with potential halonium ion donors such as Br_2 (−60 °C, $CDCl_3$) or 3,5-dichloro- and 2,4,6-trimethyl-*N*-fluoropyridinium triflate (−80 °C, CH_2Cl_2) gave numerous products, as assayed by ^{31}P and/or ^1H NMR (Scheme 3).

In the same vein, reactions with oxygen atom donors were investigated. This was further prompted by the recent interest in perfluorodialkyloxaziridines, which are powerful yet selective oxidants.[20] We were curious whether chiral transition metal derivatives such as (η^5-C_5H_5)Re(NO)(PPh_3)(NC(CF_3)$_2$O) (**8**; Scheme 3) might be accessible. However, reactions of **3** with *m*-chloroperbenzoic acid (CH_3CN) and dimethyldioxirane (0 °C, acetone) gave only triphenylphosphine oxide, as assayed by ^{31}P NMR. A reaction of **6** and *m*-chloroperbenzoic acid gave more than 10 products. In a carefully optimized experiment, the perfluorodialkyloxaziridine **9** (Scheme 3)[21] was added to a frozen $CHCl_3$ solution of **3** in an NMR tube. The sample was warmed to −20 °C, and a ^{31}P NMR spectrum showed a multitude of resonances between 10 and 15 ppm.

Discussion

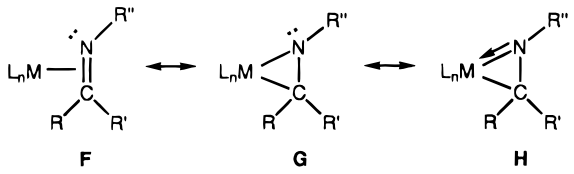
This study, together with earlier data,[5,6] establishes that imine complexes of **I** show a *much* stonger preference for a σ-binding mode than ketone or aldehyde complexes of **I**. By all presently available criteria, but subject to the IR detection limits noted above, *N*-protio acetaldimine (HN═$CHCH_3$),[5a] bis(trifluoromethyl)ketimine (HN═C(CF_3)$_2$), and trifluoroacetaldimine (HN═C(CF_3)H) ligands give only σ isomers. In contrast, acetaldehyde,[10a] 1,3-difluoroacetone,[8] and trifluoroacetaldehyde ligands give only π isomers.

After the fact, these differences can be easily rationalized on the basis of electronic effects. First, nitrogen donor ligands are usually much stronger σ bases than analogous oxygen donor ligands. In contrast, there are to our knowledge no data that show C═N π linkages to be markedly better donors than C═O π linkages. Second, the rhenium fragment **I** is a strong π donor, with the d orbital HOMO shown in Scheme 1. As would be expected from overlap considerations, and evidenced by the trends in IR ν_{NO} values described above, back-bonding to ligand acceptor orbitals is more pronounced in π isomers. These interactions would be stronger with the more electronegative C═O linkages.

Steric factors also deserve consideration. Aldehydes and ketones have two C═X substituents, whereas imines have three. Thus, there is greater potential for destabilizing steric interactions with the metal fragment in π-imine complexes. However, imines also have an additional substituent on the ligating atom in the σ binding mode. Hence, steric effects on π/σ ratios for C═O vs C═N donor ligands are likely to be small.

As noted above, some π-imine complexes have been reported.[3] However, to our knowledge, these all involve metal fragments that (1) are highly electropositive, such as (η^5-C_5H_5)$_2$Zr(L),[3b,e] or (2) have less than 16 valence electrons, such as (η^5-C_5Me_5)Ta(CH_3)$_2$,[3a,f] Ta(OAr)$_2$(Cl)$_2$,[3c] Ta(OAr)$_2$(L),[3d] W(NR)(NR′R″)(CH_3),[3g] (bipy)Ni,[3h] and (Ph_3P)$_2$Pd.[3i] In the latter category, the π-binding mode may be stabilized by a donor interaction involving the nitrogen lone pair, as illustrated in **H** in Chart 3.

Chart 3. Possible Resonance Forms for η^2-Imine Complexes



Finally, there is currently much interest in metal-catalyzed hydrogenations of imines, particularly with regard to enantioselective syntheses of chiral amines.[11,22] Especially for mid- and late-transition-metal catalysts such as rhodium(I), there are major questions concerning the nature of the hydride transfer steps. Many proposals feature an initial σ to π isomerization of the imine ligand. Although our data do not exclude this possibility, they do indicate that such processes would normally be distinctly endothermic. There have been insightful suggestions that π isomers may in certain cases be stabilized by hydrogen bonding between the imine nitrogen and an alcohol ligand.[11] Regardless, there do not at this time appear to be any well-precedented mechanistic alternatives, leaving open the tantalizing possibility that some heretofore unrecognized type of bond activation or insertion process may be operative.

Experimental Section

General Data. General procedures were given in an earlier paper.[5a] Solvents were treated as follows: CH_2Cl_2, distilled from CaH_2; THF and ether, distilled from K/benzophenone, chlorobenzene, distilled from P_2O_5; acetone, benzene, heptane, pentane, $CDCl_3$, and CD_3NO_2, used as received. Reagents were used as received from common commercial sources, except for **9** (Scheme 3),[21] which was generously provided by Dr. István Horváth (Exxon). The *n*-BuLi was standardized.[23] NMR spectra were recorded at ambient probe temperature and referenced as follows: ^1H, $Si(CH_3)_4$ (δ 0.00), CHD_2NO_2 (δ 4.33); ^{13}C, $CDCl_3$ (77.0 ppm); ^{31}P, external 85% H_3PO_4 (0.00 ppm); ^{19}F, $CFCl_3$ (0.00 ppm). All coupling constants (*J*) are in hertz. Mass spectra were obtained on a Finnigan MAT 95 high-resolution instrument ((+)-FAB, 5 kV, 3-nitrobenzyl alcohol/CH_2Cl_2 matrix).

(η^5-C_5H_5)Re(NO)(PPh_3)(N̈═C(CF_3)$_2$) (3). A Schlenk flask was charged with [(η^5-C_5H_5)Re(NO)(PPh_3)(NH_3)]$^+$TfO$^-$ (**1**;[12,13] 0.783 g, 1.10 mmol) and THF (25 mL) and cooled to −80 °C (acetone/CO_2). Then *n*-BuLi (0.148 mL, 1.11 mmol, 7.5 M in hexanes) was added dropwise with stirring. In a second flask, hexafluoroacetone trihydrate (2 mL) was added to stirred concentrated H_2SO_4 that had been cooled to −80 °C. The cold bath was removed, and after ca. 1 h was replaced with a 60 °C bath. The gaseous hexafluoroacetone[24] was condensed into the first flask. The cold bath was removed from the first flask. After 1 h, solvent was removed by rotary evaporation. The residue was dissolved in benzene (30 mL), and the solution was filtered through a silica gel plug. The plug was rinsed with benzene (100 mL), leaving a brown-red band (**1**; elutes with acetone). Heptane (20 mL) was added to the filtrate, and solvent was removed by rotary evaporation. The orange powder was collected by filtration, washed with pentane, and dried by oil pump vacuum to give **3** (0.452 g, 0.639 mmol, 58%), mp 221−223 °C dec. A portion was dissolved in benzene, and pentane was slowly added by vapor diffusion. This gave deep red crystals of **3**. Anal. Calcd for $C_{26}H_{20}F_6N_2OPRe$: C, 44.12; H, 2.85. Found: C, 44.25; H, 2.75. IR (cm^{-1}, KBr/CH_2Cl_2): ν_{NO} 1648/1649 (vs). NMR ($CDCl_3$): ^1H (δ) 7.36−7.17 (m, 3Ph), 5.49 (s, C_5H_5); $^{13}C\{^1H\}$ (ppm) 133.6 (d, $^2J_{CP}$ = 11.1, *o*-Ph), 132.4 (d, $^1J_{CP}$ = 55.8, *i*-Ph), 130.8 (d,

(20) (a) DesMarteau, D. D.; Donadelli, A.; Montanari, V.; Petrov, V. A.; Resnati, G. *J. Am. Chem. Soc.* **1993**, *115*, 4897. (b) Reiser, O. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 69.

(21) Petrov, V. A.; DesMarteau, D. D. *J. Org. Chem.* **1993**, *58*, 4754.

(22) Leading references to a rapidly growing literature: (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703. (b) Lensink, C.; de Vries, J. G. *Tetrahedron: Asymmetry* **1992**, *3*, 235. (c) Burk, M. J.; Feaster, J. E. *J. Am. Chem. Soc.* **1992**, *114*, 6266. (d) Bakos, J.; Orosz, A.; Heil, B.; Laghmari, M.; Lhoste, P.; Sinou, D. *J. Chem. Soc., Chem. Commun.* **1991**, 1684. (e) Ng Cheong Chan, Y.; Osborn, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9400.

(23) Winkle, M. R.; Lansinger, J. M.; Ronald, R. C. *J. Chem. Soc., Chem. Commun.* **1980**, 87.

(24) Haszeldine, R. N. *J. Chem. Soc.* **1954**, 1273.

$^4J_{CP}$ = 2.1, *p*-Ph), 128.5 (d, $^3J_{CP}$ = 10.9, *m*-Ph), 116.7 (q, $^1J_{CF}$ = 284, $2CF_3$), 95.7 (s, C_5H_5); $^{13}C\{^{19}F\}$ (ppm, partial) 154.6 (s, C═N), 116.7 (s, $2CF_3$); ^{19}F (ppm) 109.7 (s, $2CF_3$); $^{31}P\{^1H\}$ (ppm) 19.6 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(η^1-N(H)═C(CF_3)$_2$)]$^+$TfO$^-$ (4). A. A 5-mm NMR tube was charged with **3** (0.064 g, 0.090 mmol) and capped with a septum. Then $CDCl_3$ (0.8 mL) and TfOH (0.008 mL, 0.090 mmol) were sequentially added. The deep red solution contained only **4**, as assayed by NMR.

B. A Schlenk flask was charged with **3** (0.134 g, 0.189 mmol), ether (10 mL), and a stir bar and cooled to −45 °C (CH_3CN/CO_2). Then TfOH (0.018 mL, 0.202 mmol) was added dropwise with stirring, and the cold bath was removed. After 3 h, the red-orange powder was collected by filtration, washed with pentane, and dried by oil pump vacuum to give **4** (0.156 g, 0.182 mmol, 96%), mp 161−163 °C dec. Anal. Calcd for $C_{27}H_{21}F_9N_2O_4PReS$: C, 37.80; H, 2.47. Found: C, 37.97; H, 2.55. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1723 (vs). MS: *m*/*z* 709 (M^+, 100%). NMR ($CDCl_3$): ^1H (δ) 14.78 (s, NH), 7.63−7.44 (m, 9H of 3Ph), 7.40−7.26 (m, 6H of 3Ph), 5.75 (s, C_5H_5); $^{13}C\{^1H\}$ (ppm) 153.3 (d sep, $^2J_{CF}$ = 37.4, $^3J_{CP}$ = 3.1, C═N), 133.3 (d, $^2J_{CP}$ = 10.9, *o*-Ph), 131.9 (d, $^4J_{CP}$ = 2.6, *p*-Ph), 129.4 (d, $^3J_{CP}$ = 10.9, *m*-Ph), 129.2 (d, $^1J_{CP}$ = 57.6, *i*-Ph), 120.3 (q, $^1J_{CF}$ = 322.2, SCF_3), 117.3, 116.1 (2q, $^1J_{CF}$ = 278, 279, 2CCF_3), 94.8 (s, C_5H_5); $^{13}C\{^{19}F\}$ (ppm, partial) 153.1 (dd, $^2J_{CH}$ = 8, $^3J_{CP}$ = 3, C═N), 117.3, 116.1 (2d, $^3J_{CH}$ = 14.1, 8.6, 2CCF_3); ^{19}F (ppm) 110.6, 109.7 (2q, $^4J_{FF}$= 7, 7, 2CCF_3), 98.3 (s, SCF_3); $^{31}P\{^1H\}$ 12.2 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(η^1-N(H)═C(CF_3)H)]$^+$TfO$^-$ (5). A. A 5-mm NMR tube was charged with **6** (0.021 g, 0.033 mmol) and capped with a septum. Then CH_2Cl_2 (0.8 mL) and TfOH (0.003 mL, 0.033 mmol) were sequentially added. The yellow-orange solution contained only **5** (98:2 mixture of isomers), as assayed by ^{31}P NMR.

B. A Schlenk flask was charged with **1** (0.802 g, 1.13 mmol) and THF (50 mL) and cooled to −80 °C. Then *t*-BuO$^-$K$^+$ (1.25 mL, 1.25 mmol, 1.0 M in THF) was added dropwise with stirring. In a second flask, trifluoroacetaldehyde hydrate (1 mL) was added to stirred concentrated H_2SO_4. The mixture was refluxed using a heat gun. The gaseous trifluoroacetaldehyde[17] was passed over P_2O_5 and condensed into the first flask. The mixture was stirred for 1 h; then the cold bath was removed. After 2 h, TfOH (0.200 mL, 2.26 mmol) was added and solvent was removed by oil pump vacuum. The residue was dissolved in CH_2Cl_2 (ca. 50 mL), stirred over charcoal (0.5 h), and filtered through Celite. The filtrate was concentrated by rotary evaporation to ca. 2 mL, and hexane was added (100 mL). A bright yellow precipitate formed, which was collected by filtration, washed with pentane, and dried by oil pump vacuum to give **5** (0.753 g, 0.954 mmol, 84%; 98:2 mixture of isomers), mp 210−212 °C dec. Anal. Calcd for $C_{26}H_{22}F_6N_2O_4PReS$: C, 39.55; H, 2.81. Found: C, 39.59; H, 2.85. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1703 (vs). NMR ($CDCl_3$): ^1H (δ) 14.07 (d, $^3J_{HH}$ = 18.7, NH), 7.59−7.50 (m, 9H of 3Ph), 7.38−7.25 (m, 6H of 3Ph), 7.05 (ddq, $^4J_{HP}$ = 1.9, $^3J_{HF}$ = 4.8, $^3J_{HH}$ = 18.7, HC═N), 5.75/5.56 (2s, C_5H_5, major/minor); $^{13}C\{^1H\}$ (ppm) 156.6 (dq, $^2J_{CF}$ = 41.5, $^3J_{CP}$ = 2.6, C═N), 133.6 (d, $^2J_{CP}$ = 10.4, *o*-Ph), 132.0 (d, $^4J_{CP}$ =2.1, *p*-Ph), 129.6 (d, $^3J_{CP}$ = 11.1, *m*-Ph), 129.2 (d, $^1J_{CP}$ = 57.9, *i*-Ph), 120.7 (q, $^1J_{CF}$ = 320, SCF_3), 116.1 (dq, $^4J_{CP}$ = 1.1, $^1J_{CF}$ = 277, CCF_3), 94.1/93.5 (2s, C_5H_5, major/minor); ^{19}F (ppm) 108.3/107.8 (2d, $^3J_{FH}$ = 5.9, 4.6 CCF_3, minor/major), 98.3 (s, SCF_3); $^{31}P\{^1H\}$ (ppm) 19.6/14.7 (2s, major/minor).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(N̈═C(CF_3)H) (6). A. A 5-mm NMR tube was charged with **5** (0.020 g, 0.025 mmol) and capped with a septum. Then CH_2Cl_2 (0.8 mL) and *t*-BuO$^-$ K$^+$ (0.025 mL, 0.025 mmol, 1.0 M in THF) were sequentially added. The orange solution contained only **6**, as assayed by $^{31}P\{^1H\}$ NMR.

B. A Schlenk flask was charged with **5** (0.232 g, 0.294 mmol) and THF (40 mL) and cooled to 0 °C. Then *t*-BuO$^-$K$^+$ (0.323 mL, 0.323 mmol, 1.0 M in THF) was added dropwise with stirring. After 1 h, the cold bath was removed. After another 1 h, solvent was removed by oil pump vacuum. Benzene (50 mL) was added to the residue, and the sample was filtered through Celite. Heptane (10 mL) was added to the filtrate, and the solution was slowly concentrated by rotary evaporation. A bright orange precipitate formed, which was collected by filtration, washed with pentane, and dried by oil pump vacuum to give **6** (0.133 g, 0.208 mmol, 82%), mp 217−219 °C dec. Anal. Calcd for $C_{25}H_{21}F_3N_2OPRe$: C, 46.95; H, 3.31. Found: C, 47.02; H, 3.32. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1640 (vs). NMR ($CDCl_3$): ^1H (δ) 7.48−7.31 (m, 3Ph, HC═N), 5.44 (s, C_5H_5); $^{13}C\{^1H\}$ (ppm) 141.5 (dq, $^2J_{CF}$ = 35.8, $^3J_{CP}$ = 4.2, C═N), 134.0 (d, $^2J_{CP}$ = 10.4, *o*-Ph), 132.5 (d, $^1J_{CP}$ = 55.0, *i*-Ph), 130.8 (d, $^4J_{CP}$ = 2.1, *p*-Ph), 128.7 (d, $^3J_{CP}$ = 10.9, *m*-Ph), 117.5 (dq, $^1J_{CF}$ = 279, $^4J_{CP}$ = 2.1, CF_3), 94.8 (d, $^2J_{CP}$ = 1.6, C_5H_5); ^{19}F (ppm) 105.6 (s, CF_3); $^{31}P\{^1H\}$ (ppm) 24.9 (s).

[(η^5-C_5H_5)Re(NO)(PPh$_3$)(η^2-O═C(CF_3)H)]$^+$X$^-$ (7$^+$X$^-$). A. A Schlenk flask was charged with (η^5-C_5H_5)Re(NO)(PPh_3)(CH_3) (0.574 g, 1.03 mmol)[25] and chlorobenzene (20 mL) and cooled to −45 °C (acetonitrile/CO_2). Then HBF_4·OEt_2 (0.188 mL, 1.13 mmol, 6.0 M) was added dropwise with stirring.[18] In a second flask, trifluoroacetaldehyde was generated as described above, and it was then condensed into the first flask. The mixture was stirred for 12 h while the bath slowly warmed to room temperature. A tan precipitate formed, which was collected by filtration, washed with pentane, and dried by oil pump vacuum to give **7**$^+$$BF_4^-$ (0.593 g, 0.814 mmol, 79%; 95:5 mixture of isomers).[10f,19] IR (cm^{-1}, CH_2Cl_2/KBr): ν_{NO} 1762/1769 (vs). MS: *m*/*z* 642 (**7**$^+$, 52%), 544 (**I**$^+$, 100%); theoretical mass = 642.08216 amu, measured mass = 642.07833 amu.

B. A round-bottom flask was charged with **7**$^+$$BF_4^-$ (0.081 g, 0.111 mmol), $Bu_4N^+TfO^-$ (0.870 g, 2.22 mmol), and acetone (200 mL). The mixture was stirred for 1 h, and solvent was removed by rotary evaporation. The olive oily residue was kept at room temperature, and light yellow crystals began to form. After 2 h, these were collected on a frit, washed with ether/CH_2Cl_2 (100 mL, 50:50 v/v), and pentane (50 mL), and dried by oil pump vacuum to give **7**$^+$TfO$^-$ (0.010 g, 0.013 mmol, 12%; 95:5 mixture of isomers).[10f,19] The ^1H, ^{31}P, and ^{19}F NMR spectra ($CDCl_3$) were identical with those of the byproduct that often accompanied **5** (vide supra). The ^{19}F NMR spectrum also showed that metathesis (BF_4^-/TfO^-) was complete. IR (cm^{-1}, CH_2Cl_2): ν_{NO} 1764 (vs). NMR (**7**$^+$$BF_4^-$, CD_3NO_2, partial): ^1H (δ) 7.80−7.48 (m, 3Ph), 6.36/6.29 (2s, C_5H_5, major/minor), 5.46/5.25 (2dq, $^3J_{HP}$ = 2.3/0.9, $^3J_{HF}$ = 6.0/6.2, HC═O, major/minor); ^{19}F (ppm) 108.5/109.3 (2d, $^3J_{FH}$ = 5.8/6.0, CCF_3, major/minor), 26.3 (s, BF_4); $^{31}P\{^1H\}$ (ppm) 12.9/12.3 (2s minor/major). NMR (**7**$^+$$TfO^-$, $CDCl_3$, partial): ^1H (δ) 7.59−7.25 (m, 3Ph), 6.23/6.21 (2s, C_5H_5, major/minor), 5.56 (dq, $^4J_{HP}$ = 2, $^3J_{HF}$ = 6, HC═O); $^{13}C\{^1H\}$ (ppm) 133.4 (d, $^4J_{CP}$ = 2.8, *p*-Ph), 130.1 (d, $^3J_{CP}$ = 11.9, *m*-Ph), 126.1 (d, $^1J_{CP}$ = 61.1, *i*-Ph), 100.7/90.9 (2s, C_5H_5, major/minor), 64.5 (q, $^2J_{CF}$ = 41, C═O); ^{19}F (ppm) 107.4/108.3 (2d, $^3J_{FH}$ = 4.6/5.9 CCF_3, major/minor), 98.3 (s, SCF_3); $^{31}P\{^1H\}$ (ppm) 11.6/10.9 (2s, minor/major).

Acknowledgment. We thank DOE for support of this research.

IC960302V

(25) Agbossou, F.; O'Connor, E. J.; Garner, C. M.; Quirós Méndez, N.; Fernández, J. M.; Patton, A. T.; Ramsden, J. A.; Gladysz, J. A. *Inorg. Synth.* **1992**, *29*, 211.