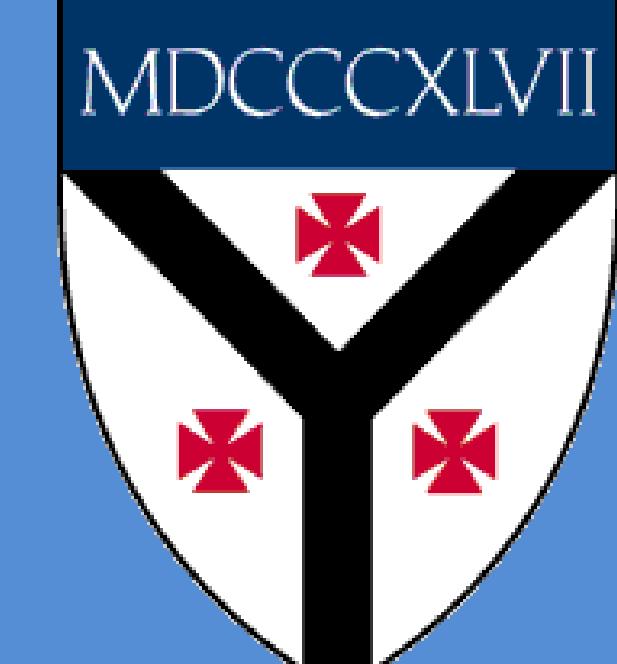




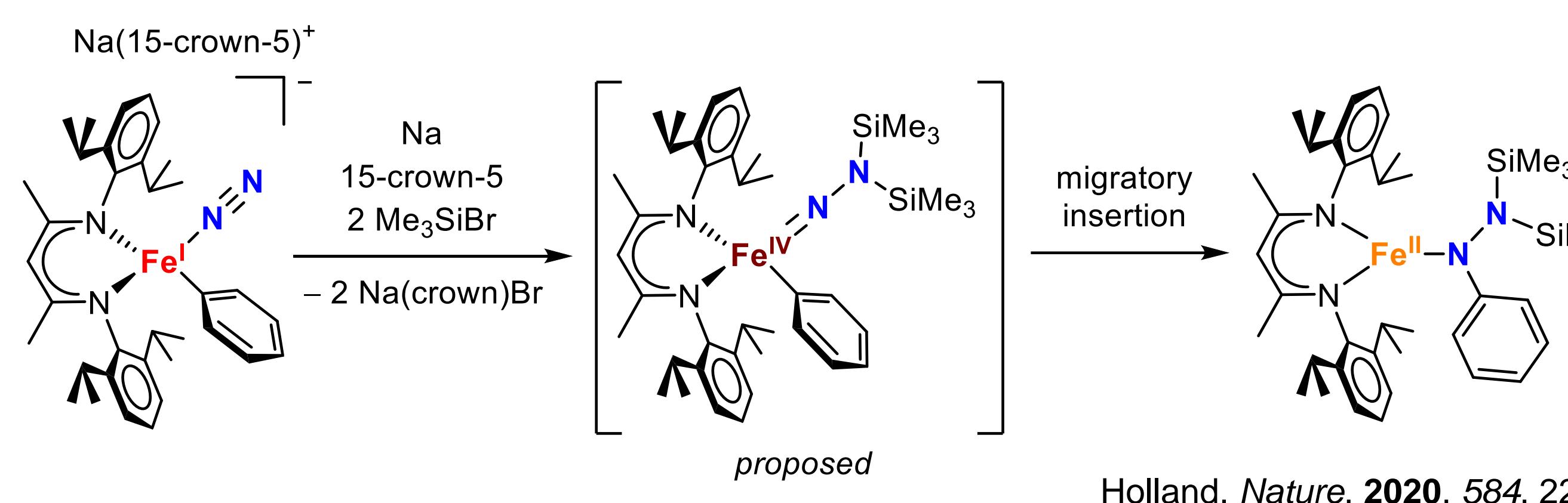
Migratory Insertion of Hydrocarbyl Groups to Dinitrogen Via a High-Valent Iron(IV) Hydrazido Intermediate



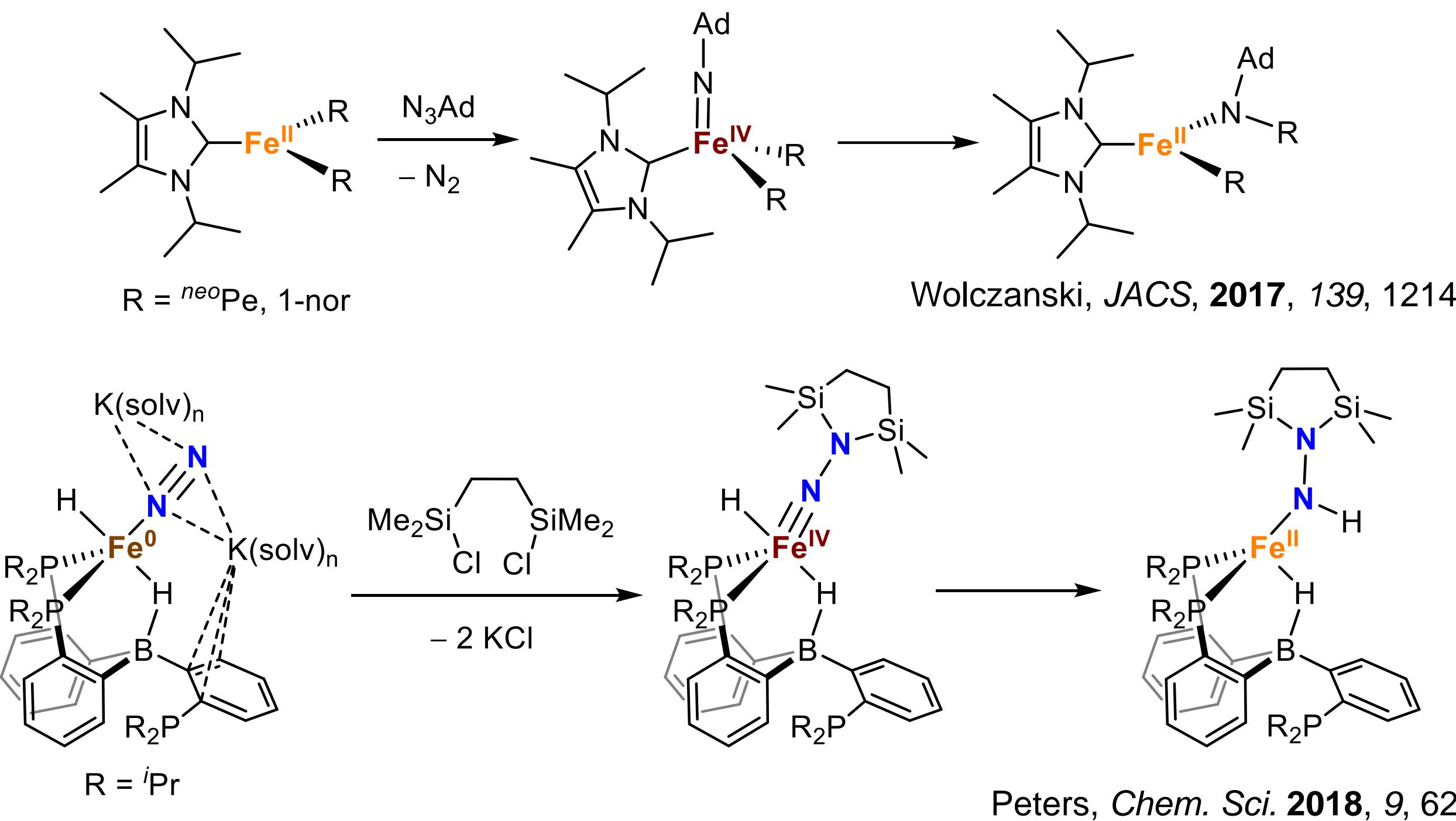
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1. Background

The Holland group recently reported a system in which the C–H activation of benzene was coupled with N₂ binding to form aniline. N–C bond formation was proposed to occur via aryl group migration from Fe to N₂ after disilylation to give a transient iron(IV) hydrazido species



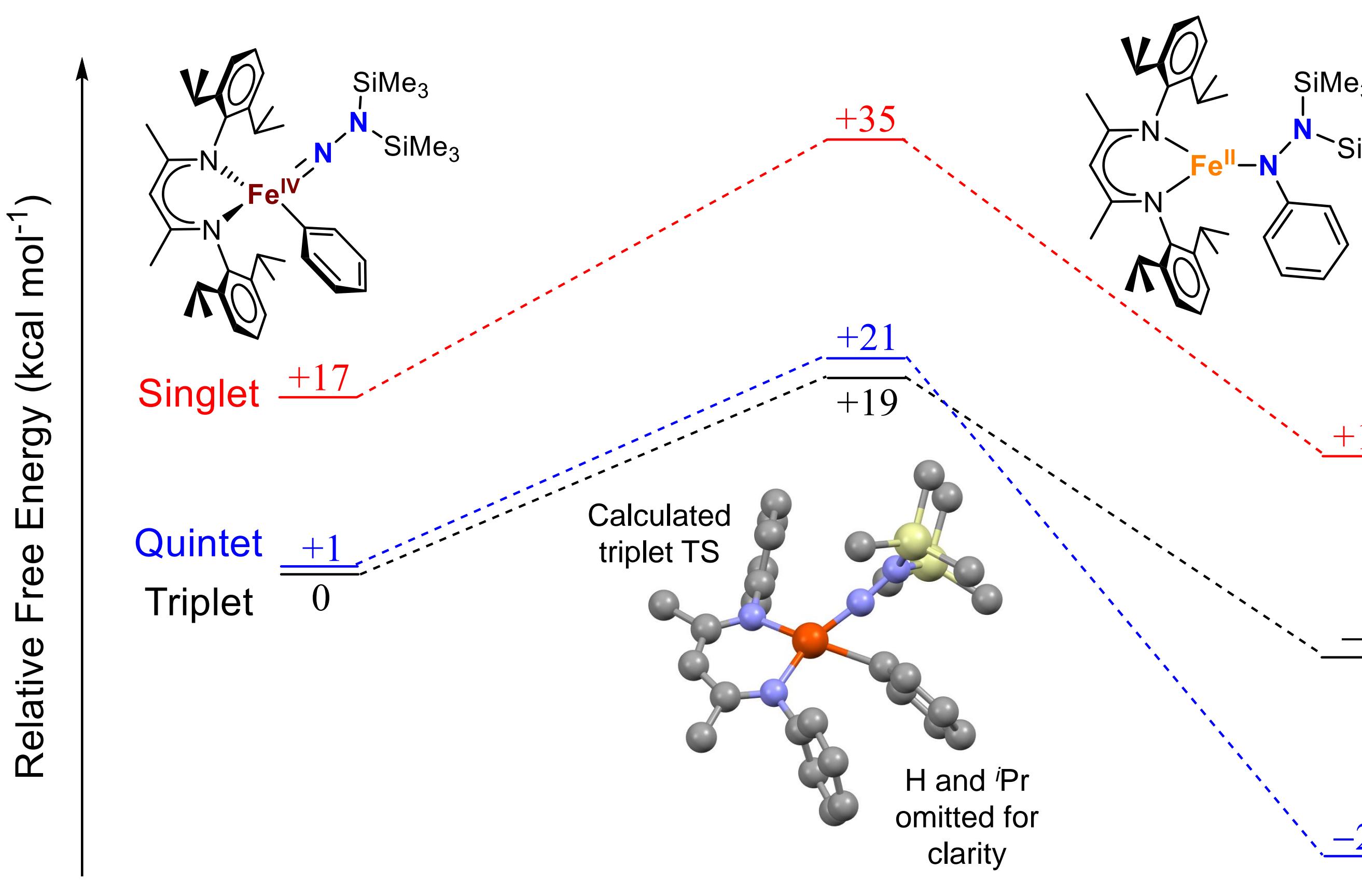
Literature precedent for migration to N from iron(IV):



Understanding this transformation may allow for generalization of hydrocarbyl migration to N₂ to other systems

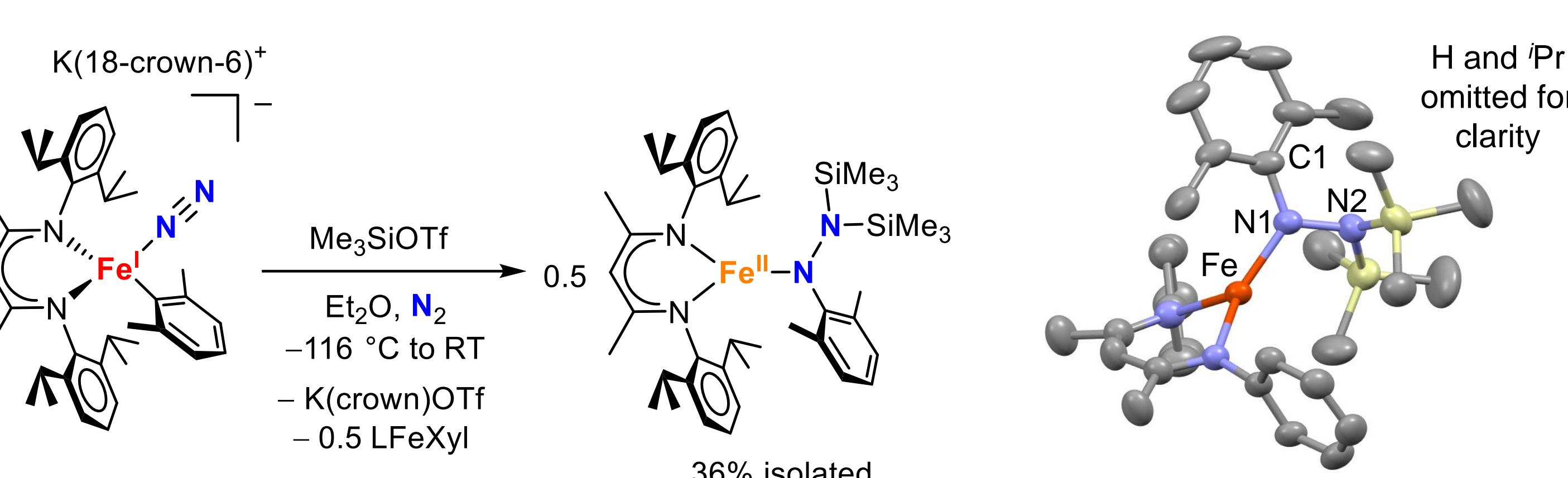
2. DFT Calculation of Aryl Migration

Relaxed surface scan calculations indicate barrierless silylation of N₂
Energy barrier of aryl migration investigated by DFT (B3LYP, def2-TZVP)



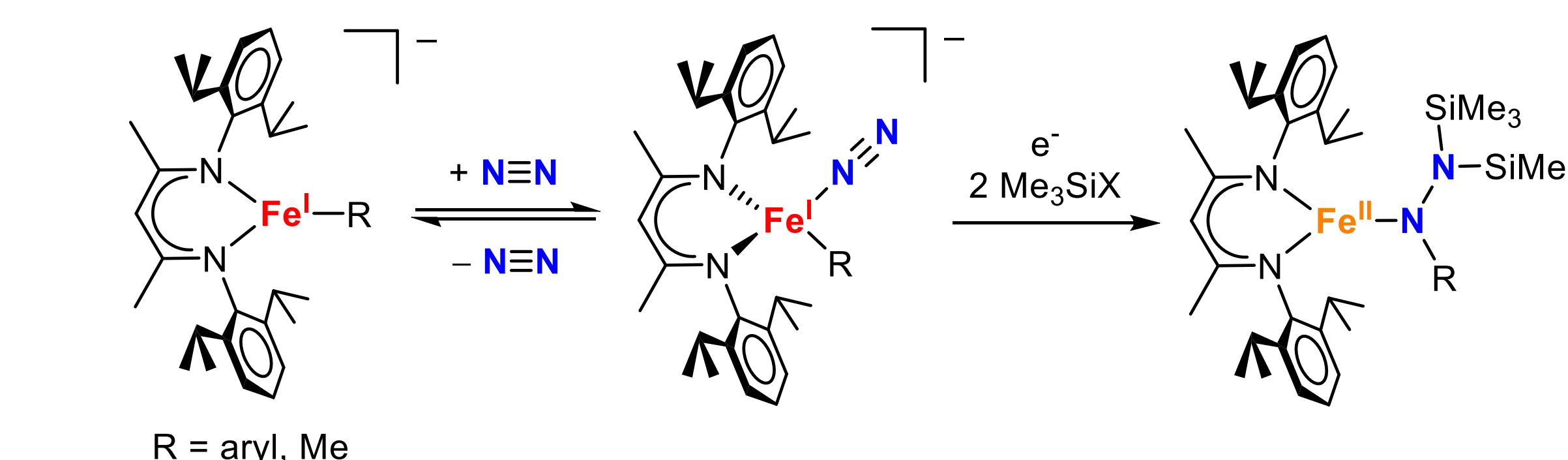
3. Variation of Migrating Group

Increase of steric bulk on aryl group may slow down migration, allow for isolation of proposed iron(IV) intermediate

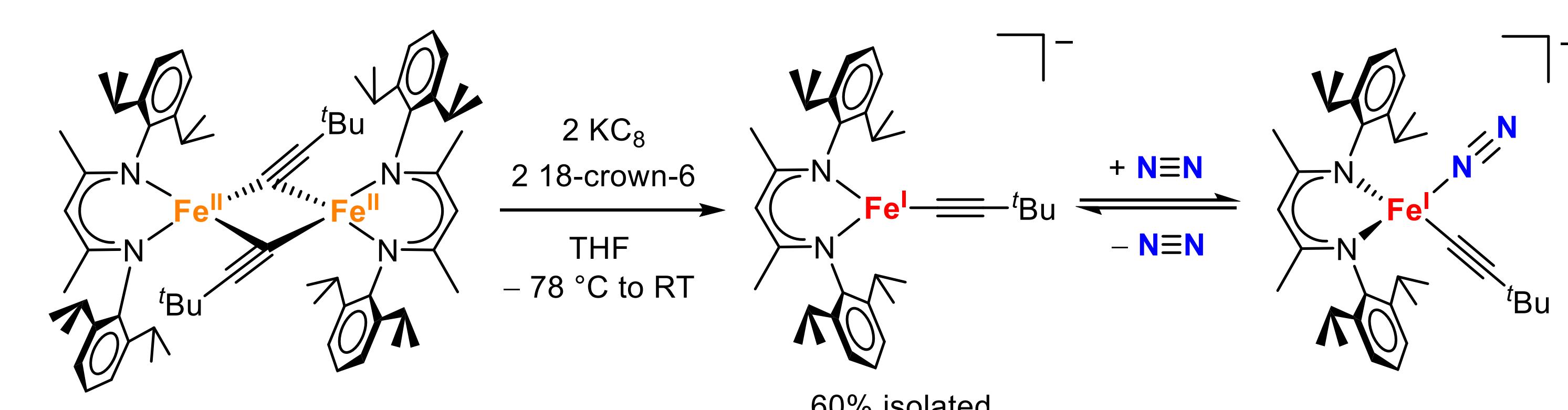


Ortho-methyl groups on phenyl ring not sterically bulky enough to prevent fast migratory insertion, i.e. proposed iron(IV) hydrazido species could not be isolated

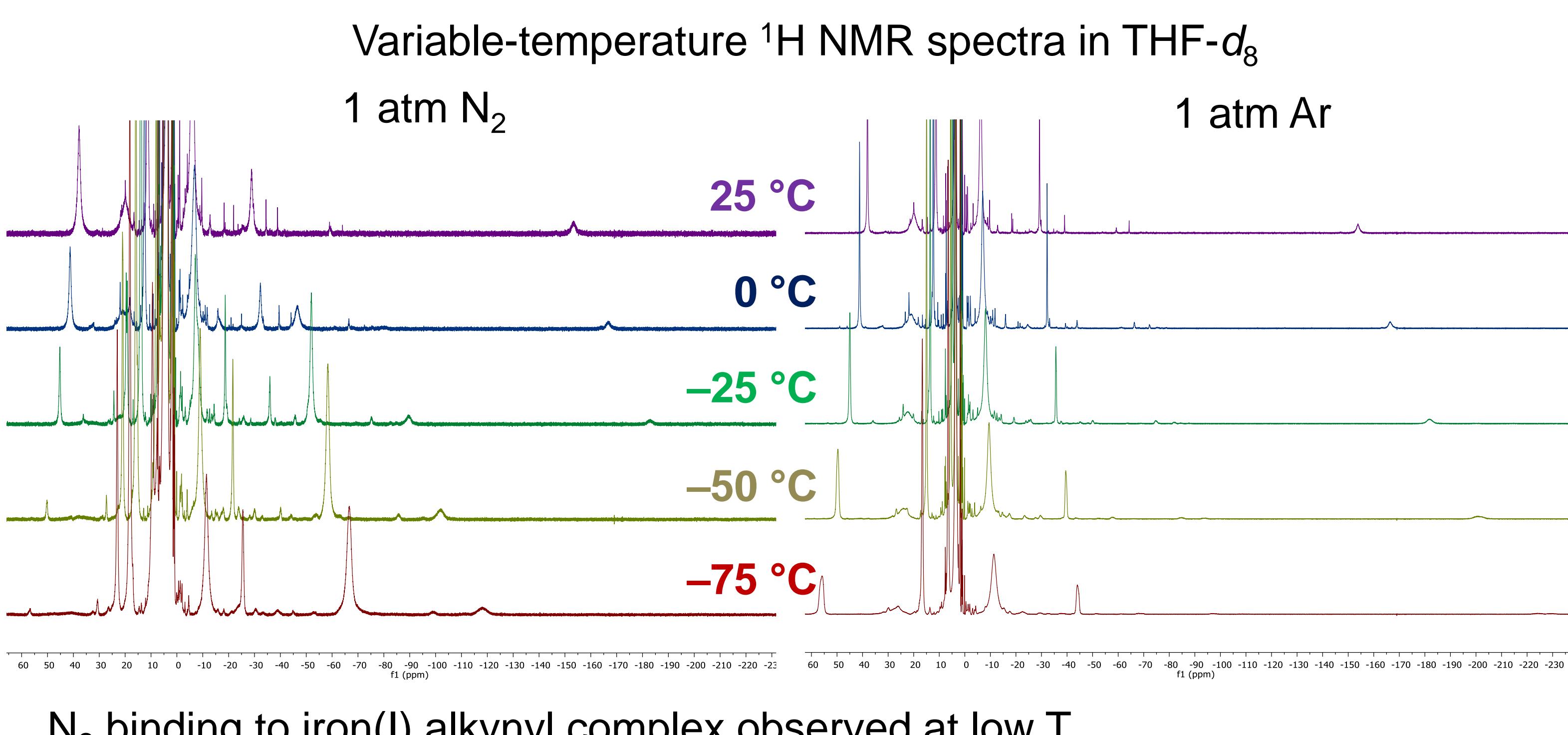
Bond	Dist. (Å)
Fe–N1	1.9593(15)
N1–C1	1.410(2)
N1–N2	1.478(2)



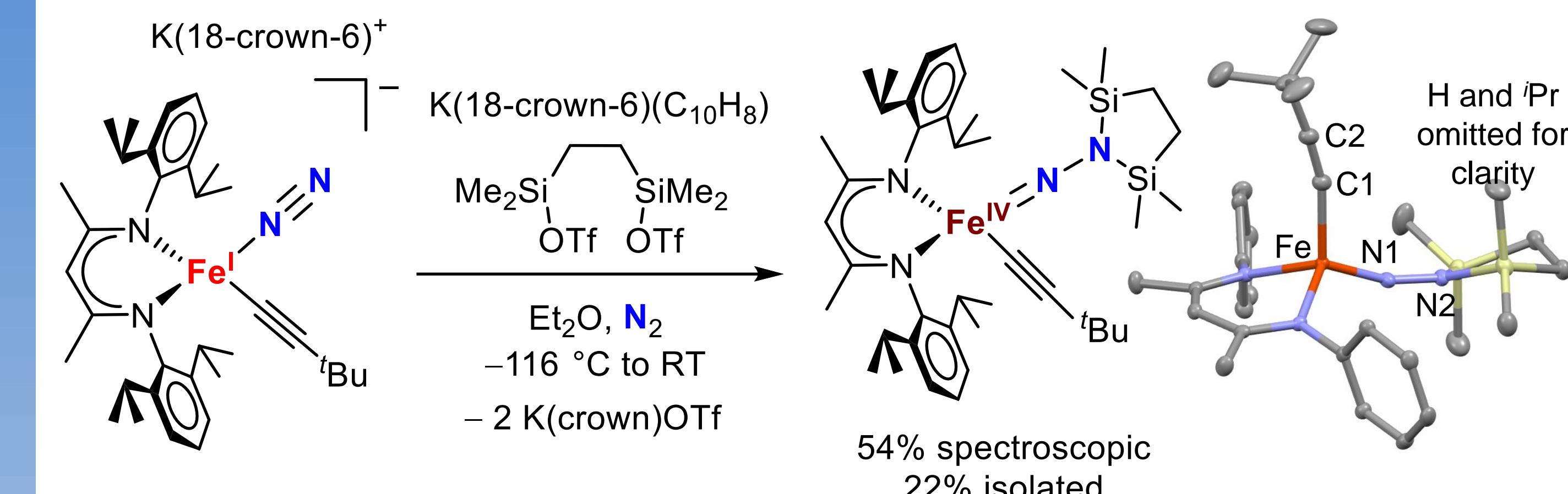
N₂ binding has been observed for iron(I) aryl and alkyl complexes at low T, and migration of the respective ligand occurs upon silylation of N₂; do other hydrocarbyl ligands undergo similar reactivity?



Reduction of iron(II) alkynyl dimer leads to mononuclear three-coordinate iron(I) alkynyl complex



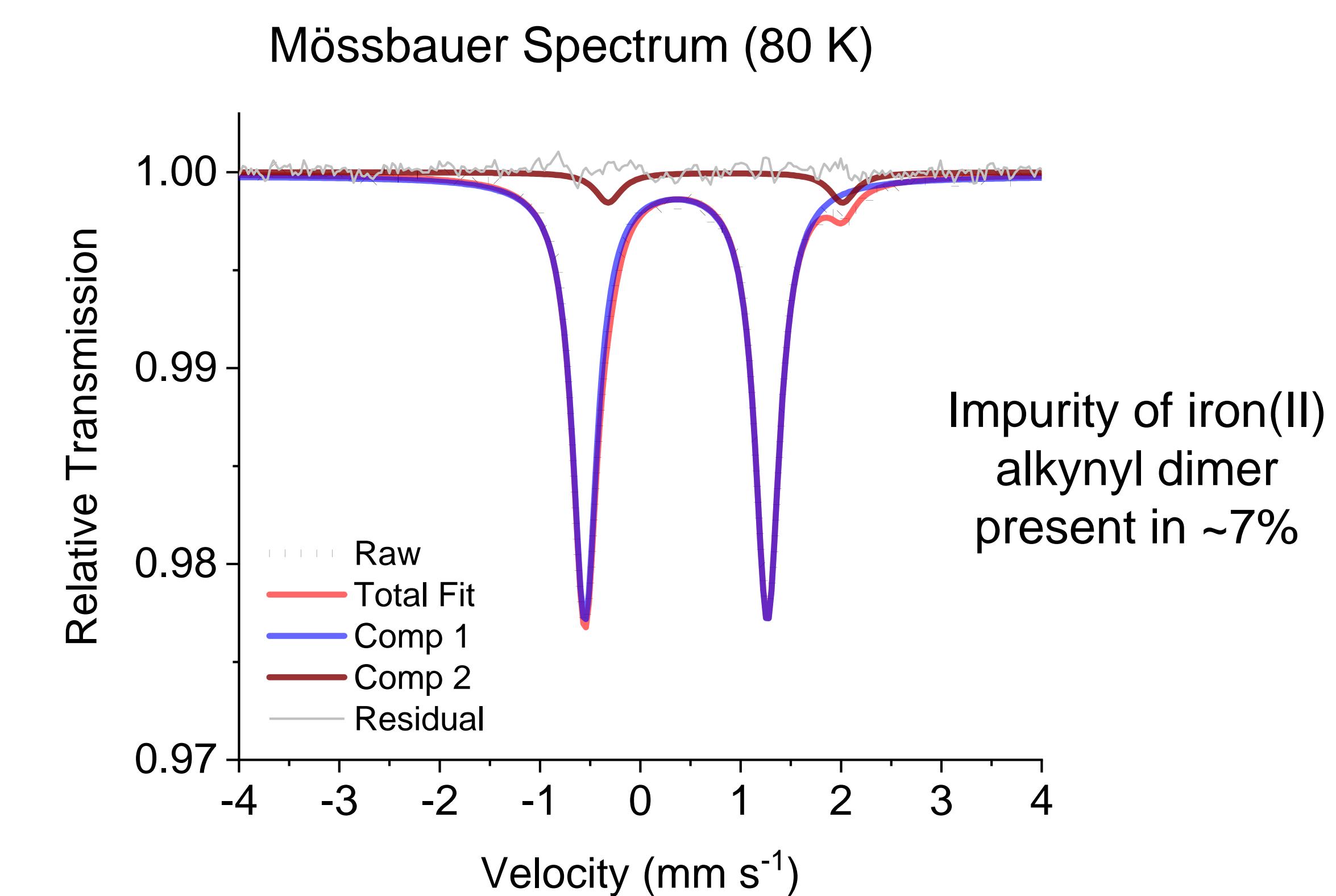
4. Isolation of an Iron(IV) Hydrazido



Use of bis(silyl)ethane reagent allows for favorable intramolecular second silylation

Addition of external reductant increases yield of desired iron(IV) product

Stronger σ-donation from alkynyl ligand likely helps stabilize high-valent iron center



	Expt.	Calc. S = 0	Calc. S = 1	Calc. S = 2
δ (mm s ⁻¹)	0.36	0.039	0.128	0.310
$ \Delta E_Q $ (mm s ⁻¹)	1.83	3.242	1.193	1.759

B3LYP, def2-TZVP

DFT-calculated Mössbauer parameters indicate a high-spin quintet state, differing from calculated lowest energy iron(IV) aryl analogue

Conclusions

- DFT calculations suggest aryl migration is spin-forbidden
- Iron(IV) hydrazido species isolated with alkynyl ligand
- Quintet state of isolated iron(IV) disagrees with calculated lowest energy spin state for analogous aryl species

Acknowledgements

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