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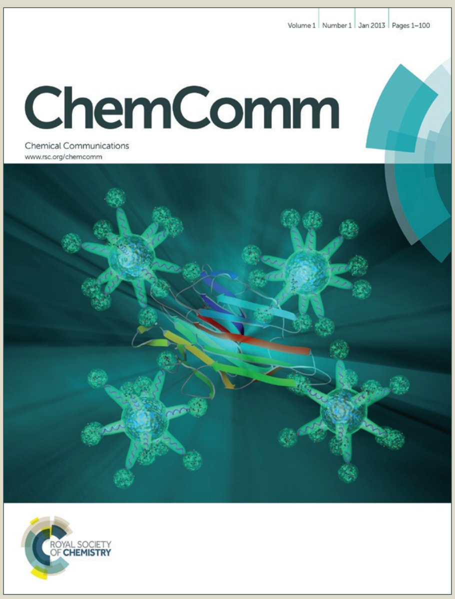

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Neutral Fe(IV) alkylidenes, including some that bind dinitrogen†

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Neutral, formally Fe(IV) alkylidene species are sought as plausible olefin metathesis catalysts, and the synthesis of several is described herein. The complexes are prepared via nucleophilic attack (Nu = MeLi, $PhCH_2K$, 2-picolyllithium, Me_2PCH_2Li, $MePhPCH_2Li$, Ph_2PCH_2Li) at the imine of cationic [*mer*-{κ-C,N,C-(C_6H_4-yl-2-CH=N(2-C_6H_4-C(^{i}Pr)=}$Fe(PMe_3)_3$][B(3,5-CF_3-C_6H_3)$_4$]. In contrast, MeMgCl and mesityllithium displaced and deprotonated bound PMe_3, respectively. Structural details are provided for *mer*-{κ-C,N,C-(C_6H_4-yl-2-CH(Bn)N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_2$}N_2 and {κ-C,N,C,P-(C_6H_4-yl-2-CH(CH_2PMe_2)N(2-C_6H_4-C(^{i}Pr)=}$Fe(PMe_3)_2$.

A Holy Grail of base metal catalysis is the generation of iron complexes capable of catalysing olefin metathesis,[1-3] a reaction currently moderated best by Ru[2,4] and Mo[3,5] species. Hoffmann's critique of olefin metathesis[6] convincingly suggests that d^n ($n \leq 4$) is a necessary constraint for active catalysts, hence Fe(IV) species are crucial targets. Recent work from these laboratories[7] has featured Fe(IV) tetra- and tri-dentate cationic chelates that contain alkylidene fragments created via the protonation[8-12] of Fe(II) vinyl precursors. While the compounds were not metathesis-active, they are the only non-diphenylcarbene,[13-16] alkylidene complexes to be structurally characterized besides [Cp*(dppe)Fe=CH(Me)]PF_6.[17]

In order to eventually obtain catalytically active Fe(IV) alkylidenes, it was suggested[7] that some or all of three additional criteria must be met: 1) coordinative unsaturation is significant, based on the known $16e^-$ Ru precursors and $14e^-$ Mo catalysts; 2) complexes must be neutral or anionic, such that the 3d orbitals of Fe are not contracted; and 3) hydrogen substituted alkylidenes, e.g., Fe=CHR, are more likely to react. In this communication, neutral alkylidenes have been generated, and some reveal instabilities likely associated with coordinative unsaturation.

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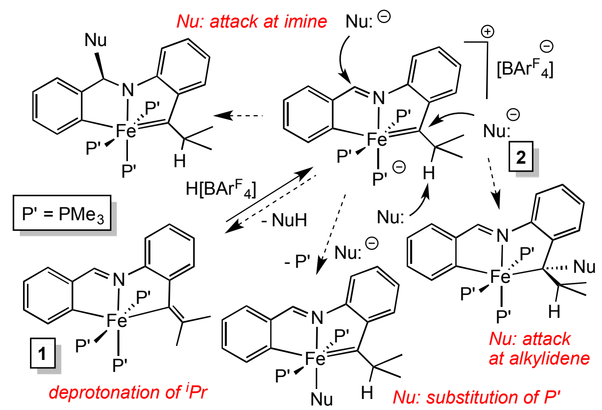
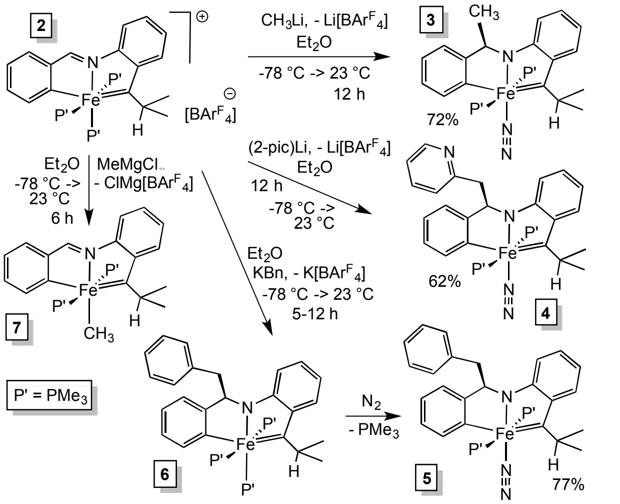
†Electronic Supplementary Information (ESI) available: synthetic details, reproductions of NMR spectra, and crystallographic information (CCDC-1430256, 1430257). See DOI: 10.1039/x0xx00000x



Scheme 1. Plausible reactions of a Nu: with the cationic Fe(IV) alkylidene, [*mer*-{κ-C,N,C-(C_6H_4-yl-2-CH=N(2-C_6H_4-C(^{i}Pr)=}$Fe(PMe_3)_3$] [B(3,5-CF_3-C_6H_3)$_4$] (**2**).

Scheme 1 illustrates possible outcomes of a reaction of an anionic nucleophile with the cationic alkylidene [*mer*-{κ-C,N,C-(C_6H_4-yl-2-CH=N(2-C_6H_4-C(^{i}Pr)=}$Fe(PMe_3)_3$][B(3,5-CF_3-C_6H_3)$_4$] (**2**): 1) deprotonation by $Nu:^-$ can regenerate the Fe(II) vinyl precursor (**1**); 2) the $Nu:^-$ can substitute for PMe_3; 3) $Nu:^-$ attack at the alkylidene affords an Fe(II) species; and 4) $Nu:^-$ attack at the imine provides an Fe(IV) amide complex. Complex **2**[7] was chosen as the starting alkylidene because its bulky isopropyl substituent should hamper deprotonation and attack at the Fe=C(Ar)^{i}Pr. Since substitution is likely to be a dissociative process, imine to amide conversion is the favoured outcome.

Scheme 2 illustrates the synthesis of several neutral Fe(IV) alkylidenes derived from [*mer*-{κ-C,N,C-(C_6H_4-yl-2-CH=N(2-C_6H_4-C(^{i}Pr)=}$Fe(PMe_3)_3$] [B(3,5-CF_3-C_6H_3)$_4$] (**2**).[7] Treatment of **2** with MeLi, 2-picolyllithium,[18] and potassium benzyl afforded the Fe(IV) dinitrogen alkylidenes *mer*-{κ-C,N,C-(C_6H_4-yl-2-CH(R)N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_2$}N_2 (R = Me, **3** (red); 2-pic, **4** (red-orange) Bn, **5** (red-brown)). The substitution of a bulky PMe_3 opposite the amide is expected, based on dinitrogen substitutions in Fe(II) imine-phosphine complexes.[7,19] The bulky ^{i}Pr group labilizes the PMe_3 opposite the N-donor, enabling binding by the thin dinitrogen ligand. Curiously, in the case of MeMgCl, direct substitution of the



Scheme 2. Syntheses of neutral Fe(IV) alkylidene complexes via attack at the chelate imine and substitution of PMe_3.

unique PMe_3 occurred, affording thermally unstable *mer*-{κ-C,N,C-(C_6H_4-yl-2-CH=N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_2$}CH_3 (**7**) in ~80% purity. A triplet (J_{PH} = 11 Hz) at δ -0.65 characterized the Fe-CH_3 in the ^{1}H NMR, and only one ^{31}P signal was observed, consistent with C_s symmetry.

In order to show that the initial product of imine attack is the *mer*-$(PMe_3)_3$ species, dinitrogen was scrupulously kept out of the reaction of **2** with KBn, and magenta *mer*-{κ-C,C-(C_6H_4-yl-2-CH(R)N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_3$ (**6**) was generated in ~80-90% purity. A key feature is an ABC pattern in the ^{31}P NMR spectrum that reflects the low symmetry of the *mer*-$(PMe_3)_3$ derivative.

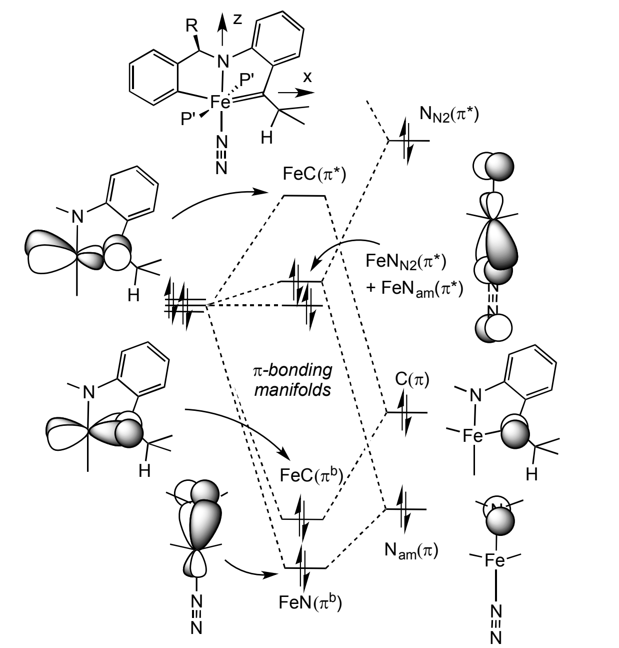


Fig. 1. The iron-alkylidene and amide-iron-dinitrogen π-bonding manifolds of **3**-R-N_2.

The new amide-alkylidenes manifest alkylidene ^{13}C shifts significantly lower[20,21] than previous cationic derivatives (e.g., **2**, δ 348.4): **3**, δ 313.77, J_{PC} = 14 Hz; **4**, δ 313.95, J_{PC} = 13 Hz; **5**, δ 315.55, J_{PC} = 14 Hz; **6**, δ 313.17, td, J_{PC} = 12, 23 Hz; **7**, δ 321.15, J_{PC} = 31 Hz. The asymmetry of each dinitrogen-amide complex is revealed by inequivalent ^{31}P signals at ~13 and ~15 ppm, with J_{PP} ~ 124-127 Hz.

Fig. 1 illustrates the π-bonds affiliated with the alkylidene, amide and dinitrogen. While the Fe=C bond is readily understood as a classic d_{xy}±C(pπ) interaction, the π-bonding to N_2 is more complicated. The dinitrogen ligands exhibit considerable backbonding, with ν(NN) = 2058, 2056, and 2058 cm^{-1} for the respective methyl, 2-picolyl, and benzyl derivatives. The amide d_{yz}-N(pπ) interaction renders the predominantly d_{yz}-orbital closer in energy to the N_2 π*-orbital. This three-orbital interaction is responsible for increased overlap for backbonding to dinitrogen, and some net N(pπ)->Fe(d_{yz}) bonding.

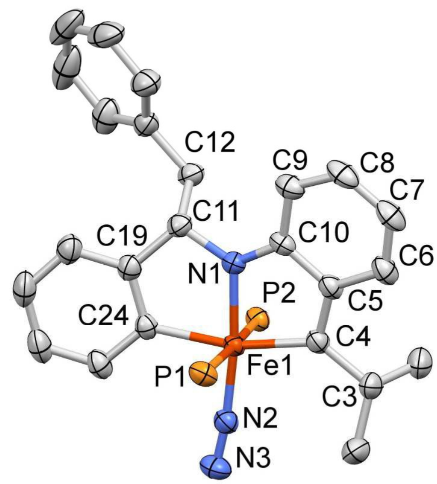


Fig. 2. Molecular view of *mer*-{κ-C,N,C-(C_6H_4-yl-2-CH(Bn)N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_2$}N_2 (**5**). Pertinent interatomic distances (Å) and angles (°): Fe-N1, 1.9299(13); Fe-N2, 1.7925(15); Fe-C4, 1.9535(16); Fe-C24, 2.0206(16); Fe-P1, 2.2679(5); Fe-P2, 2.2523(5); N1-C11, 1.471(2); N1-C10, 1.326(2); C9-C10, 1.434(2); C8-C9, 1.362(3); C7-C8, 1.405(3); C6-C7, 1.364(3); C5-C6, 1.434(2); C5-C10, 1.441(2); C4-C5, 1.420(2); C19-C24, 1.413(2); C11-C19, 1.515(2); N1-Fe-N2, 173.91(6); P1-Fe-P2, 175.45(2); C4-Fe-C24, 163.25(7); L/X-Fe-L/X, 90.0(58) (ave).

Fig. 2 illustrates a molecular view of pseudo-octahedral *mer*-{κ-C,N,C-(C_6H_4-yl-2-CH(Bn)N(2-C_6H_4-C(^{i}Pr)=}Fe{*trans*-$(PMe_3)_2$}N_2 (**5**), and pertinent metrics are listed in its caption. Of crucial importance are the d(N1-C10) = 1.326(2) Å and d(C4-C5) = 1.420(2) Å, which are 0.01-0.02 Å and 0.05 Å shorter than expected,[22] and arene distances that hint at a significant contribution from an Fe(II) representation (Fig. 3). The valence bond structures of the Fe(IV) and Fe(II) resonance forms in Fig. 3. depict whether the respective FeC(π*) (i.e., d^4) or FeC(π^b) (i.e., d^6) in Fig. 1 carry the brunt of the d-orbital contribution.

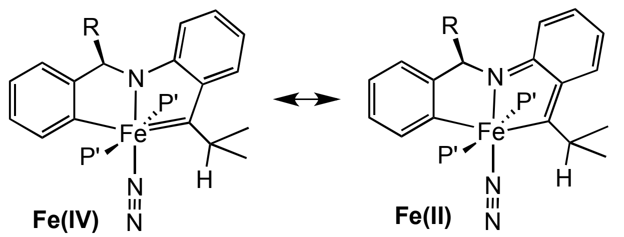
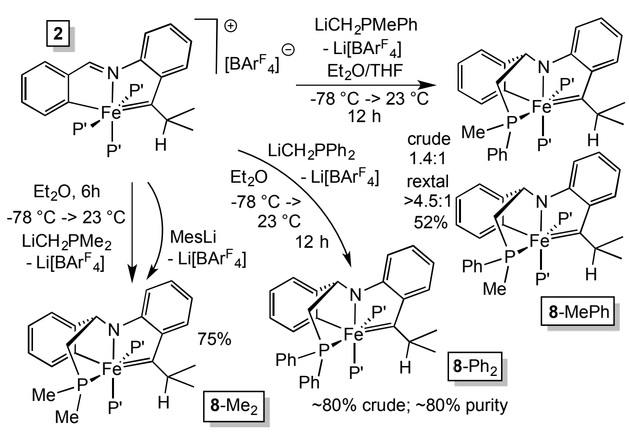


Fig. 3. Fe(IV) and Fe(II) resonance structures for **3**-**5** and related complexes.

The d(Fe=C) is long (1.9535(16) Å) relative to compound **2** (1.899(2) Å), consistent with the change from cation to neutral. The Fe-N$_{am}$ distance of 1.9299(13) Å is normal, as is the iron-nitrogen (N_2) distance of 1.7925(15) Å. The remaining metrics reflect the pseudo-octahedral arrangement, although the C4-Fe-C24 angle is 163.25(7)°, which enables a trace of σ*-character to d_{xz}, a factor that also contributes to effective dinitrogen backbonding.[7]

The use of 2-picolyl in Scheme 2 stemmed from the possibility that it could act as a chelate arm in displacing one of the *trans*-PMe_3 groups. Even though py is a weaker donor than PMe_3, the latter can be removed *in vacuo*, thereby generating a potentially labile py ligand *cis* to the alkylidene.

When the same approach was taken with nucleophiles $LiCH_2PRR'$ (R = R' = Me,[23] Ph;[24] R = Me, R' = Ph)[22] and **2**, displacement of a PMe_3 was affected, resulting in {κ-C,N,C,P-(C_6H_4-yl-2-CH(CH_2PRR')N(2-C_6H_4-C(^{i}Pr)=}Fe(PMe_3)$_2$ (R = R' = Me, **8**-Me$_2$ (magenta); R = Me, R' = Ph, **8**-MePh (red-purple); R = R' = Ph, **8**-Ph$_2$ (oily red), as illustrated in Scheme 3. In a surprising reaction, treatment of **2** with mesityllithium[25] did not result in attack at the imine, but deprotonation of PMe_3 occurred, providing an alternate route to **8**-Me$_2$. While the tetradentate chelate **8**-PMe$_2$ showed appreciable thermal stability, and the diastereomeric mixture **8**-PMePh was also reasonably stable, **8**-Ph$_2$ was thermally sensitive, and any attempts at purification simply increased the amount of degradation products.



Scheme 3. Syntheses of tetradentate chelate complexes {κ-C,N,C,P-(C_6H_4-yl-2-CH(CH_2PRR')N(2-C_6H_4-C(^{i}Pr)=}Fe(PMe_3)$_2$ (**5**-R,R').

The chelates were readily identified by an ABC pattern in the ^{31}P NMR spectrum, with shifts at δ ~12-14, 19-22 and 40-42 for **8**-Me$_2$ and **8**-MePh, while related signals for **8**-Ph$_2$ resonated at δ 13.35, 17.42, and 56.62. The alkylidene ^{13}C NMR resonances for **8**-R,R' are again lower than the related cationic chelates: **8**-Me$_2$, δ 305.79, "t"d, J_{PC} = 18, 11 Hz; **8**-MePh (major), δ 306.48, "t"d, J_{PC} = 20, 12 Hz; **8**-Ph$_2$, δ 306.48, "t"d, J_{PC} = 20, 12 Hz.

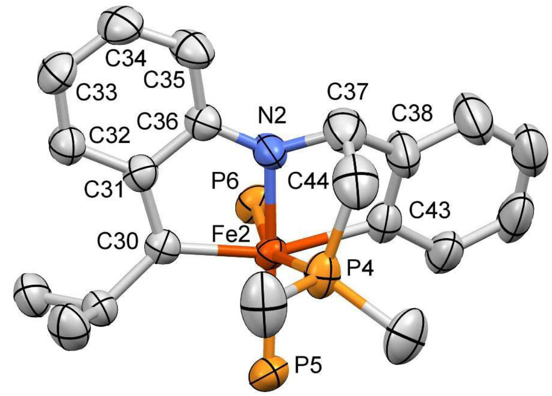


Fig. 4. Molecular view of one of two independent enantiomers of {κ-C,N,C,P-(C_6H_4-yl-2-CH(CH_2PMe_2)N(2-C_6H_4-C(^{i}Pr)=}Fe(PMe_3)$_2$ (**8**-Me$_2$) with PMe_3 methyl groups removed for clarity. Pertinent interatomic distances (Å) and angles (°): Fe2-C30, 1.947(3); Fe2-C43, 2.083(3); Fe2-N2, 1.916(2); Fe2-P4, 2.2142(9); Fe2-P5, 2.2008(9); Fe2-P6, 2.2254(9); N2-C36, 1.329(4); C35-C36, 1.409(4); C34-C35, 1.344(5); C33-C34, 1.390(5); C32-C33, 1.364(4); C31-C32, 1.421(4); C31-C36, 1.420(4); C30-C31, 1.421(4); N2-C37, 1.472(4); C37-C38, 1.493(5); C38-C43, 1.383(5); C37-C44, 1.583(6); P4-C44, 1.820(4); N2-Fe2-P5, 174.84(8); C30-Fe2-C43, 161.30(12); P4-Fe2-P6, 159.69(4).

Two independent enantiomers occupy the asymmetric unit of {κ-C,N,C,P-(C_6H_4-yl-2-CH(CH_2PMe_2)N(2-C_6H_4-C(^{i}Pr)=}Fe(PMe_3)$_2$ (**8**-Me$_2$), and the view of one in Fig. 4 shows the unusual tetradentate chelate that ligates to all but *cis*-sites on an octahedron. The average metrics for **8**-Me$_2$ essentially parallel those of **5**, except that P4, P6, C30 and C43 are all canted away (97.8(29)° ave) from P5. The alkylidene is again long (1.943(6) Å ave), and the short N-C$_{ar}$ (1.329(4) Å ave) and long C$_{alk}$-C$_{ar}$ of 1.426(6) Å (ave) also suggest that the Fe(II) resonance form in Fig. 3 plays a significant role.

The incipient coordinative unsaturation evidenced by the thermal instability of **8**-Ph$_2$ was tested by exposure to alkynes and alkenes. No evidence of olefin metathesis or carbene transfer[26] was obtained, and similar tests of the remaining **8**-R,R' failed to elicit evidence of alkylidene reactivity. Dinitrogen is typically a labile ligand in related systems,[7,27,28] and **3**-**5** was subjected to olefins, but again no substantive reactivity was observed up to degradation temperatures.

Previously, it was suggested that the switch from cationic Fe(IV) alkylidenes to neutral might be crucial to the observation of metathesis reactivity. While the compounds herein have some Fe(II) character (Figs. 1 and 3), the requisite orbital for acceptance of an olefin and generation of a metallacyclobutane is present. It appears certain that the substituents on the alkylidene, in particular the ^{i}Pr group on the neutral species, are deleterious to productive reactivity. As a consequence, the next steps in this synthetic series will be to prepare related Fe(IV)=CHR species that are coordinatively unsaturated or labile.

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Notes and references

Crystal data for **2**-Bn-N$_2$: $C_{30}H_{41}N_3P_2Fe$, *M* = 561.45, monoclinic, P2$_1$/n, *a* = 10.6131(6) Å, *b* = 14.2296(9) Å, *c* = 19.7148(12) Å, β = 97.830(3)°, *V* =

2949.6(3) Å^3, T = 223(2) K, λ = 0.71073 Å, Z = 4, 35866 reflections, 8606 independent, R_{int} = 0.0320, R_1(all data) = 0.0571, wR_2 = 0.1183, GOF = 1.032, CCDC- 1430257.

Crystal data for **5**-Me_2: $C_{26}H_{42}NP_3Fe$, M = 517.37, monoclinic, $P2_1/c$, a = 17.283(3) Å, b = 19.422(3) Å, c = 15.933(3) Å, β = 92.103(8)°, V = 5344.5(16) Å^3, T = 223(2) K, λ = 0.71073 Å, Z = 8, 49309 reflections, 10926 independent, R_{int} = 0.0520, R_1(all data) = 0.0698, wR_2 = 0.1331, GOF = 1.040, CCDC-1430256.

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