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Allenylidene Iron(II) Complexes and Their Deprotonation, Nucleophilic Addition Reactions, and Cathodic Protonation toward Alkynyl Derivatives: A Chemical and Electrochemical Study

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The allenylidene complexes *trans*-[FeBr(=C=C=CRR′)(depe)$_2$][Y] (R = Me, R′ = Ph, **1**; R = R′ = Ph, **2**; R = R′ = Et, **3**; depe = $Et_2PCH_2CH_2PEt_2$; Y = BF_4, BPh_4) were obtained by reaction of *trans*-[FeBr$_2$(depe)$_2$] with the appropriate alkynol HC≡CCRR′(OH), in MeOH and in the presence of Na[BF_4] or Na[BPh_4]. Deprotonation of **3** or nucleophilic γ-addition to **2** led to the neutral enynyl and alkynyl complexes *trans*-[FeBr{−C≡CC(=CHMe)Et}-(depe)$_2$] (**4**) and *trans*-[FeBr(−C≡CCPh$_2$R″)(depe)$_2$] (R″ = CN (**5a**), MeO (**5b**)), respectively. Complex **2** (Y = BPh_4) also leads to the cationic alkynyl compounds *trans*-[Fe(NCMe){−C≡CCPh$_2$(X)}(depe)$_2$][BPh$_4$] (X = NMe$_2$ (**6a**), NHMe (**6b**)) and *trans*-[Fe(NCMe){−C≡CCPh$_2$-(PMe$_3$)}(depe)$_2$]Y$_2$ (Y$_2$ = [BPh$_4$]$_2$ (**7a**), [BPh$_4$]$_{2-x}$Br$_x$ (**7b**)), in acetonitrile solution, upon reaction with NHMe$_2$, NH$_2$Me, and PMe$_3$, respectively. The complexes have been characterized by multinuclear NMR and IR spectroscopy, FAB-MS, and elemental analysis and, in the cases of **5a** and **6a**, also by X-ray diffraction analysis. Controlled-potential electrolysis of **2** yields the alkynyl species *trans*-[FeBr{−C≡CCPh$_2$(H)}(depe)$_2$] (**8**) via a $2e^-/H^+$ process, and the oxidation potential of the complexes, measured by cyclic voltammetry, has allowed us to estimate the electrochemical Pickett (P_L) and Lever (E_L) ligand parameters for the cumulenic ligands. These are then ordered (together with related ligands) according to their net π-electron acceptor minus σ-donor ability as follows: carbynes > aminocarbyne > CO > vinylidenes > aryl allenylidene > alkyl allenylidene > NCR ≫ phosphonium alkynyl > cyanoalkynyl, Br$^-$, NCO$^-$ > alkynyl, enynyl, aminoalkynyl.

Introduction

The dehydration of propargylic alcohols (alkynols), HC≡CCRR′(OH), by transition metals was discovered by Selegue[1] in 1982, providing a general method for the synthesis of compounds containing cumulenic chains such as allenylidene complexes (M=C=C=CRR′), although the first allenylidene complex was synthesized in a different way by Fischer[2] and Berke.[3] The chemistry of the allenylidene complexes has attracted a great deal of interest,[1−64] various factors, such as (i) the significance of complexes with such an unsaturated carbon chain as potential precursors for molecular wires or polymers in the field of new materials with optoelectronics properties (namely liquid crystals and species with nonlinear optical properties),[7,10,14,18−27] (ii) their application in the organic synthesis field[8,28−35] and in

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particular as catalysts, especially Ru complexes, in alkene ring-closing metathesis and ring-opening metathesis polymerization,[8,20,31,34,36−54] and (iii) the search its continuous growth being due to for new or unusual reactivity patterns in stoichiometric processes.[8,55,56]

The allenylidene ligand can undergo further functionalization, which can proceed in a regioselective manner,[27] in view of the electron-deficient character of the C_α and the C_γ carbon atoms (providing nucleophilic attacks) and the electron-rich character of the C_β atom (providing electrophilic attacks).

Nevertheless, allenylidene complexes of iron are still scarce[8,12,21,24,47,57,58,62,64] and, within our interest in the chemistry of alkyne-derived multiple metal−carbon bonded species,[65−71] we have been investigating[60,61] the reactions of alkynols with the iron(II) phosphinic center $\{FeBr(depe)_2\}^+$ (depe = $Et_2PCH_2CH_2PEt_2$). To this end, the cyclic alkynol HC≡CC(C_5H_{10})OH leads to a cyclic allenylidene complex, whereas the linear primary alkynols HC≡C(CH_2)$_n$OH (n = 1, 2) do not undergo dehydration and afford η^2-alkyne complexes.[61] The study with tertiary alkynols, HC≡CC(R)(Ph)OH (R = Me, Ph), was also initiated and shown[60] to yield, in the presence of Na[BPh_4], the corresponding allenylidene complexes with the $[BPh_4]^-$ counterion. We have now extended this type of study and further investigated the effect of the R/R′ groups of the alkynol on the formation and reactivity of allenylidene complexes with various nucleophiles and a Brønsted base. Allenylidene activation by electron transfer, toward the formation of various functionalized neutral and mono- or dicationic alkynyl complexes of iron(II), has also been investigated. An electrochemical study has been performed in order to measure the net electron donor/acceptor properties of the allenylidene, alkynyl, and enynyl ligands (estimate of the corresponding P_L and E_L ligand parameters) and compare them with those of other unsaturated carbon ligands such as carbynes, vinylidenes, carbon monoxide, and nitriles.

Results and Discussion

1. Syntheses and Characterization. 1.1. Cationic Allenylidene Complexes *trans*-[FeBr(=C=C=CRR′)(depe)$_2$][Y] (R = Me, R′ = Ph, Y = BF_4 (1); R = R′ = Ph, Y = BF_4 (2); R = R′ = Et, Y = BF_4 (3a), BPh_4

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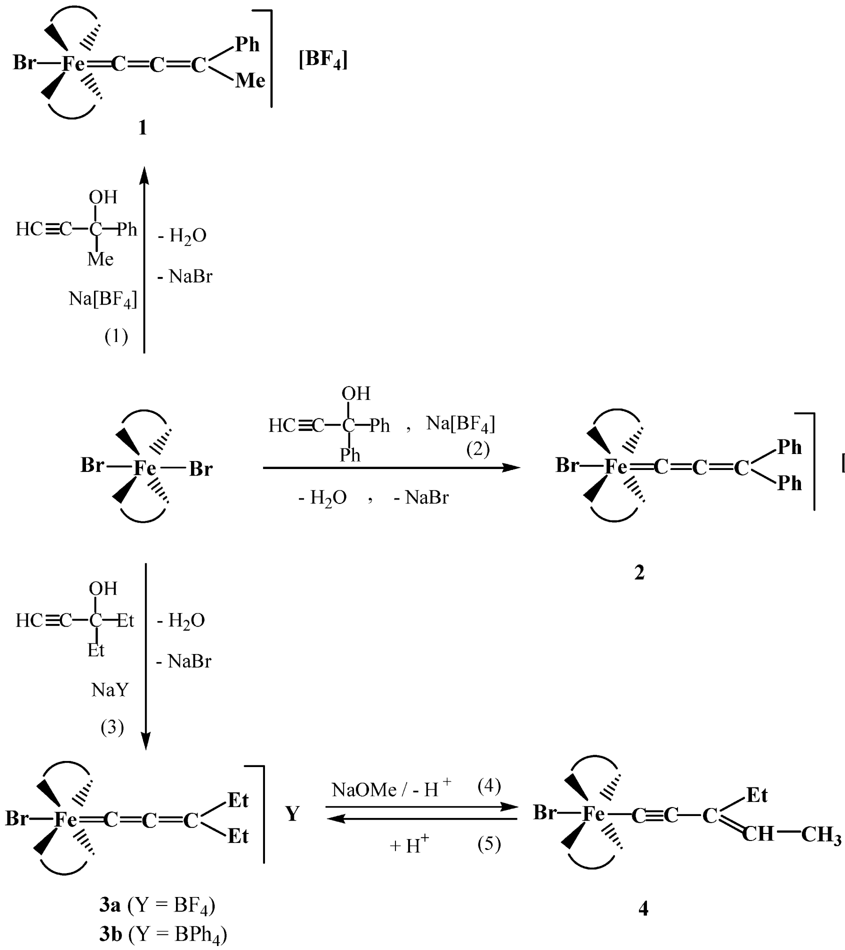
Scheme 1. Syntheses of the Allenylidene Complexes 1−3 and Enynyl Derivative *trans*-[FeBr{−C≡CC(=CHMe)Et}(depe)$_2$] (4)



(3b)). These complexes were obtained according to a procedure recently described[60] by treatment of a MeOH solution of *trans*-[FeBr$_2$(depe)$_2$], in the presence of Na[BF$_4$] or Na[BPh$_4$], with the appropriate alkynol HC≡CCRR′(OH) (e.g. reaction 3, Scheme 1, for R = R′ = Et). The reaction proceeds smoothly at 40 °C, leading to dark blue (**1** and **2**) or red (**3a** and **3b**) products with isolated yields of 58−34%. They have been characterized by IR and multinuclear NMR spectroscopy, FAB$^+$-MS spectrometry, and elemental analysis. For **1** and **2**, the IR and NMR data are identical with or very similar to those of the corresponding compounds with [BPh$_4$]$^-$ as the counterion,[60] obviously without the data associated to this ion. In the IR spectra, the characteristic asymmetric stretching vibration ν(C=C=C) is observed as a strong- or medium-intensity band at 1897 (**1**), 1880 (**2**), 1908 (**3a**), or 1907 cm^{-1} (**3b**), within the usual range (1988−1870 cm^{-1})[7] for allenylidene complexes.

The trans geometry of not only these complexes but also of all the others of this work has been assigned on the basis of the singlet observed in the ^{31}P{^{1}H} NMR spectra (except for complex **7**; see below). In the ^{13}C{^{1}H} NMR spectra the carbon atoms of the cumulenic chain are observed at ca. δ 306−307 (C$_\alpha$), 220−245 (C$_\gamma$ or C$_\beta$), and 149−171 (C$_\beta$ or C$_\gamma$). The assignment to C$_\alpha$ of the lowest field resonance (a quintet, $^2J_{CP}$ = ca. 36 Hz, for **1** and **2**) is based on the comparable data reported[72−74] for other allenylidene complexes. However, the other two resonances cannot be unambiguously assigned, although the order of the corresponding J_{CP} values (4−5 and 6.5 Hz) for their quintet structures could suggest their assignment to C$_\gamma$ and C$_\beta$, respectively, as reported earlier[73] for some Ru allenylidene complexes. The resonance structures did not display a sufficient resolution for the detection of any clear $^nJ_{CH}$, and thus the confirmation of that C$_\gamma$ and C$_\beta$ assignment was not possible.

It is noteworthy to mention that in our complexes the change of a group at C$_\gamma$ results only in a minor effect on δ(C$_\alpha$) but in substantial ones on δ(C$_\beta$) and δ(C$_\gamma$), in contrast to what has been observed[73,74] in other Ru allenylidene complexes, for which the influence of the group at C$_\gamma$ on the chemical shift is maximum for C$_\alpha$.

For **3b** the resonances of the CH$_2$ and CH$_3$ groups of the allenylidene (=C=C=CEt$_2$) are observed as quintets (J_{CP} = ca. 2 Hz) at δ 41.2 and 11.2. All the other resonances of the allenylidene and depe ligands have also been assigned in ^{1}H, ^{13}C{^{1}H}, and ^{13}C NMR spectra, including those of the ipso, ortho, meta, and para atoms of the phenyl rings.

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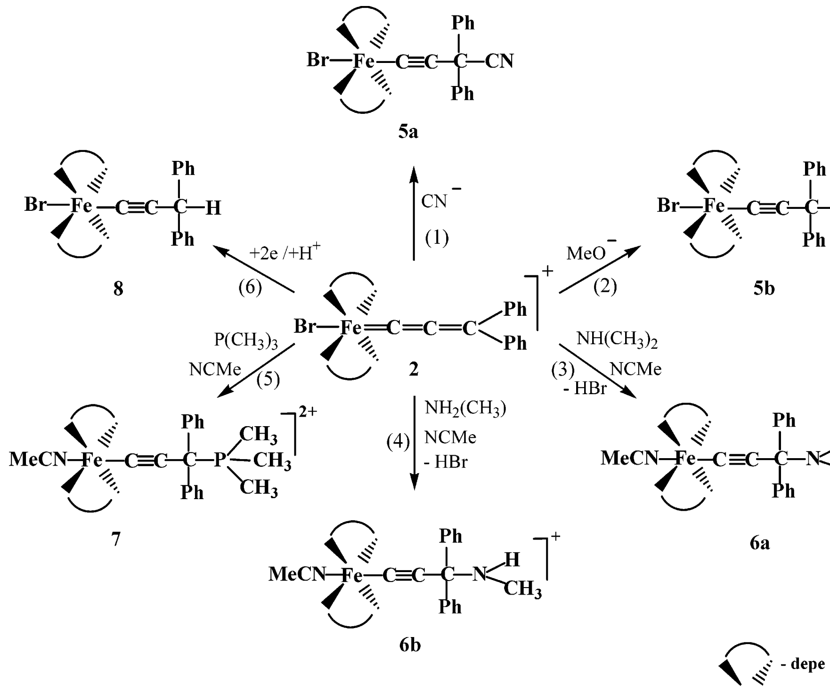
Scheme 2. Syntheses of Neutral and Mono- and Dicationic Alkynyl Complexes



Further, the FAB$^+$-MS spectra of the complexes exhibit the corresponding molecular ion $[M]^+$, whose fragmentation pattern is initiated by the stepwise elimination of the bromide, $[M - Br]^+$, allenylidene, $[M - C{=}C{=}CRR']^+$, or depe, $[M - depe]^+$, ligands.

1.2. Neutral Alkynyl Complexes. The diethylallenylidene complex *trans*-$[FeBr({=}C{=}C{=}CEt_2)(depe)_2][BPh_4]$ (**3b**) undergoes deprotonation in CH_2Cl_2 by NaOMe, which acts as a Brønsted base toward an ethyl group, yielding the neutral enynyl complex *trans*-$[FeBr\{-C{\equiv}CC({=}CHCH_3)Et\}(depe)_2]$ (**4**) (Scheme 1, reaction 4) isolated as a pink solid, in ca. 85% yield. When **4** and HBF_4 are combined in thf, protonation occurs to regenerate the parent diethylallenylidene complex **3a** (Scheme 1, reaction 5).

In the IR spectrum of **4**, the $\nu(C{\equiv}C)$ and $\nu(C{=}C)$ bands appear at 2024 and 1610 cm^{-1}, respectively, values comparable with those for the related complex *trans*-$[FeBr\{-C{\equiv}CC({=}CH_2)Ph\}(depe)_2]$ (2020 and 1552 cm^{-1}),[60] obtained by deprotonation of the methyl group of *trans*-$[FeBr\{{=}C{=}C{=}C(Me)Ph\}(depe)_2][BPh_4]$. The unsaturated $-C{\equiv}CC({=}CHMe)Et$ ligand has been clearly identified by ^1H and $^{13}C\{^1H\}$ NMR and, for example, the latter spectrum exhibits a quintet ($^2J_{CP} = 28$ Hz, C_α) at δ 132.5, a quintet ($J_{CP} = 2$ Hz, C_β or C_γ) at δ 131.2, a multiplet at δ 122.5 (C_γ or C_β), a multiplet at δ 118.6 (${=}CHCH_3$), and a singlet at δ 16.0 (${=}CHCH_3$), whereas, for the ethyl group, the CH_2CH_3 resonance is a quintet ($^5J_{CP} = 2$ Hz) at 33.9 and CH_2CH_3 gives a singlet at 15.2 ppm. In the ^{13}C NMR spectrum, those resonances split into the expected structures.

In the FAB$^+$-MS spectrum, the molecular ion was detected, $[M]^+$ (*m/z* 640), as well as a fragmentation pattern initiated by the stepwise elimination of the bromide $[M - Br]^+$ (*m/z* 561), the alkynyl $[M - (-C{\equiv}CC({=}CHMe)Et)]^+$ (*m/z* 547), and the depe $[M - depe]^+$ (*m/z* 434) ligands.

In contrast with the proton abstraction reactions exhibited by the ligated alkylallenylidenes ${=}C{=}C{=}CEt_2$ and ${=}C{=}C{=}C(Me)Ph$ in **3** and **1**, respectively, the diphenylallenylidene ligand in *trans*-$[FeBr({=}C{=}C{=}CPh_2)(depe)_2]^+$ (**2**) undergoes nucleophilic addition to the C_γ atom upon treatment, in a CH_2Cl_2 or MeOH solution, with $[NBu_4]CN$ or NaOMe. This leads to the formation of the neutral alkynyl complexes *trans*-$[FeBr(-C{\equiv}CCPh_2R'')(depe)_2]$ (R″ = CN (**5a**), MeO (**5b**)), respectively (Scheme 2, reactions 1 and 2), isolated as salmon (**5a**) or red (**5b**) solids, in ca. 80% yields.

They exhibit, in the IR spectra, a strong- (**5a**) or medium-intensity (**5b**) $\nu(C{\equiv}C)$ vibration at 2043 and 2087 cm^{-1}, respectively, and, for **5a**, $\nu(C{\equiv}N)$ appears as a weak band at 2229 cm^{-1}. These features are comparable with those quoted for other Ru π-ligand complexes.[39,75−79] In the ^1H NMR spectrum, the resonance of the methoxy protons at the acetylenic chain $C{\equiv}CCPh_2(OCH_3)$ in **5b** overlaps with those of the methylenic phosphinic protons at δ 2.2−1.3, in accord with the chemical shift (δ 2.2) reported[78] for *trans*-$[RuCl\{-C{\equiv}CCPh_2(OCH_3)\}(Ph_2PCH_2PPh_2)_2]$. In the $^{13}C\{^1H\}$ and ^{13}C NMR spectra of **5a**, the C_α, C_β, and C_γ resonances of the alkynyl ligand appear at much higher fields, δ 132.0 (qnt, $^2J_{CP} = 27$ Hz), 110.8 (m), and 49.8 (m), respectively, compared with those of the allenylidene precursor *trans*-$[FeBr({=}C{=}C{=}CPh_2)(depe)_2]^+$ (C_α 305.5, C_γ 244.9, and C_β 149.4 ppm),[60] and the $C{\equiv}N$ resonance occurs as a quintet ($^5J_{CP} = 1$ Hz) at 122.2 ppm. All the other resonances of the alkynyl and depe ligands have also been assigned in the ^1H, $^{13}C\{^1H\}$, and ^{13}C NMR spectra. Comparable ^{13}C chemical shifts have

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been quoted for the cyanoalkynyl ligand in some Ru π-ligand complexes.[39,76,77]

The FAB$^+$-MS spectra of complexes **5a**,**b** show the corresponding molecular ion, $[M]^+$ (*m/z* 763 (**5a**), 767 (**5b**)), which by loss of Br, R″, alkynyl, or depe leads to the derived fragments.

1.3. Cationic Alkynyl Complexes. Treatment of a NCMe solution of *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]-[BPh$_4$] with dimethylamine, methylamine, or trimethylphosphine leads to the formation of the monocationic alkynyl complexes *trans*-[Fe(NCMe){$-$C≡CC(NR$_1$R$_2$)-Ph$_2$}(depe)$_2$][BPh$_4$] (R$_1$, R$_2$ = Me (**6a**); R$_1$ = H, R$_2$ = Me (**6b**)) (Scheme 2, reactions 3 and 4) or to the dicationic complexes*trans*-[Fe(NCMe){$-$C≡CC(PMe$_3$)Ph$_2$}(depe)$_2$]-Y$_2$ (Y$_2$ = [BPh$_4$]$_2$ (**7a), **[BPh$_4$]$_{2-x}$Br$_x$ (**7b**)), respectively (Scheme 2, reaction 5), isolated as yellow (**6a**), yellowish green (**6b**), or dark green (**7**) solids, in ca. 80% (**6a**,**b**) and 60% (**7**) yields. Thus, the replacement of the effective electron donor Br$^-$ ligand by the much weaker donor NCMe conceivably favors the nucleophilic attack at the C$_\gamma$ atom of the cumulenic chain of the diphenylallenylidene complex. Moreover, the bromide may somehow assist the N deprotonation.

In the IR spectra, the characteristic ν(N≡C) and ν(C≡C) vibrations are observed as medium- and strong-intensity bands, respectively, at 2246 and 2048 (**6a**), 2239 and 2054 (**6b**), and 2247 and 2012 cm^{-1} (**7a**). The ν(C≡C) values are comparable with those quoted for Ru alkynyl π-ligand complexes.[33,80] in the ^{1}H NMR spectra, the presence of the methyl protons at the alkynyl ligand is accounted for by the multiplet observed at δ ca. 2 (6 H, N(CH$_3$)$_2$, **6a**; 3 H, NH(C*H*$_3$), **6b**) or the doublet ($^2J_{HP}$ = 12 Hz) at δ 1.0 (P(C*H*$_3$)$_3$, **7a**).

In accord with the trans geometry, in the ^{31}P{^{1}H} NMR spectrum of complex **7**, the four equivalent P nuclei of depe are observed as a doublet (4P, $^5J_{PP'}$ = 5 Hz) at δ 70.3 and the *P*Me$_3$ resonance as a quintet (1P, $^5J_{P'P}$ = 6 Hz) at 31.9 ppm. The latter δ value shows a significant shift from the value for free *P*Me$_3$ (δ -60.8 ppm) and is comparable to those of some Ru π-ligand complexes.[33,80]

In the ^{13}C{^{1}H} NMR spectra, the carbon atoms of the alkynyl chain are also observed at much higher fields, δ 119.0 (**6a**), 120.2 (**6b**), or 116.8 (**7b**) ppm (m, C$_\alpha$, respectively), δ 110.7 (**6a**), 110.0 (**6b**), or 107.1 (**7b**) ppm (qnt, $^3J_{CP}$ = 28 (**6a**), 30 (**6b**) Hz; d, $^2J_{CP'}$ = 7 Hz (**7b**), C$_\beta$), and δ 72.0 (**6a**), 66.6 (**6b**), or 65.7 (**7b**) ppm (qnt, $^4J_{CP}$ = 1 (**6a**), 2 (**6b**) Hz; m (**7b**), C$_\gamma$), than for the allenylidene precursor *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]$^+$ (C$_\alpha$ 305.5 ppm,, C$_\gamma$ 244.9 ppm, and C$_\beta$ 149.4 ppm).[60] The methylamine carbons, in the ^{13}C{^{1}H} NMR spectra, occur as a broad singlet (**6a and 6b**) at δ ca. 40 ppm which, in the ^{13}C NMR spectra, splits into the expected quartet, $^1J_{CH}$ = ca. 134 Hz (quartet of quartets, $^3J_{CH}$ = 5 Hz, for **6a**). The $-$P(*C*H$_3$)$_3$$^+$ resonance appears as a doublet ($^1J_{CP'}$ = 41 Hz) at much higher field, 9.5 ppm, and splits into the corresponding quartet ($^1J_{CH}$ = 128 Hz) of doublets in the ^{13}C NMR spectrum. All of the other resonances of the alkynyl and depe ligands have also been assigned (see Experimental Section) in the ^{1}H, ^{13}C{^{1}H} and ^{13}C NMR spectra, including those of ipso, ortho, meta, and para atoms of the phenyl rings.

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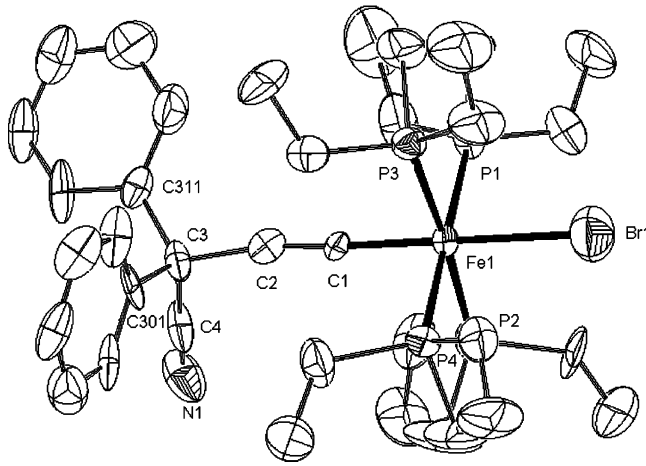

Figure 1. Molecular structure of *trans*-[FeBr{$-$C≡CCPh$_2$-(CN)}(depe)$_2$] (**5a**).

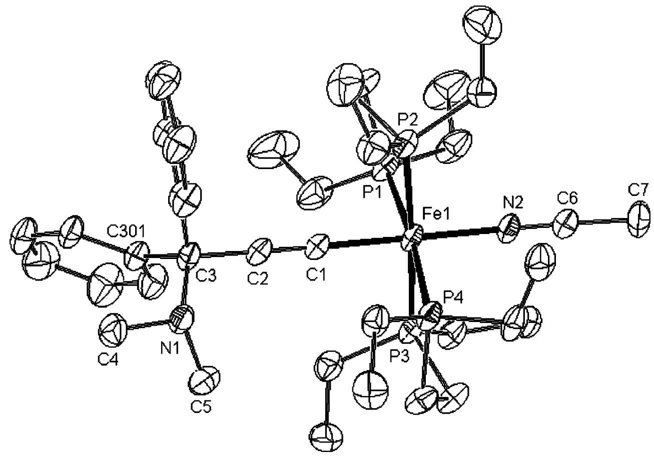

Figure 2. Molecular structure of the cation *trans*-[Fe-(NCMe){$-$C≡CCPh$_2$(NMe$_2$)}(depe)$_2$]$^+$ of compound **6a**.

In the FAB$^+$-MS spectra of the cationic alkynyl complexes, the molecular ion, $[M]^+$, is not observed, but their corresponding fragments derived from the stepwise elimination of the amine (**6a**,**b**) or the phosphine (**7b**) and the acetonitrile ligand, [M $-$ NMe$_2$ $-$ NCMe]$^+$ (*m/z* 659), [M $-$ NHMe $-$ NCMe]$^+$ (*m/z* 659), or [M $-$ NCMe $-$ PMe$_3$]$^+$ (*m/z* 658), respectively, are clearly observed.

2. Crystal Structure Analyses. The molecular structures of **5a** and **6a** (Figures 1 and 2 and Tables 1 and 2 for selected bond distances and angles, respectively) were unambiguously established by X-ray diffraction analyses.

For both molecules **5a** and **6a**, the overall geometry around iron can be described as an octahedron with the two diphosphine ligands chelating at the equatorial positions. The axial positions are occupied by the alkynyl ligand and a bromide (**5a**) or an acetonitrile (**6a**). In the neutral complex **5a** the metal$-$P distances are slightly shorter (2.227(4)$-$2.246(4) Å) than those observed for the cationic **6a** (2.2411(14)$-$2.2919(15) Å), as is known in other cases.[81,82] The Fe$-$C distances (1.877(11) Å (**5a**) and 1.929(5) Å (**6a**)) are not un-

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complexes *trans*-[FeBr{−C≡CCPh$_2$(CN)}(depe)$_2$] (5a) and *trans*-[Fe(NCMe){−C≡CCPh$_2$(NMe$_2$)}(depe)$_2$][BPh$_4$]·C$_6$H$_6$ (6a·C$_6$H$_6$)

	5a	**6a**·C$_6$H$_6$
C(1)−C(2)	1.192(14)	1.206(6)
C(1)−Fe(1)	1.877(11)	1.929(5)
C(2)−C(3)	1.540(16)	1.494(6)
C(3)−C(4)	1.48(2)	
C(3)−N(1)		1.496(6)
C(4)−N(1)	1.118(17)	1.470(6)
C(5)−N(1)		1.471(6)
C(6)−N(2)		1.136(6)
C(6)−C(7)		1.461(6)
Fe(1)−N(2)		1.937(4)
P(1)−Fe(1)	2.246(4)	2.2411(14)
P(2)−Fe(1)	2.227(4)	2.2528(15)
P(3)−Fe(1)	2.240(4)	2.2886(14)
P(4)−Fe(1)	2.242(4)	2.2919(15)
Fe(1)−Br(1)	2.527(3)	
C(2)−C(1)−Fe(1)	176.1(11)	175.2(4)
C(1)−C(2)−C(3)	170.9(14)	176.6(5)
C(2)−C(3)−N(1)		109.1(4)
C(4)−C(3)−C(2)	105.8(10)	
N(1)−C(4)−C(3)	178.4(16)	
N(2)−C(6)−C(7)		178.6(6)
C(1)−Fe(1)−N(2)		175.36(17)
C(1)−Fe(1)−P(1)	90.3(4)	89.12(13)
C(1)−Fe(1)−P(2)	87.5(4)	84.27(14)
N(2)−Fe(1)−P(1)		94.46(11)
N(2)−Fe(1)−P(2)		93.14(13)
C(1)−Fe(1)−P(3)	88.4(4)	92.59(14)
N(2)−Fe(1)−P(3)		90.23(12)
C(1)−Fe(1)−P(4)	90.5(4)	86.28(13)
N(2)−Fe(1)−P(4)		90.34(11)
C(1)−Fe(1)−Br(1)	179.2(4)	
P(2)−Fe(1)−Br(1)	92.00(12)	
P(3)−Fe(1)−Br(1)	92.20(12)	
P(4)−Fe(1)−Br(1)	90.04(12)	
P(1)−Fe(1)−Br(1)	89.16(11)	
C(4)−N(1)-C(5)		108.9(4)
C(4)−N(1)−C(3)		113.8(4)
C(5)−N(1)−C(3)		113.6(4)
C(6)−N(2)−Fe(1)		176.5(4)

usual,[83,84] and the C(1)−C(2) alkynyl bond distances (1.192(14) Å (**5a**) and 1.206(6) Å (**6a**)) clearly indicate a triple-bond character and are comparable to those observed in other alkynyl complexes.[83,84]

The X-ray analysis of **6a** also revealed the expected presence of a [BPh$_4$]$^-$ anion together with a C$_6$H$_6$ molecule of crystallization, whose refinement gave large anisotropic displacement parameters for all C atoms which influenced the final R1 parameter. The presence of the C$_6$H$_6$ molecule probably results from [BPh$_4$]$^-$ decomposition in acidic medium (note the liberation of HBr in reactions 3 and 4 of Scheme 2), a possible[85,86] type of reaction shown to occur in other cases.

3. Electrochemical Behavior. Interestingly, the alkynyl complex *trans*-[FeBr{−C≡CCPh$_2$(H)}(depe)$_2$] (**8**), previously obtained[60] by nucleophilic hydride addition at *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$][BPh$_4$], can also be formed upon electrochemical reduction of the latter compound. This complex exhibits (Figure 3a), by cyclic voltammetry (CV) in 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$, a single-electron reversible reduction wave (I) at $^{I}E_{1/2}^{red}$ = −0.63 V vs SCE which is followed, at a lower

Table 2. First Oxidation Potential[a] of the Complexes *trans*-[FeBr(L)(depe)$_2$]^n (1−3, L = Allenylidene, *n* = +1; 4, 5, 8, 9, L = Alkynyl, *n* = 0), *trans*-[Fe(NCMe)(L)(depe)$_2$]$^+$ (6, L = Alkynyl), and *trans*-[Fe(NCMe)(L)(depe)$_2$]$^{2+}$ (7, L = Phosphonium Alkynyl) and Estimated P_L and E_L Parameters for the Allenylidene and Alkynyl Ligands

complex	ligand	$E_{1/2}^{ox}$ [a]	P_L [b]	E_L [c]
1	C=C=C(Me)Ph	0.93	−0.35	0.42
2	C=C=CPh$_2$	0.97	−0.32	0.45
3	C=C=CEt$_2$	0.90	−0.38	0.40
4	C≡CC(=CHMe)Et	−0.16	−1.34	−0.40
5a	C≡CCPh$_2$(C≡N)	0.02	−1.18	−0.27
6a	C≡CCPh$_2$(NMe$_2$)	0.47	−1.35	−0.49
6b	C≡CCPh$_2$(NHMe)	0.48	−1.34	−0.47
7	C≡CCPh$_2$(P$^+$Me$_3$)	0.74	−1.08	−0.28
8	C≡CCPh$_2$(H)	−0.13	−1.32	−0.38
9	C≡CC(=CH$_2$)Ph	−0.06	−1.25	−0.33

[a] Potential values in V (±0.02) vs SCE; they can be converted to V vs NHE by adding 0.245 V. The first oxidation is followed, at higher potential (ca. 0.7−1.3 V more anodic) by a second one, reversible or irreversible, assigned to the Fe$^{III/IV}$ redox couple; for ionic compounds with the [BPh$_4$]$^-$ counterion, the oxidation waves of this ion are observed at ca. 1.0 and 2.2 V. [b] Pickett's electrochemical ligand parameter,[94] in V, estimated from eq 1. [c] Lever's electrochemical ligand parameter,[96] in V vs NHE, estimated from eq 2 and using $^{I}E_{1/2}^{ox}$ values vs NHE.

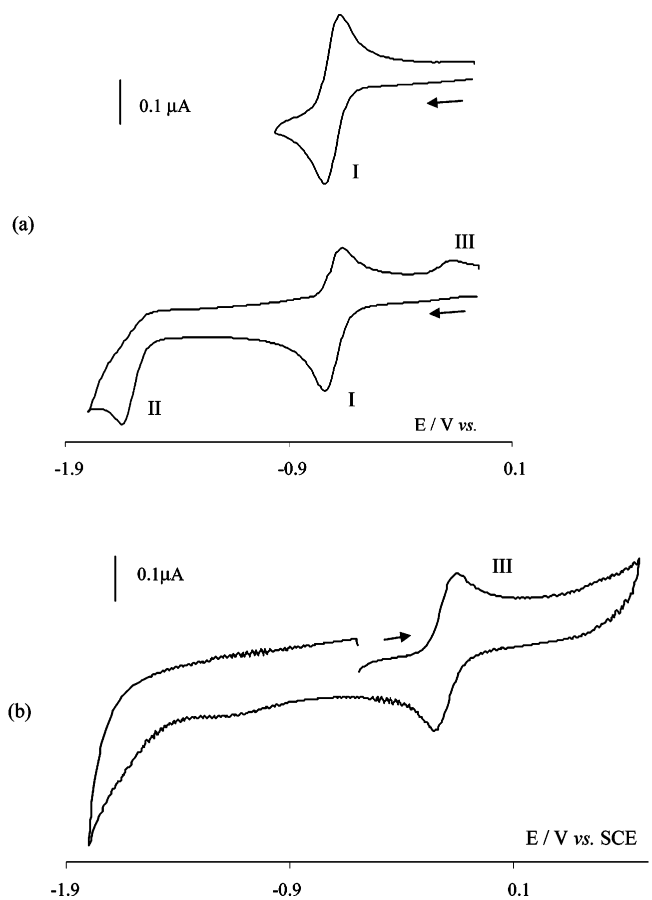

Figure 3. Cyclic voltammograms for a solution of *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]$^+$ (**2**; $c = 0.48 \times 10^{-3}$ M) in 0.2 M [NBu$_4$][BF$_4$]/CH$_2$Cl$_2$, recorded at a scan rate of 0.2 V s^{-1}, at a Pt-disk working electrode: (a) before the controlled-potential electrolysis; (b) after exhaustive controlled-potential electrolysis at ca. −1.5 V vs SCE.

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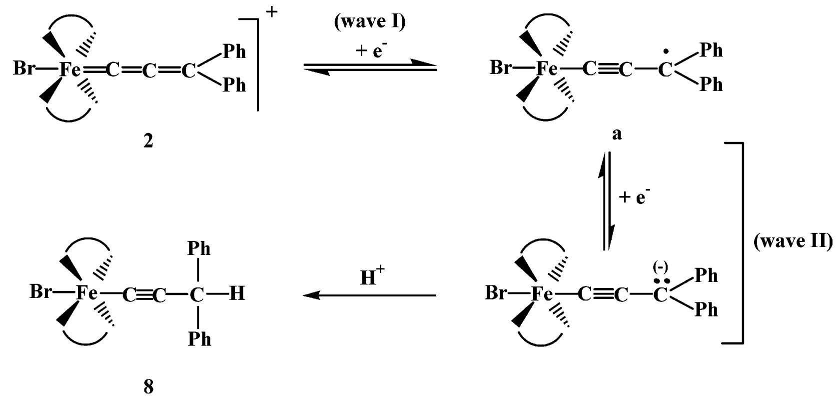
Scheme 3. Cathodic Behavior of *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]$^+$ (2)



potential, by a single-electron irreversible reduction wave (II) ($^{II}E_p{}^{red} = -1.53$ V, measured at a scan rate of 0.2 V s^{-1}). The reduction process at wave II generates a product (see below) that is oxidized at the anodic wave III.

Exhaustive controlled-potential electrolysis (CPE) of a CH_2Cl_2 solution of *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$]-[BPh$_4$] at the potential of the reduction wave II consumes 2 F/mol of complex and leads to the formation of the neutral alkynyl product *trans*-[FeBr{−C≡CCPh$_2$-(H)}(depe)$_2$] (**8**). This is indicated by the following evidence: (i) detection, in the electrolyzed solution, of a reversible oxidation wave (III, Figure 3b) at an $E_{1/2}{}^{ox}$ value identical with that (−0.13 V) observed for **8**, (ii) detection, by $^{31}P\{^1H\}$ NMR of the electrolyzed solution, of a singlet at a chemical shift (70.3 ppm) identical with that of **8**, and (iii) similarity of the colors (both are orange) of the electrolyzed solution and of a genuine solution of **8** (along the electrolysis, the electrolytic solution color gradually changes from dark blue, that of the starting allenylidene complex, to orange, i.e., that of the final product **8**).

The cathodic conversion of *trans*-[FeBr(=C=C=CPh$_2$)-(depe)$_2$][BPh$_4$] into *trans*-[FeBr{−C≡CCPh$_2$(H)}(depe)$_2$] (**8**) follows an overall 2e$^-$/H$^+$ process (Scheme 2, reaction 6) which is believed to involve the initial formation of the neutral radical *trans*-[FeBr(CCCPh$_2$)(depe)$_2$] (**a**) derived from the first electron transfer. The reversibility of the reduction wave I of *trans*-[FeBr(=C=C=CPh$_2$)-(depe)$_2$][BPh$_4$] (Figure 3a and Scheme 3) indicates that this radical (**a**) is stable in the cyclic voltammetric time scale. The unpaired electron in **a** is expected to be located on the terminal trisubsituted carbon atom (C_γ) of the cumulene chain, i.e. *trans*-[FeBr(−C≡CCPh$_2$)-(depe)$_2$] (**a**), as proved by others[44] by EPR for the related one-electron reductions of the metallacumulenes *trans*-[RuCl(=C=C=CR$_2$)(dppe)$_2$][PF$_6$] (R = Me, Ph) and *trans*-[RuCl(=C=C=C=C=CPh$_2$)(dppe)$_2$][PF$_6$].

The neutral species **a** undergoes a further one-electron reduction at a lower potential (wave II, Figure 3a and Scheme 3), leading to the corresponding anionic species, which is unstable. The latter undergoes a chemical reaction (irreversible wave II) to give the alkynyl product *trans*-[FeBr{−C≡CCPh$_2$(H)}(depe)$_2$] (**8**), whose formation is detected by cyclic voltammetry (oxidation wave III) upon scan reversal following a cathodic scan comprising the reduction wave II. The chemical reaction at the cathodic process of wave II, i.e., the conversion of the anionic species formed therein into the final alkynyl complex, consists of a proton addition, conceivably from traces of moisture in the electrolytic medium.

The observed cathodic process is quite distinct from the electron-transfer-induced C−C coupling reactions known[87−91] to occur in some cases with vinylidene and other cumulenylidene ligands.

In contrast to the above ligand-based irreversible reductions, both the allenylidene and the alkynyl complexes undergo metal-centered reversible one-electron oxidations ($Fe^{II/III}$ redox couple), in accord with the reported studies for related iron(II) nitrile[92] and isocyanide[12] complexes and for ruthenium(II) allenylidene compounds.[27,44] The first reversible oxidation is followed, at a higher potential (at least 0.7 V more anodic), by a second one, reversible or irreversible, assigned to the $Fe^{III} \rightarrow Fe^{IV}$ oxidation, which was not further investigated. The anodic behavior has been preliminarily reported[93] for complexes **1**−**3** and **8**.

The first oxidation potential values ($E_{1/2}{}^{ox}$) are listed in Table 2 and follow the overall order cationic allenylidene−bromo complexes **1**−**3** (0.97−0.90 V vs SCE) > cationic alkynyl−acetonitrile complexes **7** and **6a**,**b**, (0.74−0.47 V vs SCE) > neutral alkynyl−bromo complexes **4**, **5a**, and **8** (0.02 to −0.16 V vs SCE). This is in agreement with the expected stronger electron donor character of the formally anionic alkynyl and bromide ligands in comparison with the neutral ligated allenylidenes (see also below).

3.1. Estimate of Electrochemical Ligand Parameters. The measured oxidation potentials ($E_{1/2}{}^{ox}$) of the above complexes viewed as closed-shell octahedral-type complexes [M$_S$L] with the allenylidene or alkynyl ligand L bound to the 16-electron {M$_S$} = *trans*-{FeBr(depe)$_2$}$^+$ site (complexes **1**, **2**, **3a**, **4**, **5a**, and **8**) or {M$_S$} = *trans*-{Fe(NCMe)(depe)$_2$}$^{2+}$ center (**6a**,**b** and **7b**) allows us to

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estimate, for the allenylidene and alkynyl ligands, the electrochemical P_L ligand parameter. This has been defined by Pickett et al.[94] as the shift of the Cr^0 oxidation potential upon replacement of one CO ligand in $[Cr(CO)_6]$ by the ligand L under consideration and constitutes a measure of the net π-electron acceptor minus σ-donor character of the ligand. By applying the linear relationship (1)[94] between $E_{1/2}^{ox}$ and P_L to our complexes and considering the known values of the electron richness (E_S) and polarizability (β) for their iron(II) binding site ($E_S = 1.32$ V, $\beta = 1.10$ for the former site[92] and $E_S = 1.81$ V, $\beta = 0.99$ for the latter site[95]), we have estimated the P_L values for those ligands (Table 2).

$$E_{1/2}^{ox}[M_SL] = E_S + \beta P_L \qquad (1)$$

Another redox potential parametrization approach for octahedral complexes was developed by Lever,[96] who proposed the linear relationship (2), in which the redox potential (in volts vs NHE) of a complex is related to electrochemical parameters determined by the ligands and the metal redox center. $\sum E_L$ is the sum of the values

$$E_{1/2}^{ox} = I_M + S_M(\sum E_L) \text{ (V vs NHE)} \qquad (2)$$

of the E_L ligand parameter for all the ligands, S_M and I_M are the slope and intercept, respectively (dependent upon the metal, redox couple, spin state, and stereochemistry). The E_L values were normally obtained[96] through a statistical analysis of the reported redox potentials of the large number of known complexes with the standard $Ru^{III/II}$ redox couple (for which ideally $I_M = 0$ and $S_M = 1$) and the possible ligands.

From the application of eq 2 to our complexes (with oxidation potentials converted to volts vs NHE) and the knowledge of I_M (−0.57 in V vs NHE) and S_M (1.32) for the Fe^{II}/Fe^{III} redox center[92] and of E_L for the various coligands[96] (−0.22, 0.34, 0.28 for Br^-, NCMe, and depe, respectively), we have obtained the E_L values for the various allenylidene and alkynyl ligands indicated in Table 2.

The P_L and E_L ligand parameters are normally related (except for strong π-acceptor ligands, e.g. CO,[96] isocyanides,[96,97] and carbynes[68]) by the empirical equation (3), also proposed by Lever,[96] which generally also reasonably fits our data.

$$P_L \text{ (V)} = 1.17E_L - 0.86 \qquad (3)$$

As indicated by their P_L and E_L values, the L ligands can be ordered as follows according to their net electron donor character: alkynyls and aminoalkynyls $C{\equiv}CCPh_2(R)$ (R = H, NHMe, NMe_2), alkylenynyl $C{\equiv}CC({=}CHMe)Et$ ($P_L = -1.35$ to -1.32 V; $E_L = -0.49$ to -0.38 V vs NHE) > phenylenynyl $C{\equiv}CC({=}CH_2)Ph$ ($P_L = -1.25$ V, $E_L = -0.33$ vs NHE) > cyanoalkynyl $C{\equiv}CCPh_2(C{\equiv}N)$ ($P_L = -1.18$ V, $E_L = -0.27$ V vs NHE) > phosphonium alkynyl $C{\equiv}CCPh_2(P^+Me_3)$ ($P_L = -1.08$ V, $E_L = -0.28$ V vs NHE) ≫ dialkylallenylidene $C{=}C{=}CEt_2$ ($P_L = -0.38$ V, $E_L = 0.40$ V vs NHE) ≥ alkylphenylallenylidene $C{=}C{=}C(Me)Ph$ ($P_L = -0.35$ V, $E_L = 0.42$ V vs NHE) ≥ diphenylallenylidene $C{=}C{=}CPh_2$ ($P_L = -0.32$ V, $E_L = 0.45$ V vs NHE).

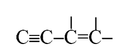
The alkynyls and the enynyl are the strongest net electron donors, and they can be even more effective than phenylalkynyl $C{\equiv}CPh$ ($P_L = -1.22$ V)[98] or bromide ($P_L = -1.17$ V).[94] However, those complexes with the electron-acceptor cyano or phosphonium groups are not strong electron donors, the former behaving similarly to bromide or NCO^- ($P_L = -1.17$ or -1.16 V, respectively)[94] and the latter being a slightly weaker electron donor.

The allenylidenes are much weaker net electron donors: i.e., they present a higher net π-electron acceptor minus σ-donor ability which is even slightly stronger than that of organonitriles (with P_L values in the range from −0.44 to −0.55 V, at the same metal center[92]). However, they behave as significantly less effective net π-electron acceptors than vinylidenes $C{=}CHR$ ($P_L = -0.21$ to -0.27 V for R = H, alkyl, aryl)[68] and are much weaker than carbonyl ($P_L = 0$ V), aminocarbyne ($P_L = +0.09$ V),[99] or carbyne CCH_2R ($P_L = +0.21$ to $+0.23$ V for R = H, alkyl, aryl).[68,69,98] Hence, such ligands can be ordered as follows on account of their net π-electron acceptance: $N{\equiv}CR < C{=}C{=}CRR' < C{=}CHR < CO < C{\doteq}NH_2 < CCH_2R$.

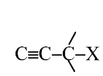
Within the allenylidene ligands, the observed order of P_L or E_L values follows the expected net π-electron acceptance, i.e. $C{=}C{=}CEt_2 < C{=}C{=}C(Me)Ph < C{=}C{=}CPh_2$.

Conclusions

Alkyl, aryl, or mixed alkyl/aryl allenylidene ($C{=}C{=}CRR'$) complexes of Fe(II) can be readily obtained from reaction of the dibromo complex *trans*-$[FeBr_2(depe)_2]$ with the appropriate alkynol. They can behave either as (i) a Brønsted acid when they present an alkyl (R) group which undergoes deprotonation or as (ii) a Lewis acid (when R, R′ = aryl) adding, at C_γ, various nucleophiles. The former type of behavior (i) provides an easy entry to enynyl species



with an extra (ene) functional site available for further reactivity. The latter behavior (ii) allows the preparation of a variety of neutral or mono- or dicationic alkynyl species



functionalized at the C_γ with a cyano, alkoxy, amino, or phosphonium group (X).

The labile bromide ligand in a trans position can also play an active role by assisting the addition of the nucleophile (amine or phosphine) upon replacement by acetonitrile, a weaker electron donor. For a sufficiently strong nucleophile, such as cyanide or methoxide, the addition occurs without requiring bromide displacement.

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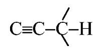
The type of reactivity of the diphenylallenylidene ligand can be reversed on reduction of the complex: i.e., the C_γ character changes from electrophilic to basic, undergoing protonation via a $2e^-/H^+$ process to yield an alkynyl



derivative, thus disclosing the synthetic significance of electrochemical methods to achieve electron-transfer-induced reactions. These methods can also be applied to investigate the electronic properties of the allenylidene, enynyl, and alkynyl ligands by allowing the estimation of their electrochemical P_L and E_L ligand parameters and thus to compare their net π-electron-acceptor/σ-electron-donor characters (also with those of related ligands). The following order of such a character has thus been established alkynyls, aminoalkynyls, enynyls < cyanoalkynyl, Br^-, NCO^- < phosphonium alkynyl ≪ NCR < dialkylallenylidene ≤ alkylphenylallenylidene ≤ diphenylallenylidene < vinylidenes < CO < amonicarbyne (CNH_2) < carbynes (CCH_2R).

Experimental Section

All the manipulations and reactions were carried out in the absence of air using standard inert-gas-flow and high-vacuum techniques. Solvents were purified and dried by standard methods and freshly distilled under dinitrogen. The complex *trans*-[$FeBr_2$(depe)$_2$] was prepared by a published method,[100,101] and the alkynols were used as purchased from Aldrich. The IR spectra (4000−400 cm^{-1}) were recorded on a Bio-Rad FTS 3000MX instrument in KBr pellets and the NMR spectra (run in CD_2Cl_2 unless stated otherwise) on a Varian UNITY 300 spectrometer at room temperature. ^{1}H, ^{13}C, and ^{13}C{^{1}H} and ^{31}P{^{1}H} chemical shifts (δ) are reported in ppm relative to TMS and H_3PO_4, respectively. In the ^{13}C NMR data, assignments and coupling constants common to the ^{13}C{^{1}H} NMR spectra are not repeated. Abbreviations: s = singlet; d = doublet; t = triplet; q = quartet; qnt = quintet; dq = doublet of quartets; dd = doublet of doublets; dt = doublet of triplets; dm = doublet of multiplets; tqnt = triplet of quintets; tm = triplet of multiplets; qq = quartet of quartets; qqnt = quartet of quintets; qm = quartet of multiplets; m = multiplet; b = broad. C, H, and N elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico. Positive-ion FAB mass spectra were obtained on a Trio 2000 instrument by bombarding 3-nitrobenzyl alcohol matrixes of the samples with 8 keV (ca. 1.28×10^{-15} J) of Xe atoms. Nominal molecular masses were calculated using the isotopes ^{56}Fe and ^{79}Br. However, further complexity due to addition (from matrix) or loss of hydrogen was not taken into account. Mass calibration for data system acquisition was achieved using CsI.

Linear Allenylidene Complexes *trans*-[FeBr(=C=C=CRR′)(depe)$_2$][Y] (R = Me, R′ = Ph, Y = BF$_4$ (1); R = R′ = Ph, Y = BF$_4$ (2); R = R′ = Et, Y = BF$_4$ (3a), BPh$_4$ (3b)). Complexes **1** and **2** were obtained according to the procedure described in a previous work,[60] but by using Na[BF$_4$] instead of Na[BPh$_4$], and these products were recrystallized from CH_2Cl_2/Et_2O to give dark blue solids. Yield: 58% (0.070 g) for **1** and 50% (0.065 g) for **2**. NMR spectra of the complex cations are identical with those[60] of the corresponding compounds with [BPh$_4$]$^-$ as the counterion.

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Data for compound **1** are as follows. Anal. Calcd for $C_{30}H_{56}BF_4BrP_4Fe$: C, 47.2; H, 7.4. Found: C, 46.8; H, 7.8. IR (KBr, cm^{-1}): ν(C=C=C) 1897 (m).

Data for compound **2** are as follows. Anal. Calcd for $C_{35}H_{58}BF_4BrP_4Fe$: C, 50.9; H, 7.1. Found: C, 50.6; H, 7.1. IR (KBr, cm^{-1}): ν(C=C=C) 1880 (m).

The preparation of **3** is as follows. To a stirred solution of *trans*-[$FeBr_2$(depe)$_2$] (0.200 g, 0.318 mmol) in MeOH (50 mL), under dinitrogen and at room temperature, was added an excess (molar ratio 2:1) of a methanolic solution of the HC≡CCEt$_2$(OH) alkynol (0.636 mmol in 10 mL). The solution was stirred at 40 °C for ca. 3−4 h, and during this time its color changed from pale green to dark red. Addition of a MeOH solution (10 mL) of Na[BF$_4$] (0.038 g, 0.350 mmol) or Na[BPh$_4$] (0.120 g, 0.350 mmol) led to the precipitation, as a dark red solid, of the allenylidene compound **3a** or **3b,** respectively. It was separated by filtration, recrystallized from CH_2Cl_2/Et_2O, and dried in vacuo. Yield: 34% (0.078 g) for **3a** and 44% (0.136 g) for **3b**.

Data for **3a** are as follows. Anal. Calcd for $C_{27}H_{58}BF_4BrP_4Fe$: C, 44.5; H, 8.0. Found: C, 44.3; H, 8.1. IR (KBr, cm^{-1}): ν(C=C=C) 1908 (m).

Data for **3b** are as follows. Anal. Calcd for $C_{51}H_{78}BBrP_4Fe$: C, 62.0; H, 8.4. Found: C, 61.9; H, 8.6. IR (KBr, cm^{-1}): ν(C=C=C) 1907 (m). ^{1}H NMR (CDCl$_3$): δ 7.29 (m, 8H, H_o from BPh$_4^-$), 6.99 (t, J_{HH} = 7.1 Hz, 8H, H_m from BPh$_4^-$), 6.85 (t, J_{HH} = 6.8 Hz, 4H, H_p from BPh$_4^-$), 2.43 (dq, J_{HP} = 13.8, J_{HH} = 6.9 Hz, 4H, $^1/_4$ (CH$_3$C*H*$_2$)$_2$PCH$_2$CH$_2$P(C*H*$_2$CH$_3$)$_2$), 2.08 (m, 4H, $^1/_2$(CH$_3$CH$_2$)$_2$PC*H*$_2$C*H*$_2$P(CH$_2$CH$_3$)$_2$), 1.84 (m, 4H, $^1/_2$(CH$_3$CH$_2$)$_2$PC*H*$_2$C*H*$_2$P(CH$_2$CH$_3$)$_2$), 1.77−1.59 (m, 16H, C=C=C(C*H*$_2$Me)$_2$ and $^3/_4$(CH$_3$C*H*$_2$)$_2$PCH$_2$CH$_2$P(C*H*$_2$CH$_3$)$_2$), 1.29−1.07 (m, 30H, C=C=C(CH$_2$C*H*$_3$)$_2$ and (C*H*$_3$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 56.0 ppm (s). ^{13}C{^{1}H} NMR: δ 307.4 (m, C_α), 219.6 (m, C_γ or C_β), 170.7 (m, C_β or C_γ), 164.1 (q, $^1J_{CB}$ = 49 Hz, C_i from BPh$_4^-$), 136.0 (s, C_m from BPh$_4^-$), 125.8 (m, C_o from BPh$_4^-$), 121.9 (s, C_p from BPh$_4^-$), 41.2 (qnt, J_{CP} = 2 Hz, C=C=C(*C*H$_2$Me)$_2$), 21.7 (qnt, J_{CP} = 6 Hz, $^1/_2$(CH$_3$CH$_2$)$_2$P*C*H$_2$*C*H$_2$P(CH$_2$CH$_3$)$_2$), 20.0 (qnt, J_{CP} = 11 Hz, (CH$_3$CH$_2$)$_2$PCH$_2$CH$_2$P(*C*H$_2$CH$_3$)$_2$), 19.6 (qnt, J_{CP} = 6 Hz, $^1/_2$(CH$_3$CH$_2$)$_2$P*C*H$_2$CH$_2$P(CH$_2$CH$_3$)$_2$), 11.2 (qnt, J_{CP} = 2 Hz, C=C=C(CH$_2$*C*H$_3$)$_2$), 9.7 (s, $^1/_2$(*C*H$_3$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$*C*H$_3$)$_2$), 9.3 (s, $^1/_2$(CH$_3$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$CH$_3$)$_2$). ^{13}C NMR: δ 307.4 (m), 219.6 (m), 170.7 (m), 164.1 (q), 136.0 (dt, $^1J_{CH}$ = 153, $^2J_{CH}$ = 6 Hz), 125.8 (dm, $^1J_{CH}$ = 153 Hz), 121.9 (dt, $^1J_{CH}$ = 158, $^2J_{CH}$ = 7 Hz), 41.2 (tm, $^1J_{CH}$ = 128 Hz), 21.7 (tm, $^1J_{CH}$ = 130 Hz), 20.0 (tm, $^1J_{CH}$ = 133 Hz), 19.6 (m), 11.2 (m), 9.7 (q, $^1J_{CH}$ = 127 Hz), 9.3 (q, $^1J_{CH}$ = 130 Hz). FAB$^+$-MS (*m/z*): 641 [M]$^+$, 562 [M − Br]$^+$, 547 [M − (=C=C=CEt$_2$)]$^+$, 435 [M − depe]$^+$, 341 [M − depe − (=C=C=CEt$_2$)]$^+$.

Enynyl Complex *trans*-[FeBr{−C≡CC(=CHMe)Et}(depe)$_2$] (4). To a solution containing the diethylallenylidene compound *trans*-[FeBr(=C=C=CEt$_2$)(depe)$_2$][BPh$_4$] (0.200 g, 0.201 mmol) in CH_2Cl_2 (40 mL) was added NaOMe in a 2-fold molar amount (0.021 g, 0.402 mmol). The solution was stirred, at room temperature and under dinitrogen, for 2 h and its color changed from dark red to pink. The solvent was removed in vacuo, yielding an oily residue. Extraction with diethyl ether followed by filtration, concentration, and cooling at ca. −20 °C resulted in the precipitation of **4** as a crystalline pink solid. This precipitate was isolated by filtration and dried in vacuo. Yield: 85% (0.113 g).

Data for **4** are as follows. Anal. Calcd for $C_{27}H_{57}BrP_4Fe$: C, 51.3; H, 9.4. Found: C, 50.9; H, 9.8. IR (KBr, cm^{-1}): ν(C≡C) 2024 (s), ν(C=C) 1610 (m). ^{1}H NMR (C$_6$D$_6$): δ 5.14 (q, J = 6.5 Hz, 1H, −C≡CC(=C*H*Me)Et), 2.54 (dq, J_{HP} = 15.2 and J = 7.6 Hz, 8H, $^1/_2$(CH$_3$C*H*$_2$)$_2$PCH$_2$CH$_2$P(C*H*$_2$CH$_3$)$_2$), 2.08 (q, J = 7.8 Hz, 2H, −C≡CC(=CHMe)(C*H*$_2$Me)), 1.88 (d, J = 6.9 Hz, 3H, −C≡CC(=CHC*H*$_3$)Et), 1.86−1.71 (m, 12H, $^1/_4$(CH$_3$C*H*$_2$)$_2$PCH$_2$CH$_2$P(C*H*$_2$CH$_3$)$_2$ and (CH$_3$CH$_2$)$_2$PC*H*$_2$C*H*$_2$P(CH$_2$CH$_3$)$_2$), 1.63 (dq, J_{HP} = 15.4 and J = 7.7 Hz, 4H, $^1/_4$(CH$_3$C*H*$_2$)$_2$PCH$_2$CH$_2$P(C*H*$_2$CH$_3$)$_2$), 1.11 (m, 27H, (C*H*$_3$CH$_2$)$_2$PCH$_2$CH$_2$P(CH$_2$C*H*$_3$)$_2$

and $-C{\equiv}CC(=CHMe)(CH_2CH_3)$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 70.1 ppm (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 132.5 (qnt, $J_{CP} = 28$ Hz, C_α), 131.2 (qnt, $J_{CP} = 2$ Hz, C_γ or C_β), 122.5 (m, C_β or C_γ), 118.6 (m, $-C{\equiv}CC(=CHMe)Et$), 33.9 (qnt, $^5J_{CP} = 2$ Hz, $-C{\equiv}CC(=CHMe)(CH_2Me)$), 21.6 (qnt, $J_{CP} = 11$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 21.3-21.0 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 16.0 (s, $-C{\equiv}CC(=CHCH_3)Et$), 15.2 (s, $-C{\equiv}CC(=CHMe)(CH_2CH_3)$), 11.0 (qnt, $J_{CP} = 2$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.4 (qnt, $J_{CP} = 2$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). ^{13}C NMR (C_6D_6): δ 132.5 (qnt), 131.2 (m), 122.5 (m), 118.6 (dm, $^1J_{CH} = 152$ Hz), 33.9 (tm, $^1J_{CH} = 126$ Hz), 21.6 (tm, $^1J_{CH} = 124$ Hz), 21.3-21.0 (tm, $^1J_{CH} = 128$ Hz), 16.0 (qd, $^1J_{CH} = 125$, $^2J_{CH} = 5$ Hz), 15.2 (qts, $^1J_{CH} = 124$, $^2J_{CH} = 4$ Hz), 11.0 (qm, $^1J_{CH} = 127$ Hz), 10.4 (qm, $^1J_{CH} = 127$ Hz). FAB$^+$-MS (m/z): 640 $[M]^+$, 561 $[M - Br]^+$, 547 $[M - (-C{\equiv}CC(=CHMe)Et)]^+$, 434 $[M - depe]^+$, 341 $[M - depe - (-C{\equiv}CC(=CHMe)Et)]^+$.

Neutral Alkynyl Complexes *trans*-[FeBr(−C≡CCPh₂R″)(depe)₂] (R″ = CN (5a), OMe (5b)). **5a** was prepared as follows. To a solution of *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (0.200 g, 0.189 mmol) in CH_2Cl_2 (20 mL) was added a CH_2Cl_2 solution (2 mL) of $[NBu_4]CN$ (0.079 g, 0.284 mmol). The color of the solution changed immediately from dark blue to pink, and the mixture was stirred at room temperature for 30 min. It was taken to dryness by evaporation of the solvent in vacuo, resulting in an oily product. Extraction with diethyl ether followed by filtration, concentration, and cooling to ca. −18 °C led to precipitation of a pink solid of **5a** ,which was separated by filtration and dried in vacuo. Yield: 80% (0.116 g).

Data for **5a** are as follows. Anal. Calcd for $C_{36}H_{58}NBrP_4Fe$: C, 54.3; H, 7.4; N, 1.7%. Found: C, 54.0; H, 8.2; N, 1.6. IR (KBr, cm^{-1}): $\nu(C{\equiv}N)$ 2229 (w), $\nu(C{\equiv}C)$ 2043 (s). ^1H NMR (C_6D_6): δ 7.53 (d, $J = 7.5$ Hz, 4H, H_o from alkynyl), 7.04 (t, $J = 7.4$ Hz, 4H, H_m from alkynyl), 6.95 (t, $J = 7.0$ Hz, 2H, H_p from alkynyl), 2.48 (dq, $J_{HP} = 15.4$ and $J = 7.7$ Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 2.25 (dq, $J_{HP} = 15.2$ and $J = 7.6$ Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.82−1.62 (m, 12H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.52 (dq, $J_{HP} = 15.0$ and $J = 7.5$ Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.07 (m, 12H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$, 1.05 (m, 12H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 67.7 ppm (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 144.1 (m, C_i), 132.0 (qnt, $J_{CP} = 27$ Hz, C_α), 129.1 (s, C_o), 127.9 (s, C_p), 127.8 (s, C_m), 122.2 (qnt, $J_{CP} = 1$ Hz, CN), 110.8 (m, C_β), 49.8 (m, C_γ), 21.6 (qnt, $J_{CP} = 12$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 21.1 (qnt, $J_{CP} = 4$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 11.0 (qnt, $J_{CP} = 2$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.4 (qnt, $J_{CP} = 2$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$). ^{13}C NMR (C_6D_6): δ 144.1 (m), 132.0 (qnt), 129.1 (dd, $^1J_{CH} = 168$, $^2J_{CH} = 1$ Hz), 127.9 (dm, partially overlapped with the solvent resonance), 127.8 (dm, $^1J_{CH} = 158$ Hz), 122.2 (m), 110.8 (m), 49.8 (m), 21.6 (m), 21.1 (tm, $^1J_{CH} = 128$ Hz), 11.0 (qm, $^1J_{CH} = 127$ Hz), 10.4 (qm, $^1J_{CH} = 127$ Hz). FAB$^+$-MS (m/z): 763 $[M]^+$, 737 $[M - CN]^+$, 684 $[M - Br]^+$, 557 $[M - depe]^+$, 547 $[M - (-C{\equiv}CCPh_2(CN))]^+$, 341 $[M - depe - (-C{\equiv}CCPh_2(CN))]^+$.

5b was prepared as follows. To a MeOH solution (30 mL) of the allenylidene complex *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (0.200 g, 0.189 mmol) was added a MeOH solution (5 mL) of NaOMe (0.122 g, 226.9 mmol), and the system was stirred at room temperature and kept under dinitrogen for ca. 6 h. The color changed gradually from dark blue to dark violet. The solution was cooled to ca. −18 °C, leading to the precipitation of a red solid, which was separated by filtration and dried in vacuo. ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopic analyses revealed that this solid is the *trans*-$[FeBr\{-C{\equiv}CCPh_2(OMe)\}(depe)_2]$ alkynyl complex **5b** contaminated with $Na[BPh_4]$. Recrystallization from CH_2Cl_2 leads to decomposition into the starting material *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$. It was also proved (by ^1H and $^{31}P\{^1H\}$ NMR and IR) that the alkynyl complex **5b** is converted into the respective allenylidene, even in the solid state. For these reasons it was not possible to obtain an analytically pure sample for elemental analysis and the reaction yield could not be estimated.

Data for **5b** are as follows. IR (KBr, cm^{-1}): $\nu(C{\equiv}C)$ 2087 (m). ^1H NMR: δ 7.60−6.85 (m, H_o, H_m, H_p from alkynyl, partially overlapped with the $[BPh_4]^-$ impurity resonance), 2.24 (dq, $J_{HP} = 16.0$ and $J = 8.0$ Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 2.20−1.32 (m, 23H, $^3/_4$ $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and OCH_3), 1.13 (m, 12H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.11 (m, 12H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$. $^{31}P\{^1H\}$ NMR: δ 66.1 ppm (s). $^{13}C\{^1H\}$ and ^{13}C NMR spectra could not be obtained, due to the instability of the compound. FAB$^+$-MS (m/z): 767 $[M]^+$, 737 $[M - OMe]^+$, 688 $[M - Br]^+$, 547 $[M - (-C{\equiv}CCPh_2(OMe))]^+$, 341 $[M - depe - (-C{\equiv}CCPh_2(OMe))]^+$.

Cationic Alkynyl Complexes *trans*-[Fe(NCMe){−C≡CCPh₂(X)}(depe)₂][BPh₄] (X = NMe₂ (6a), NHMe (6b)). **6a** was prepared as follows. The allenylidene complex *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (0.200 g, 0.189 mmol) was dissolved in a minimum of NCMe (ca. 10 mL), and an excess of a 40% aqueous solution of dimethylamine (6 mL, 0.048 mol) was added. The color of the solution changed from dark blue to green, and after 30−60 min we observed the formation of a green suspension from which complex **6a** was separated by filtration as a crystalline green-yellow solid, which was dried in vacuo. Yield: 90% (0.180 g).

Data for **6a** are as follows. Anal. Calcd for $C_{63}H_{87}N_2P_4Fe$: C, 71.2; H, 8.2; N, 2.6%. Found: C, 71.3; H, 8.5; N, 2.2%. IR (KBr, cm^{-1}): $\nu(N{\equiv}C)$ 2246 (m), $\nu(C{\equiv}C)$ 2048 (s). ^1H NMR: δ 7.35 (m, 12H, H_o from BPh_4^- and alkynyl), 7.20 (t, $J = 7.4$ Hz, 4H, H_m from alkynyl), 7.00 (t, $J = 6.9$ Hz, 2H, H_p from alkynyl), 6.99 (t, $J = 7.4$ Hz, 8H, H_m from BPh_4^-), 6.85 (t, $J = 7.2$ Hz, 4H, H_p from BPh_4^-), 2.22 (dq, $J_{HP} = 15.6$ and $J = 7.8$ Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.96 (m, 6H, $N(CH_3)_2$), 1.83 (m, 4H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.64−1.54 (m, 16H, $^3/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.13 (m, 27H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $NCCH_3$). $^{31}P\{^1H\}$ NMR: δ 70.3 ppm (s). $^{13}C\{^1H\}$ NMR: δ 164.4 (q, $^1J_{CB} = 49$ Hz, C_i from BPh_4^-), 143.5 (bs, C_i from alkynyl), 136.2 (s, C_m from BPh_4^-), 128.8 (s, C_m from alkynyl), 128.0 (bs, NCMe), 127.4 (s, C_o from alkynyl), 126.3 (s, C_p from alkynyl), 125.9 (q, $^2J_{CB} = 3$ Hz, C_o from BPh_4^-), 122.0 (s, C_p from BPh_4^-), 119.0 (m, C_α or C_β), 110.7 (qnt, $J_{CP} = 28$ Hz, C_β or C_α), 72.0 (qnt, $^4J_{CP} = 1$ Hz, C_γ), 40.4 (bs, $N(CH_3)_2$), 20.8 (qnt, $J_{CP} = 11$ Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 19.7 (qnt, $J_{CP} = 6$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 19.5 (qnt, $J_{CP} = 4$ Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.6 (m, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.4 (m, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 4.2 (s, $NCCH_3$). ^{13}C NMR: δ 164.4 (q), 143.5 (m), 136.2 (dt, $^1J_{CH} = 153$, $^2J_{CH} = 6$ Hz), 128.8 (dt, $^1J_{CH} = 159$, $^2J_{CH} = 6$ Hz), 128.0 (q, $^2J_{CH} = 10$ Hz), 127.4 (dd, $^1J_{CH} = 159$, $^2J_{CH} = 7$ Hz), 126.3 (dt, $^1J_{CH} = 160$, $^2J_{CH} = 8$ Hz), 125.9 (dm, $^1J_{CH} = 153$ Hz), 122.0 (dt, $^1J_{CH} = 157$, $^2J_{CH} = 8$ Hz), 119.0 (m), 110.7 (qnt), 72.0 (m), 40.4 (qq, $^1J_{CH} = 134$, $^3J_{CH} = 5$ Hz), 20.8 (tm, $^1J_{CH} = 132$ Hz), 19.7 (m), 19.5 (tm, $^1J_{CH} = 125$ Hz), 9.6 (qm, $^1J_{CH} = 127$ Hz), 9.4 (qm, $^1J_{CH} = 128$ Hz), 4.2 (q, $^1J_{CH} = 138$ Hz). FAB$^+$-MS (m/z): 812 $[M - 3Me - depe + BPh_4]^+$, 685 $[M - NMe_2 - Me]^+$, 659 $[M - NMe_2 - NCMe]^+$, 478 $[M - NMe_2 - Me - depe]^+$.

6b was prepared as follows. To a solution of *trans*-$[FeBr(=C=C=CPh_2)(depe)_2][BPh_4]$ (0.200 g, 0.189 mmol) in NCMe (20 mL) was added, drop by drop, an excess of a 35% aqueous solution of NH_2Me (12 mL, 0.121 mol), leading to a color change, after ca. 1 h, from dark blue to yellow. Evaporation of the solvent in vacuo led to the precipitation of a crystalline yellow solid of **6b**, which was separated by filtration, washed with Et_2O, and dried in vacuo. Yield: 80% (0.160 g).

Data for **6b** are as follows. Anal. Calcd for $C_{62}H_{85}N_2P_4Fe$: C, 71.0; H, 8.2; N, 2.7. Found: C, 71.1; H, 8.7; N, 2.4. IR (KBr, cm^{-1}): $\nu(N{\equiv}C)$ 2239 (m), $\nu(C{\equiv}C)$ 2054 (s). ^1H NMR: δ 7.29

(m, 8H, H_o from BPh_4^-), 7.23−7.11 (m, 10H, C_6H_5 from alkynyl), 6.99 (t, J = 7.5 Hz, 8H, H_m from BPh_4^- alkynyl), 6.84 (t, J = 7.2 Hz, 4H, H_p from BPh_4^-), 2.21 (dq, J_{HP} = 15.2 and J = 7.6 Hz, 4H, $^1/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 2.01 (s, 3H, $NH(CH_3)$), 1.88 (bs, 4H, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.75−1.50 (m), $^3/_4(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and NHMe), 1.11 (m, 27H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $NCCH_3$). $^{31}P\{^1H\}$ NMR: δ 70.1 ppm (s). $^{13}C\{^1H\}$ NMR: δ 164.5 (q, $^1J_{CB}$ = 49 Hz, C_i from BPh_4^-), 147.7 (bs, C_i from alkynyl), 136.3 (s, C_m from BPh_4^-), 128.1 (qnt, J_{CP} = 2 Hz, NCMe), 127.9 (s, C_o from alkynyl), 127.5 (s, C_m from alkynyl), 126.5 (s, C_p from alkynyl), 125.9 (q, $^2J_{CB}$ = 3 Hz, C_o from BPh_4^-), 122.0 (s, C_p from BPh_4^-), 120.2 (m, C_α or C_β), 110.0 (qnt, J_{CP} = 30 Hz, C_β or C_α), 66.6 (qnt, $^4J_{CP}$ = 2 Hz, C_γ), 31.0 (bs, $NH(CH_3)$), 20.7 (qnt, J_{CP} = 12 Hz, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 19.6 (qnt, J_{CP} = 6 Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 19.4 (qnt, J_{CP} = 4 Hz, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.6 (m, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.4 (m, $^1/_2(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 4.3 (s, $NCCH_3$). ^{13}C NMR: δ 164.5 (q), 147.7 (m), 136.3 (dm, $^1J_{CH}$ = 153), 128.1 (m), 127.9 (dd, $^1J_{CH}$ = 156, $^2J_{CH}$ = 6 Hz), 127.5 (dt, $^1J_{CH}$ = 158, $^2J_{CH}$ = 6 Hz), 126.5 (dt, $^1J_{CH}$ = 161, $^2J_{CH}$ = 8 Hz), 125.9 (dm, $^1J_{CH}$ = 150 Hz), 122.0 (dt, $^1J_{CH}$ = 157, $^2J_{CH}$ = 7 Hz), 120.2 (m), 110.0 (qnt), 66.6 (m), 31.0 (qm, $^1J_{CH}$ = 133 Hz), 20.7 (tm, $^1J_{CH}$ = 120 Hz), 19.6 (tm, $^1J_{CH}$ = 121 Hz), 19.4 (m), 9.6 (qm, $^1J_{CH}$ = 127 Hz), 9.4 (qm, $^1J_{CH}$ = 128 Hz), 4.3 (q, $^1J_{CH}$ = 138 Hz). FAB$^+$-MS (m/z): 813 [M − NHMe − depe + BPh_4]$^+$ or [M − 2Me − depe + BPh_4]$^+$, 812 [M − 2Me − H − depe + BPh_4]$^+$, 685 [M − NHMe − Me]$^+$, 659 [M − NHMe − NCMe]$^+$.

Dicationic Alkynyl Complexes *trans*-[Fe(NCMe){−C≡CCPh$_2$(PMe$_3$)}(depe)$_2$]Y$_2$ (Y$_2$ = [BPh$_4$]$_2$ (7a), [BPh$_4$]$_{2-x}$Br$_x$ (7b)). 7a was prepared as follows. The allenylidene complex *trans*-[FeBr(=C=C=CPh$_2$)(depe)$_2$][BPh$_4$] (0.200 g, 0.189 mmol) was dissolved in 60 mL of NCMe, and an excess of PMe_3 (1.89 mL of a 1 M toluene solution) was added. The system was stirred at room temperature and kept under dinitrogen. After ca. 24 h the color of the solution had changed from dark blue to dark green and Na[BPh$_4$] (0.065 g; 0.189 mmol) was added. The solvent was removed in vacuo, yielding an oily residue, which was recrystallized from CH_2Cl_2/Et_2O. Yield: 56% (0.150 g).

7b was prepared following the procedure described above. After the 24 h reaction, Et_2O was added but no precipitation was observed. The solution was then concentrated in vacuo, yielding a green oily residue, which was separated by decantation. The oil was dried in vacuo and recrystallized from CH_2Cl_2/Et_2O, leading to compound **7b**. It was not possible to determine accurately the relative quantities of Br^- and $[BPh_4]^-$ for the counterions $[BPh_4]_{2-x}Br_x$.

Data for **7a** are as follows. Anal. Calcd for $C_{88}H_{110}NP_5Fe$: C, 73.0; H, 7.8; N, 0.9. Found: C, 73.1; H, 8.2; N, 0.9. IR (KBr, cm^{-1}): ν(C≡N) 2247 (m), ν(C≡C) 2012 (s). ^1H NMR: δ 7.39−7.23 (m, 20H, H_o from BPh_4^- and H_o or H_m from alkynyl), 7.02−6.92 (m, 18H, H_m from BPh_4^- and H_p from alkynyl), 6.89−6.83 (m, 12H, H_p from BPh_4^- and H_m or H_o from alkynyl), 1.80 (m, 8H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.60−1.40 (m, 16H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 1.14 (m, 27H, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $NCCH_3$), 0.98 (d, $^2J_{HP}$ = 12.0 Hz, 9H, $P(CH_3)_3$). $^{31}P\{^1H\}$ NMR: δ 70.3 (d, $J_{PP'}$ = 5.3 Hz, 4P, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 31,9 (qnt, $J_{P'P}$ = 5.5 Hz, 1P, PMe_3).

Data for **7b** are as follows. $^{13}C\{^1H\}$ NMR: δ 164.1 (q, $^1J_{CB}$ = 49 Hz, C_i from BPh_4^-), 146.1 (m, C_i from alkynyl), 136.0 (s, C_m from BPh_4^-), 130.1 (m, NCMe), 129.3 (s, C_o or C_m from alkynyl), 129.1 (s, C_p from alkynyl), 128.7 (s, C_m or C_o from alkynyl), 125.7 (q, $^2J_{CB}$ = 3 Hz, C_o from BPh_4^-), 121.8 (s, C_p from BPh_4^-), 116.8 (m, C_α or C_β), 107.1 (d, J_{CP} = 7 Hz, C_β or C_α), 65.7 (m, C_γ), 22.4 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 21.2 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 20.0 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$ and $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 10.0 (m, $(CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), 9.5 (d, $^1J_{CP}$ = 41 Hz, $P(CH_3)_3$), 2.0 (s, $NCCH_3$). ^{13}C NMR: δ 164.1 (q), 146.1 (m), 136.0 (dt, $^1J_{CH}$ = 153, $^2J_{CH}$ = 8 Hz), 130.1 (m), 129.3 (dm, $^1J_{CH}$ = 162 Hz), 129.1 (m), 128.7 (dm, $^1J_{CH}$ = 158 Hz), 125.7 (dm, $^1J_{CH}$ = 155 Hz), 121.8 (dt, $^1J_{CH}$ = 157, $^2J_{CH}$ = 8 Hz), 116.8 (m), 107.1 (d), 65.7 (m), 22.4 (m), 21.2 (m), 20.0 (m), 10.0 (qm, $^1J_{CH}$ = 127 Hz), 9.5 (qd, $^1J_{CH}$ = 128 Hz), 2.0 (q, $^1J_{CH}$ = 137 Hz). FAB$^+$-MS (m/z): 1053 [M − NCMe + BPh_4]$^+$, 768/770 [M − 3Me − NCMe + Br]$^+$, 699 [M − PMe_3]$^+$, 698 [M − Ph]$^+$, 658 [M − NCMe − PMe_3), 528 [M − NCMe − depe]$^+$.

Table 3. Crystallographic Data for *trans*-[FeBr{−C≡CCPh$_2$(CN)}(depe)$_2$] (5a) and *trans*-[Fe(NCMe){−C≡CCPh$_2$(NMe$_2$)}(depe)$_2$][BPh$_4$] (6a)

	5a	6a
empirical formula	$C_{36}H_{58}NBrP_4Fe$	$C_{69}H_{93}N_2P_4Fe$
fw	764.47	1140.99
temp, K	293	298
λ, Å	0.710 69	1.541 50
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c{:}b1$ (No. 14)	$Pbca$ (No. 61)
a, Å	16.552(2)	11.311(3)
b, Å	13.2079(17)	25.042(4)
c, Å	18.9008(18)	45.647(3)
V, Å^3	3907.4(8)	12930(4)
Z	4	8
ρ_{calcd}, g/mL	1.300	1.172
μ(Mo Kα), mm^{-1}	1.597	3.104
θ range for data collecn (deg)	1.92−25.97	3.53−67.24
limiting indices	$-18 \le h \le 18$, $-15 \le k \le 0$, $0 \le l \le 21$	$0 \le h \le 13$, $0 \le k \le 29$, $-54 \le l \le 0$
R1 ($I > 2\sigma(I)$)^a	0.1159	0.0801
R1 (all data)	0.3660	0.1214

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$.

Reaction of *trans*-[FeBr{−C≡CC(=CHMe)Et}(depe)$_2$] (4) with HBF$_4$. To a solution of the enynyl complex *trans*-[FeBr{−C≡CC(=CHMe)Et}(depe)$_2$] (**4**; 0.060 g, 0.094 mmol) in CH_2Cl_2 (20 mL) was added a slight excess (1.2:1) of HBF_4 (0.112 mmol, ca. 170 μL of a 54% solution in Et_2O). The color of the solution changed immediately from pink to dark red. Concentration and addition of Et_2O (ca. 10 mL) led to the precipitation of the allenylidene complex **3a** as a pink solid, which was isolated by filtration and dried in vacuo. IR and ^1H and $^{31}P\{^1H\}$ NMR (spectra identical with those of **3b**, except for the features concerning the different counterions) confirmed the formulation.

Structural Analyses of Complexes 5a and 6a. Diffraction analyses were carried out at room temperature on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo Kα (**5a**; λ = 0.710 69 Å) or Cu Kα (**6a**; λ = 1.541 50 Å) radiation. Cell dimensions were obtained from centered reflections with θ between 1.92 and 25.97° (**5a**) and between 3.53 and 67.24° (**6a**). The intensities of 7676 (**5a**) and 11 033 (**6a**) reflections were observed, and a total of 7437 (**5a**) and 11 033 (**6a**) unique reflections were used for structure determinations. The structures were solved by direct methods by using the SHELXS-97 package[102] and refined with SHELXL-97[103] with the WinGX graphical user interface.[104] Molecular structures with their correspondent numbering schemes are shown in Figures 1 and 2. Selected bond lengths and angles are given in Table 1, and crystallographic data are summarized in Table 3.

In both structures the hydrogen atoms were inserted in calculated positions. Least-squares refinements with anisotropic thermal motion parameters for all the non-hydrogen

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atoms and isotropic for the remaining atoms gave R1 = 0.1159 (**5a**), 0.0801 (**6a**) ($I > 2\sigma(I)$) and R1 = 0.3660 (**5a**), 0.1214 (**6a**) (all data).

Electrochemical Studies. The electrochemical experiments were performed on an EG&G PAR 273A potentiostat/galvanostat connected to a computer through a GPIB interface. Cyclic voltammograms were obtained in 0.2 M solutions of $[NBu_4][BF_4]$ in CH_2Cl_2, at a platinum-disk working electrode (0.5 mm diameter) probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a Pt auxiliary electrode was employed. Controlled-potential electrolyses (CPE) were carried out in electrolyte solutions with the aforementioned composition, in a two-compartment−three-electrode cell, separated by a glass frit and equipped with platinum-gauze working and counter electrodes. A Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The CPE experiments were monitored regularly by cyclic voltammetry (CV), thus ensuring that no significant potential drift occurred along the electrolyses. The electrochemical experiments were performed under a N_2 atmosphere at room temperature.

The potentials of the complexes were measured by CV in the presence of ferrocene as the internal standard, and the redox potential values are normally quoted relative to the SCE by using the $[Fe(\eta^5\text{-}C_6H_5)_2]^{0/+}$ ($E_{1/2}^{ox}$ = 0.525 V vs SCE) redox couple in 0.2 M $[NBu_4][BF_4]$ in CH_2Cl_2. For the application of the Lever equation (2), they have been converted to volts vs NHE by adding 0.245 V.[96]

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Supporting Information Available: CIF files giving X-ray crystallographic data for *trans*-[FeBr{−C≡CCPh$_2$(CN)}-(depe)$_2$] (**5a**) and *trans*-[Fe(NCMe){−C≡CCPh$_2$(NMe$_2$)}(depe)$_2$]-[BPh$_4$]·C$_6$H$_6$ (**6a**·C$_6$H$_6$). This material is available free of charge via the Internet at http://pubs.acs.org.

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