Syntheses, Spectroscopy, and Redox Properties of Fluoro−Carbyne and Derived Fluoro−Vinylidene Complexes of Rhenium and of Analogous Chloro Complexes

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The fluoro− or chloro−carbyne complexes *trans*-[ReX(≡CCH$_2$R)(dppe)$_2$][BF$_4$] (X = F (**1**), R = H (**1a**), Bu^t (**1b**), CO$_2$Me (**1c**), CO$_2$Et (**1d**), Ph (**1e**), or C$_6$H$_4$Me-4 (**1f**); X = Cl (**2**), R = H (**2a**), Bu^t (**2b**), CO$_2$Me (**2c**), CO$_2$Et (**2d**), Ph (**2e**), or C$_6$H$_4$Me-4 (**2f**); dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) have been prepared by a single-pot reaction, in THF and under sunlight, of the appropriate 1-alkyne (HC≡CR) with *trans*-[ReCl(N$_2$)(dppe)$_2$] and [NH$_4$][BF$_4$] in the presence or in the absence, respectively, of Tl[BF$_4$]. With the exception of the less acidic *tert*-butylcarbyne complexes (**1b** and **2b**), these complexes are deprotonated by [Bu$_4$N]OH to give the corresponding vinylidene complexes *trans*-[ReX(=C=CHR)(dppe)$_2$] (X = F (**3**) or Cl (**4**)) which, by treatment with HBF$_4$, regenerate the carbyne complexes. This route is more convenient for the synthesis of the chloro−carbyne complexes **2** from the vinylidenes **4**, the latter being then prepared upon reaction of the dinitrogen complex with HC≡CR in toluene under sunlight. The electrochemical behavior of complexes **1**−**4** has been investigated by cyclic voltammetry and controlled potential electrolysis in aprotic media and at a Pt electrode. These complexes undergo single-electron reversible oxidations at half-wave oxidation potentials in the range from 1.39 to 1.48 (**1**, **2**) and −0.35 to 0.25 (**3, 4**) V vs SCE. The corresponding electrochemical P_L and E_L ligand parameters have been estimated for the carbyne (P_L = 0.21−0.24 V, E_L *ca.* 1.2 V vs NHE) and the vinylidene (P_L = −0.27 to −0.13 V, E_L = 0.50−0.62 V vs NHE) ligands and discussed in terms of redox potential−structure relationships. The former ligands behave as remarkably strong π-electron acceptors and undergo cathodically induced C−H bond cleavage to give the corresponding vinylidenes. Both the carbyne and the vinylidene ligands are effectively stabilized by the *trans*-fluoride ligand, although it presents, relative to chloride, a slightly stronger destabilizing effect on the HOMO in these complexes.

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Introduction

Since the discovery[1] of the first carbyne (alkylidyne) metal complexes nearly 25 years ago, the field has developed enormously and a few books and extensive reviews have appeared.[2,3] However, in comparison with the group 6 transition metals (Mo or W), carbyne complexes of rhenium (in particular with phosphine coligands[4,5]) are still in a limited number. They commonly involve a relatively electron-poor rhenium site and/or cyclopentadienyl-type or carbonyl coligands[6,7] and often the presence of an anionic strong electron donor ligand, such as chloride (bromide or iodide) or alkoxyde, helps the stabilization of the metal−carbon triple bond. However, in contrast with the developed chemistry of organotransition-metal complexes with such halide ligands, that of the fluoro complexes still remains relatively unexplored,[8] especially for low-valent metal centers. Particularly in carbyne chemistry, fluoride is an almost unknown ligand,[9−11] and its carbyne complexes are usually obtained[10,11] in low yields. Moreover, attempts to prepare fluorocarbyne complexes analogous to other halocarbyne compounds have failed.[12]

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

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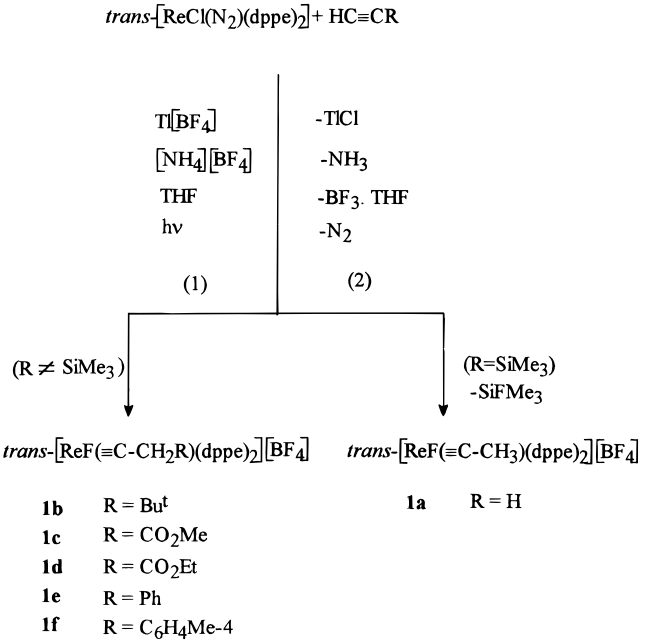
In the present study and within our interest[13] on the activation of unsaturated small molecules by electron-rich metal centers, we have succeeded in preparing a series of fluoro−carbyne complexes of rhenium, *trans*-[ReF(≡CCH$_2$R)(dppe)$_2$][BF$_4$] (R = H(**1a**), Bu^t (**1b**),CO$_2$Me (**1c**),CO$_2$Et (**1d**), Ph (**1e**), or C$_6$H$_4$Me-4 (**1f**)), in which the [BF$_4$]$^-$ anion behaved as the metal fluorinating agent. The carbyne ligands in **1** were generated from the activation of 1-alkynes (HC≡CR) toward a 1,2-hydrogen shift to give vinylidenes (C=CHR) which undergo β-protonation, a known route for such species.[1,2,14] In contrast with the usual synthetic pathways for carbyne complexes, which occur in a stepwise manner, complexes **1** are prepared in a convenient single-pot synthesis from the reaction of *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate 1-alkyne, in the presence of a chloride abstractor, Tl[BF$_4$], and suitable proton ([NH$_4$]$^+$) and fluoride ([BF$_4$]$^-$) sources, in sunlight. Deprotonation of carbyne complexes **1** leads to the corresponding fluoro−vinylidene complexes *trans*-[ReF(=C=CHR)(dppe)$_2$] (**3**). The analogous chloro−carbyne and chloro−vinylidene complexes *trans*-[ReCl(≡C−CH$_2$R)(dppe)$_2$][BF$_4$] (**2**) and *trans*-[ReCl(=C=CHR)(dppe)$_2$] (**4**), respectively, have also been prepared either in a similar manner, without using Tl$^+$, or more adequately *via* the prior formation of **4** from the above dinitrogen compound (a process that we have previously applied[15] but now have substantially improved), followed by proton addition to give **2**.

Moreover, since very few studies of the redox properties of carbyne or carbene complexes have been reported,[16−27] in spite of their expected significance in terms of defining the electron-donor/acceptor properties of those ligands[17a] and of their promising redox-induced chemistry, we have also investigated the electrochemical behavior of those rhenium carbyne and vinylidene complexes, which is also described in detail.

Some preliminary results have already been briefly reported by us,[28] including the crystal structure of **1b**,[28a] a complex that was then obtained fortuitously in an extremely low yield as a side product. We now describe in detail the systematic and extended study that developed since this report. However, the investigation of the detailed mechanisms of the formation of the carbyne complexes **1** and **2** is the subject of a subsequent publication.

Results and Discussion

Fluoro−Carbyne and Fluoro−Vinylidene Complexes. The fluoro−carbyne complexes *trans*-[ReF(≡C−CH$_2$R)(dppe)$_2$][BF$_4$] (R = H (**1a**), Bu^t (**1b**), CO$_2$Me (**1c**), CO$_2$Et (**1d**), Ph (**1e**), or C$_6$H$_4$Me-4 (**1f**)) (isolated as white or pale yellow solids in *ca.* 60−40% yields) are obtained by treatment of a THF solution of the dinitrogen complex *trans*-[ReCl(N$_2$)(dppe)$_2$] with the appropriate 1-alkyne (HC≡CR) in the presence of Tl[BF$_4$] and [NH$_4$][BF$_4$] in sunlight under argon (eq 1). The simplest



member (**1a**) of the series is derived similarly from HC≡CSiMe$_3$, although in a modest yield (*ca.* 15%) and with concomitant desilylation (eq 2). These complexes, as well as all the other complexes discussed in this study, have been characterized (see Experimental Section) by IR and NMR spectroscopies, elemental analysis, and electrochemical methods.

Their preparative reactions are of a considerable complexity, involving five reagents and a number of steps which are combined in a convenient single-pot process, starting from readily available starting materi-

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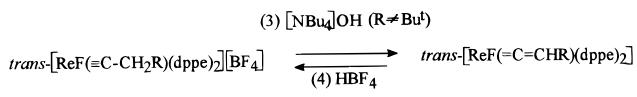
als to lead to very rare examples of fluoro−carbyne complexes. The formation of the carbyne ligands should occur through the corresponding vinylidene intermediate species derived from the replacement of N_2 (which is assisted by light in agreement with some simplified π-MO schemes[29]) by the alkyne (although no alkyne complex was isolated), followed by a 1,2-hydrogen migration, as known to occur at related d^6 metal centers.[9,14,15,30] This type of behavior has been rationalized in terms of repulsive electronic interactions[9,30] and by extended-Hückel calculations.[31] The vinylidene ligand in our system is susceptible to β-protonation to give the corresponding carbyne product, as known for related cases,[9−11,32−35] and the detailed mechanism of such a protonation will be reported in a subsequent paper.

The formation of complexes **1** also involves Cl/F exchange. The metal fluorination is unusual,[8] particularly in low-valent transition metal complexes due, *inter alia*, to the expected unfavorable combination of a soft acid (the metal center) with a hard base (fluoride). However, in our system this reaction occurs even in the absence of a deliberately added fluoride source. Nevertheless, the ability of $[BF_4]^-$ to fluorinate related metal centers has been observed[8,10,11,36] in a few cases. The preparation of the fluoro−carbyne *trans*-[WF(≡CCH$_2$Ph)(CO)$_2$(dppe)] has been reported[9] in a high yield, but it occurs by free F^- addition from $[NEt_4]F$ to the five-coordinate carbyne complex [W(≡CCH$_2$Ph)(CO)$_2$(dppe)$_2$][BF_4].

The X-ray crystal structure of **1b**, which we have previously obtained accidentally in a very low yield and as a contaminant of the analogous chloro−carbyne complex upon treatment of *trans*-[ReCl(=C=CHBu^t)(dppe)$_2$] with HBF_4, has already been reported[28a] and will not be discussed here apart from the relevant metal−ligand bonds. The rhenium−carbyne carbon distance, 1.772(7) Å, is only slighty longer than that expected (1.75−1.72 Å) for a Re≡C(sp) triple bond[5a,37] and is much shorter than that quoted[15] for the rhenium−vinylidene carbon (Re=C) distance, 2.046(8) Å, in *trans*-[ReCl(=C=CHPh)(dppe)$_2$]. The average Re−P distance in **1b**, 2.455(2) Å, is significantly longer than that, 2.418(9) Å,[15] for this vinylidene compound, in accord with the expected weaker π-electron release to the phosphine ligands from the metal center in the former complex.

The fluoro−carbyne complexes **1c**, **1d** and **1f** undergo deprotonation by a base, $[NBu_4]OH$, in CH_2Cl_2 to give (eq 3) the corresponding neutral fluoro−vinylidene compounds *trans*-[ReF(=C=CHR)(dppe)$_2$] **3c** (R = CO_2Me), **3d** (R = CO_2Et), and **3f** (R = C_6H_4Me-4) which have been isolated as yellow or rose solids in *ca.* 60−50% yields. Complex **3a** (R = H), although not isolated,



1a	R=H	**3a**	R=H
1b	R=Bu^t [not for reaction (3)]	**3b**	R=Bu^t
1c	R=CO_2Me	**3c**	R=CO_2Me
1d	R=CO_2Et	**3d**	R=CO_2Et
1f	R=C_6H_4Me-4	**3f**	R=C_6H_4Me-4

has been generated in the same way and detected *in situ* electrochemically (see below). However, **1b**, which has a weaker acid character in view of the electron-donor ability of the Bu^t group, is not deprotonated even under refluxing solvent conditions. The deprotonation reaction (eq 3) of the fluoro−carbyne complexes can be reversed on treatment of the fluoro−vinylidene products by acid (HBF_4), which readily regenerates the corresponding carbyne compounds (eq 4).

In complexes **1** and **3** the presence of the fluoride *trans* to the carbyne or vinylidene is unambiguously shown by the expected quintet ($^2J_{FP}$ = 34−44 Hz) and doublet (with identical coupling constant) resonances observed in the ^{19}F (δ −316 to −329 ppm relative to $CFCl_3$) and $^{31}P\{^1H\}$ (δ −110 to −116 ppm relative to $P(OMe)_3$) NMR spectra (CD_2Cl_2), respectively. In the ^{13}C NMR spectra, the carbyne− or vinylidene−carbon resonance occurs as a low-field multiplet (δ *ca.* 291−267 or 298−291 ppm relative to $SiMe_4$, respectively) whose quintet structure ($^2J_{CP}$ = 11 Hz) is resolved for **1d**. Moreover, the C−*C*H$_2$R or C=*C*HR resonances are the expected triplet (J_{CH} = 127−129 Hz, δ 52−65) or doublet (J_{CH} = 156 Hz, δ 97.4 for **3d**), respectively. In the $^{13}C\{^1H\}$ NMR spectra, the resonance (δ *ca.* 32−33) of the dppe methylene carbons is a quintet, due to virtual coupling to the four phosphorus nuclei (J_{CP} = *ca.* 10−12 Hz), which, in the proton-coupled spectra, splits to a triplet (J_{CH} = *ca.* 135 Hz) of quintets. In the ^1H NMR spectra, the C−C*H*$_2$R or C=C*H*R resonance is an unresolved multiplet usually at a considerable higher field (δ 0.5−2.4) than the broad multiplet resonances of the dppe methylene protons (δ 2.5−3.9).

The IR spectra of complexes **3** have strong bands in the *ca.* 1610−1480 cm^{-1} range which are assigned to ν(C=C) of the vinylidene ligand or to ν(CO) in the methyl− or ethyl−propiolate derivatives **3c** and **3d** for which the two detected bands conceivably result[15,38] from coupling of those vibrations.

Chloro−Carbyne and Chloro−Vinylidene Complexes. The chloro−carbyne complexes *trans*-[ReCl(≡C−CH$_2$R)(dppe)$_2$][BF_4] **2** can be obtained as pale yellow solids (eqs 5 and 6, with isolated yields up to *ca.*

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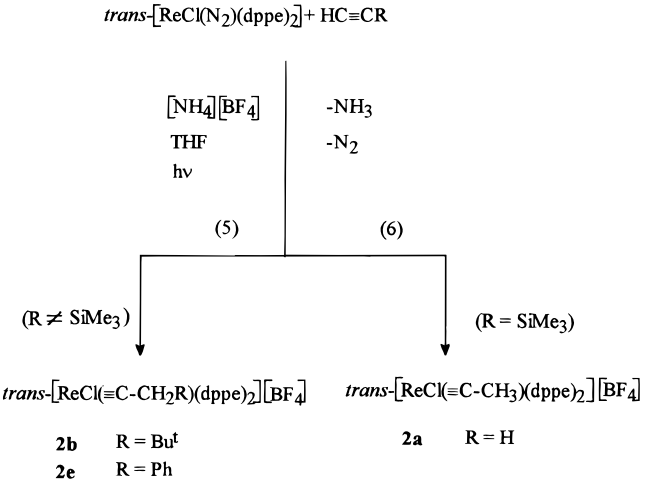
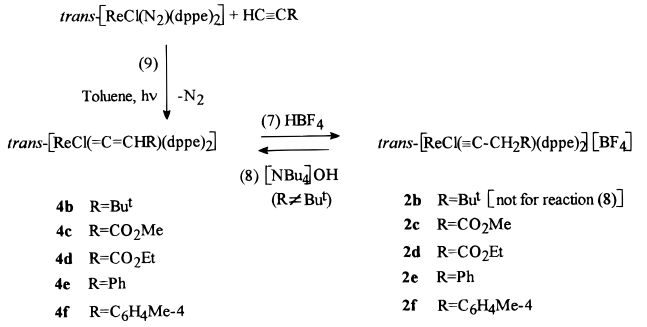
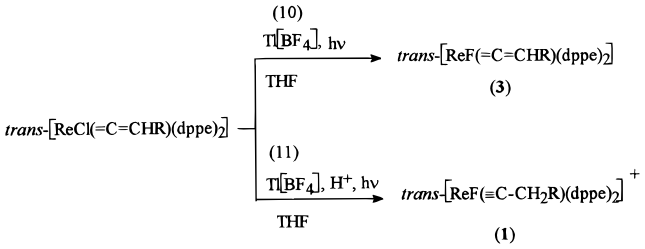
75% or *ca.* 15%, respectively) in a manner similar to that described above for the synthesis of the fluoro analogues **1** (eqs 1 and 2), without requiring the use of the chloride ligand abstractor. However, a cleaner and



higher-yield route (typically above 80% yield) for **2** consists of treatment of the corresponding vinylidene complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] **4** (in CH_2Cl_2 or in THF) with acid, commonly HBF_4 (eq 7), although a weaker acid such as $[NH_4][BF_4]$ or an alkyl derivative, *e.g.*, $[NHEt_3][BPh_4]$, can also be used.



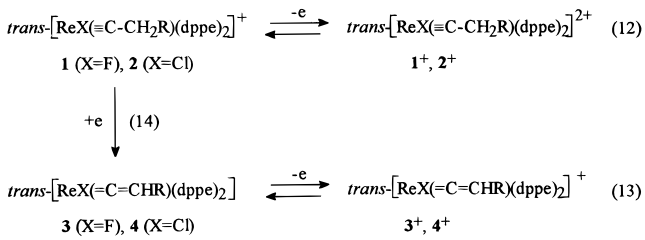
Inversely, complexes **2**, with the exception of the less acidic *tert*-butyl derivative **2b**, are susceptible to deprotonation by base, $[NBu_4]OH$, to regenerate the corresponding chloro−vinylidene complexes **4**, isolated as red solids (eq 8). However, the latter complexes are more directly prepared from the reaction of *trans*-[ReCl(N$_2$)(dppe)$_2$], in toluene, with the appropriate 1-alkyne (*ca.* 4 equiv) under argon and in sunlight for *ca.* 0.5−3 h (depending on the light intensity) (eq 9) following an improvement of the procedure we reported previously[15] in which the reaction proceeded slowly (*ca.* 4 to 6 days) in refluxing THF or in toluene under tungsten-filament bulb irradiation, even in the presence of a much higher excess of the alkyne (15−30-fold molar excess). A chloro−vinylidene complex, *e.g.*, **4e** or **4d**, can be converted into the corresponding fluoro−vinylidene (**3e**) or fluoro−carbyne (**1e** or **1d**) complex by reaction (*ca.* 1 h) in THF and under sunlight with $Tl[BF_4]$ in the absence or in the presence, respectively, of $[NH_4][BF_4]$ (eqs 10 and 11), suggesting that in the above-mentioned single-pot synthesis of **1**, replacement of the chloride ligand by fluoride can occur at an earlier stage than the protonation of the vinylidene intermediate.



In the ^{13}C NMR spectra, the carbyne or vinylidene carbon resonance, *C*−CH_2R or *C*=CHR, respectively, is observed as a low-field multiplet (δ *ca.* 297−259) which, in some of the cases, is resolved into a quintet ($^2J_{CP}$ *ca.* 8.5−12.5 Hz). By comparing the homologous complexes in the various families, one observes that replacement of the chloride ligand by fluoride results in a downfield shift for both the vinylidene and carbyne carbon resonances: fluoro−vinylidenes (δ *ca.* 298−291) > chloro−vinylidenes (δ *ca.* 297−285) > fluoro−carbynes (δ *ca.* 291−267) > chloro−carbynes (δ *ca.* 280−259). In the ^1H NMR spectra, the C−CH_2R and C=C*H*R resonances are detected at relatively high fields (δ *ca.* 0−2.2), usually resolved into a quintet ($^4J_{HP}$ *ca.* 3−5 Hz). The *trans* geometry of all of these complexes and the absence of any fluoride ligand are unambiguously confirmed by the singlet resonance observed in their $^{31}P\{^1H\}$ NMR spectra. The X-ray structure of the phenylvinylidene complex **4e** has been described previously[15] and will not be discussed further herein (see also above).

Redox Properties. The cyclic voltammograms of NCMe solutions of the complexes, at a Pt electrode (see Experimental Section), display a single-electron reversible anodic wave at oxidation potentials ($E_{1/2}^{ox}$ vs SCE, Table 1) in the ranges *ca.* 1.5−1.4 (chloro−carbynes **2**) ≥ *ca.* 1.4 (fluoro−carbynes **1**) >> *ca.* 0.3 to −0.2 (chloro−vinylidenes **4**) > 0.1 to −0.4 (fluoro−vinylidenes **3**). In the case of **3** and **4**, a second anodic wave, with only a partial reversible character, is detected at a much higher potential (in the range of 0.9−1.5 V).

The first anodic processes (eqs 12 and 13) should involve the formal Re(n) → Re(n + 1) single-electron oxidations, similar to the observed Re(+1) → Re(+2) oxidation for related isocyanide[39] or nitrile[40] complexes, to form the relatively stable (in the time scale of the cyclic voltammetry experiment) paramagnetic carbyne and vinylidene complexes *trans*-[ReX(≡C−CH_2R)(dppe)$_2$]$^{2+}$ (**1**$^+$ (X = F) or **2**$^+$ (X = Cl)) and *trans*-[ReX(=C=CHR)(dppe)$_2$]$^+$ (**3**$^+$ (X = F) or **4**$^+$ (X = Cl)). This



indicates a strong stabilization of both the carbyne and vinylidene ligands by the fluoro− and the chloro−

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Table 1. Cyclic Voltammetric Data[a] for *trans*-[ReX(≡C−CH_2R)(dppe)$_2$][BF_4] 1 (X = F) and 2 (X = Cl) and *trans*-[ReX(=C=CHR)(dppe)$_2$] 3 (X = F) and 4 (X = Cl)

complex	R	$^{I}E_{1/2}^{ox}$	$^{II}E_{1/2}^{ox}$
1a	H	1.39	
1b	Bu^t	1.39	
1c	CO_2Me	1.44	
1d	CO_2Et	1.41	
1f	C_6H_4Me-4	1.42	
2a	H	1.39	
2b	Bu^t	1.41	
2c	CO_2Me	1.48	
2d	CO_2Et	1.48	
2e	Ph	1.45	
2f	C_6H_4Me-4	1.44	
3a	H	−0.30[b]	1.37
3c	CO_2Me	0.06	1.53
3d	CO_2Et	0.09	1.44
3f	C_6H_4Me-4	−0.35[b]	1.42
4a	H	−0.02[b]	1.38
4b	Bu^t[c]	−0.24	
4c	CO_2Me	0.24[b]	1.48
4d	CO_2Et	0.25	1.41
4e	Ph[d]	−0.18	0.96[e]
4f	C_6H_4Me-4[d]	−0.21	0.85[e]

[a] Values in volts (±0.02) vs SCE, measured in 0.2 mol dm^{-3} [NBu_4][BF_4]/NCMe, unless stated for THF, at a Pt-wire electrode, by using the [Fe(η^5-C_5H_5)$_2$]$^{0/+}$ redox couple ($E_{1/2}^{ox}$ = 0.42 V vs SCE in NCMe or 0.54 V vs SCE in THF) as an internal standard; for conversion into V vs NHE, simply add 0.245 V. [b] Measured for the complex generated *in situ* by deprotonation of the corresponding carbyne complex upon addition of [NBu_4]OH to its electrolytic solution. [c] In THF due to its instability in NCMe. [d] In THF due to its low solubility in NCMe. [e] Irreversible wave ($^{II}E_{p/2}$).

rhenium centers. The much higher oxidation potential of the carbyne complexes **1** and **2** in comparison with that of the vinylidene compounds **3** and **4** reflects the much greater stabilization of the HOMO in the former relative to the latter complexes.

Complexes **1** and **2** are also reversibly oxidized at a substantially more anodic potential than that observed ($E_{p/2}^{ox}$ *ca.* 0.9 V)[18,28c] for the chemically irreversible anodic wave of *trans*-[ReCl(CNH_2)(dppe)$_2$][BF_4] in which the aminocarbyne ligand undergoes proton loss upon oxidation. Hence, the carbyne ligands CCH_2R present a stronger net electron-acceptor ability than the aminocarbyne CNH_2 and are stable toward anodically-induced deprotonation.

Interestingly, the fluoro complexes (either the carbyne or the vinylidene ones) exhibit oxidation potentials at slightly lower values than the corresponding chloro compounds (Table 1), suggesting that the HOMO is less stabilized in energy for the former complexes. Although this could conceivably account, in part, for the rarity (see above) of fluoro−carbyne and fluoro−carbene complexes in comparison with chloro complexes, our synthetic studies indicate that the former can also be readily obtained.

Although neither the carbyne nor the vinylidene complexes exhibit, by cyclic voltammetry, any clear cathodic wave at a potential distinctly above the solvent/electrolyte discharge, when we cathodically scan the potential down to this level, in the case of a carbyne complex solution, the carbyne ligand undergoes dehydrogenation, as a result of electron-transfer, to form the corresponding vinylidene complex which is detected during the subsequent anodic sweep by its characteristic reversible anodic wave (Figure 1) (eq 14).

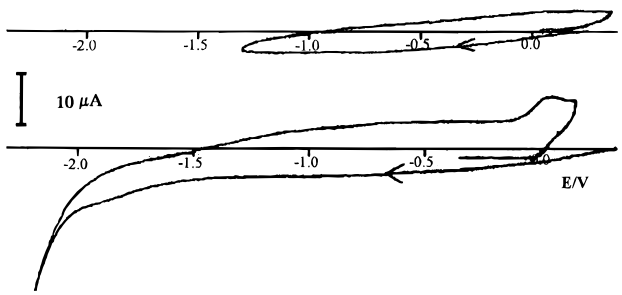

Figure 1. Cathodic cyclic voltammogram of a 0.92 mmol dm^{-3} solution of *trans*-[ReF(≡CCH_2CO_2Et)(dppe)$_2$][BF_4] **1d** in 0.2 mol dm^{-3} [NBu_4][BF_4]/NCMe, Pt-wire electrode (scan rate = 200 mV s^{-1}; potential in V vs SCE). The anodic wave is due to the corresponding cathodically-derived vinylidene complex.

We have previously detected[18] the cathodically-induced dehydrogenation of *trans*-[ReCl(CNH_2)(dppe)$_2$]$^+$ to form *trans*-[ReCl(CNH)(dppe)$_2$], *via* reduction of liberated H^+ from the former complex (which, in solution, partially dissociates to the isocyanide compound) with the resulting shift of this H^+ dissociation equilibrium. However, in the case of the carbyne complexes **1** and **2**, proton dissociation has not been detected to any extent in the electrolyte medium, and therefore, the cathodically-induced deprotonation should result from a genuine reduction of the complex. Since the LUMO is expected to be π-antibonding between the metal and carbon and mainly localized at the carbyne carbon in a cationic complex[41,42] (which accounts for the well-documented frontier-orbital-controlled nucleophilic addition to carbyne ligands, in particular at Re complexes),[43] the reduction of the complex is expected to lead to a decrease in the metal−carbon bond order and to a significant localization of the electron at the carbyne carbon; pairing this unpaired electron could then occur *via* the homolytic cleavage of a C−H bond (the hydrogen atom acceptor has not been identified) with formation of the vinylidene product:

Electrochemical Ligand (P_L and E_L) Parameters for the Carbyne and Vinylidene Ligands. Electrochemical quantifications of the relative electron-donor/acceptor abilities of ligands based on the redox potential values of their complexes have already been proposed, in particular by C. J. Pickett *et al.*[44] and A. B. P. Lever,[45,46] and the values of the defined electrochemical parameters have been quoted for a wide variety of ligands. However, very little information is still available for carbyne or carbene ligands,[16,17,28c] but this work

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(45) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271.
(46) Lever, A. B. P. *Inorg. Chem.* **1991**, *30*, 1980.

Table 2. Estimated P_L and E_L Ligand Parameters for Carbyne and Vinylidene Ligands (L)

L	P_L (V)[a]	E_L (V vs NHE)[b]
CCH_3	0.21	*ca.* 1.2
CCH_2Bu^t	0.21	*ca.* 1.2
CCH_2CO_2Me	0.24	*ca.* 1.2
CCH_2CO_2Et	0.24	*ca.* 1.2
CCH_2Ph	0.23	*ca.* 1.2
$CCH_2C_6H_4Me$-4	0.22	*ca.* 1.2
$C{=}CH_2$	−0.21	0.56
$C{=}CHBu^t$	−0.27	0.50
$C{=}CHCO_2Me$	−0.13	0.62
$C{=}CHCO_2Et$	−0.13	0.62
$C{=}CHPh$	−0.25	0.52
$C{=}CHC_6H_4Me$-4	−0.26	0.51

[a] Estimated using expression 15,[44] applied to the {ReCl(dppe)$_2$} site (E_s = 0.68 V, β = 3.4 V)[39] and to complexes **2** and **4** (see text). [b] Estimated by using expression 17[45] plus, in the case of the carbynes, a proposed[48] correction of *ca.* 0.25 V.

provides an opportunity to gain insight into the electronic properties of these types of ligands.

For several series of closed-shell octahedral-type complexes [M_sL], a linear relationship (eq 15) has been

$$E_{1/2}{}^{ox}[M_sL] = E_s + \beta P_L \qquad (15)$$

observed[44] between their redox potential and the electronic properties of the ligand L and its binding metal center {M_s}, expressed by the P_L ligand parameter, the electron-richness (E_s, that is the redox potential of the carbonyl complex [M_s(CO)]) and polarizability (β) of the metal center. The P_L parameter is considered[44] as a measure of the net electron σ-donor minus π-acceptor ability of the ligand (L): the lower is this character, the higher the oxidation potential of the complex [M_sL] and thus (eq 15) the higher P_L.

Knowing[39] E_s (0.68 V) and β (3.4) for our *trans*-{ReCl(dppe)$_2$} center and the measured values of the oxidation potential of its carbyne and vinylidene complexes **2** and **4**, we have estimated the P_L parameter for these ligands (Table 2) which, together with related ones, can be ordered as follows according to their net-electron acceptance (the P_L ranges being indicated in parentheses): carbynes (CCH_2R, 0.21−0.24 V) > aminocarbyne (CNH_2, *ca.* 0.1V)[28c] > CO (0) > isocyanides (CNR, −0.10 to −0.18 V)[47] ≥ vinylidenes (C=CHR, −0.13 to −0.27 V) >> aminocarbenes or other related heterosubstituted carbenes (−0.6 to −0.8 V).[17a] The carbynes behave as very strong π-electron acceptors, even more effective than carbonyl although not as strong as NO^+ (P_L = 1.40 V).[44]

Another ligand electrochemical parameter (E_L) has been proposed[45] for which the empirical linear correlation (eq 16) was shown to be followed by many redox couples. The redox potential of the complex (E) is

$$E = S_M(\sum E_L) + I_M \qquad (16)$$

expressed in volts vs the normal hydrogen electrode (NHE), $\sum E_L$ is the sum of the E_L values for all the ligands (additive effects),whereas S_M and I_M depend upon the metal and redox couple, the spin state, and stereochemistry.[45] Values of E_L have been proposed for a wide variety of ligands[45] but not for carbynes or carbenes. However, from the linear relationship (eq 17) experimentally observed[45] (for a considerable number of ligands but not for CO) between E_L and P_L, one can estimate the E_L (Table 2) by knowing P_L. The vinylidene E_L values, thus estimated (0.50−0.62 V vs NHE), are much lower than that (0.99)[45] for CO but significantly higher than those known for organonitriles (0.37−0.49 V vs NHE),[45] indicating that vinylidenes are stronger net-electron donors than CO but weaker than organonitriles. Application of eq 17 to the carbyne ligands leads to E_L values of *ca.* 1.2 V vs NHE (upon correction[48] due to their strong π-electron acceptor character), which are the highest ones so far reported.

$$P_L = 1.17E_L - 0.86 \qquad (17)$$

Application of eq 16 to our complexes presents serious difficulties. For the carbyne complexes, not knowing the I_M and S_M values for the metal redox couple prevents the use of such an expression. This difficulty should not arise for the vinylidene complexes (for the Re(+1/+2) redox couple, S_M = 0.76 and I_M = −0.95 V vs NHE),[46] but eq 16 needs correction to be valid for potentials below *ca.* 0.2 V vs NHE (corresponding to $\sum E_L$ values below *ca.* 1.6 V vs NHE).[46] In our vinylidene complexes **3** and **4**, only those with the stronger electron accepting ester groups have an oxidation potential value well above that restriction and the E_L values for the ester−vinylidenes (average 0.66 or 0.68 V vs NHE for $C{=}CHCO_2Me$ or $C{=}CHCO_2Et$), estimated by application of this equation (knowing[45] the E_L values for the other coligands), are in agreement with that (0.62 V) obtained from eq 17; however, for the other vinylidene complexes, the E_L values estimated from eq 16 are in high disagreement with those obtained by using eq 17.

Peculiarities of the Re(+1/+2) redox systems have been recognized by Lever[46] who, in terms of the two available sets of data well-separated in complex redox potentials (above *ca.* 0.2 and at *ca.* −1.0 V vs NHE), postulated that either two distinct linear relationships (an "upper" and, although with highly scattered points, a "lower" one) of the type of eq 16 but with different S_M and I_M values or a curved relationship between the redox potential and $\sum E_L$ (Figure 2, dotted lines) occurs. In such a plot, the points which represent the first oxidation of our vinylidene complexes **4**, with the exception of those with ester substituents, are situated below the upper line (Figure 2). This observation supports the hypothesis of a curved relationship, although it shoud be confirmed by studying other Re(+1/+2) systems with lower oxidation potentials. In contrast, the plot for the second oxidation potential of **4**, *i.e.*, for the oxidation potential of $\mathbf{4}^+$ (Figure 2), does not deviate much from the straight line presented by Lever[46] for other Re(+3/+2) systems (extrapolated to higher redox potentials).

(47) Carvalho, M. F. N. N.; Pombeiro, A. J. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1209.

(48) The direct application of eq 17 to the carbyne ligands in our complexes would give E_L values (0.91−0.94 V vs NHE range) which are lower than that for CO, in disagreement with the fact that the carbyne complexes have oxidation potentials (1.39−1.48 V range) (Table 1) higher than that of the carbonyl analogue (0.68 V); moreover, the proposed E_L value for CO (0.99 V vs NHE)[45] is significantly higher than that (0.74 V vs NHE, since P_L = 0 V for CO) obtained from the expression, appearing to be invalid for ligands (like carbynes and CO) that are strong π-acceptors, accounting for the recognized[45] need to introduce positive corrections to E_L for ligands with an extensive π-stabilizing influence on the energy of the HOMO. If the E_L values for the carbynes given by expression 17 would need a correction similar to that of CO (0.25 V, see above), they would lie in the 1.16−1.19 V vs NHE range.

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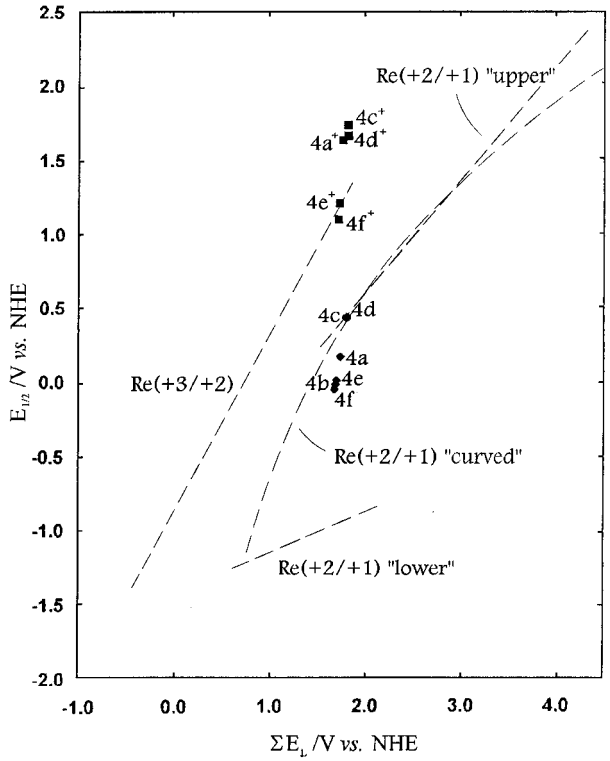

Figure 2. Plot of the first (♦) and the second (■) oxidation potentials ($^{I}E_{1/2}{}^{ox}$ and $^{II}E_{1/2}{}^{ox}$ (V vs NHE), respectively) vs $\sum E_L$(V vs NHE) for the vinylidene complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$], **4** (R = H (**4a**), Bu^t (**4b**), CO_2Me (**4c**), CO_2Et (**4d**), Ph (**4e**), or C_6H_4Me-4 (**4f**)). The dotted lines correspond to the relationships previously proposed by Lever (Figure 2 in ref 46) for other Re(+2/+1) or Re(+3/+2) redox systems.

The above curved correlation indicates that for our electron-rich vinylidene−rhenium(+1) complexes with the stronger electron donor ligands, the energy of the redox orbital is more sensitive to a change of the electronic properties of the ligands (reflecting a change in $\sum E_L$) than in the case of other less electron-rich rhenium centers. This supports the finding,[39,44] on the basis of the Pickett formalism, that in a series of related complexes, an increase of the electron-rich character of the metal site (E_s) is accompanied by an increase of its polarizability (β), the energy of the HOMO thus becoming less buffered with respect to a ligand change. Hence, the influence of a ligand on the energy of the redox orbital of a complex is a delicate function of the properties not only of the ligand but also of the metal center, including the effect of the other coligands, a situation which can invalidate the hypothesis of the additive effect of ligands on the redox potential of the complexes.

Conclusions

Series of fluoro−carbyne and fluoro−vinylidene complexes (apart from the related chloro species), which are interconvertible by acid−base reactions or upon electron transfer, have been prepared by activation of 1-alkynes by the electron-rich {ReCl(dppe)$_2$} center, in the former case through a convenient single-plot synthesis. The $[BF_4]^-$ ion behaves as a ready metal fluorinating agent, and fluoride is shown to have a good stabilizing effect on the *trans*-carbyne or -vinylidene ligand, even in the corresponding oxidized complexes generated anodically. Electrochemical methods were also shown to be successfully applicable to the activation of the carbyne ligands toward C−H bond cleavage, which is induced cathodically to generate the corresponding vinylidene species, as well as to the investigation of the electron-donor/acceptor properties of the carbyne and vinylidene ligands, the former being shown to behave as rather strong net electron acceptors. The electrochemical P_L and E_L ligand parameters have been estimated and corroborate a curved relationship between the oxidation potential and $\sum E_L$ comprising the vinylidene ligands, which is interpreted on the basis of the low ability of the electron-rich Re(I)−halide center to buffer changes in the energy of the HOMO. The fluoride ligand, in comparison with chloride, has a slightly stronger destabilizing effect on the HOMO, which, however, does not avoid the ready formation of stable fluoro−carbyne and −vinylidene complexes even with the electron-rich metal centers of this study. Hence, the still rather limited number of transition metal fluoro complexes with multiple metal−carbon bonds is expected to expand in the future.

In addition, these studies can also be of some biological importance since vinylidene complexes are recognized intermediates in some enzymatic processes (*e.g.*, in the matabolism of some chlorinated hydrocarbons)[49] and they can be postulated, with carbyne species of the type we have obtained, as conceivable intermediates[13a] in the reduction of 1-alkynes by nitrogenases.

Experimental Section

All reactions were carried out using standard inert gas flow or high-vacuum techniques. The complex *trans*-[ReCl(N$_2$)(dppe)$_2$] was prepared by a published method;[40] the acid [Et$_2$OH][BF$_4$], the alcoholic solution of [NBu$_4$]OH, and the 1-alkynes (HC≡CR) were used as purchased from Aldrich (R = Bu^t, CO_2Me, CO_2Et, Ph, or C_6H_4Me-4) or Fluorochem (R = $SiMe_3$). The solvents were purified and dried by standard methods and freshly distilled under dinitrogen. The IR spectra were recorded on a Perkin-Elmer 683 spectrophotometer and NMR spectra (run in CD_2Cl_2 unless stated otherwise) on a Varian Unity 300 spectrometer. ^1H, ^{31}P, ^{19}F, and ^{13}C chemical shifts (δ) are reported in ppm relative to TMS, $P(OMe)_3$, $CFCl_3$, and TMS, respectively. In the ^{13}C NMR data, assignments and coupling constants common to the $^{13}C\{^1H\}$ NMR spectra are not repeated. Abbreviations: s = singlet; d = doublet; t = triplet; q =quartet; qnt = quintet; m = complex multiplet; br = broad; tqnt = triplet of quintets; dm = doublet of multiplets; tm = triplet of multiplets; qt = quartet of triplets; *o*, *m*, or *p* = the *ortho*-, *meta*- or *para*-phenyl proton, respectively; sh = shoulder.

The electrochemical experiments were carried out either on an EG & G PAR 173 potentiostat/galvanostat and an EG & G PARC 175 Universal programmer or on an HI-TEK DT 2101 potentiostat/galvanostat and an HI-TEK PP RI waveform generator. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum wire or disc or a vitreous carbon working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. Controlled-potential electrolyses were carried out in a three-electrode H-type cell with platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a

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(50) Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1973**, 612.

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silver wire pseudo-reference electrode. The first anodic wave in the cyclic voltammograms of the complexes has ΔE_p of *ca.* 100 mV, i_p (anodic)/i_p (cathodic) close to one, and the current-function $i_pC^{-1}v^{-1/2}$ (C = concentration, v = scan rate) without appreciable variation in the 50−1000 mV s^{-1} scan rate range, thus following the usual criteria for a single-electron reversible process. Controlled potential electrolysis at this anodic wave corresponds to the consumption of 1 *F*/mol, confirming the involvement of a single-electron process. The oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][BF_4]$/NCMe or THF, and the redox potential are quoted relative to the SCE (saturated calomel electrode) by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple (0.42 or 0.54 V vs SCE in 0.2 mol dm^{-3} $[NBu_4][BF_4]$/NCMe or THF, respectively, as an internal reference). To convert to the NHE (normal hydrogen electrode), this reference redox couple, in NCMe or THF, is considered[45] to lie at 0.665 or 0.785 V vs NHE respectively; hence, the values of the oxidation potentials of the complexes relative to NHE were estimated by adding 0.245 V to the corresponding ones quoted relative to SCE.

Preparation of *trans*-[ReF(≡C−CH_2R)(dppe)$_2$][BF_4] 1a (R = H), 1b (R = Bu^t), 1c (R = CO_2Me), 1d (R =CO_2Et), 1e (R = Ph), or 1f (R = C_6H_4Me-4). These fluoro−carbyne complexes have been prepared in a single-pot synthesis by treating a THF solution of *trans*-[ReCl(N_2)(dppe)$_2$] with the appropriate 1-alkyne and $[NH_4][BF_4]$ in the presence of Tl[BF_4], under sunlight, in an argon atmosphere. They are also formed, eventually, in lower yields and as side products in the syntheses of the chloro−carbyne complexes **2** described below. Complex **1a** was obtained from HC≡$CSiMe_3$ which underwent desilylation.

As a typical example, the synthesis of *trans*-[ReF(≡C−CH_2-CO_2Me)(dppe)$_2$][BF_4], **1c**, can be described as follows: A THF solution (250 cm^3) of *trans*-[ReCl(N_2)(dppe)$_2$] (0.30 *g*, 0.29 mmol), under argon, was treated with Tl[BF_4] (0.13 *g*, 0.43 mmol), $[NH_4][BF_4]$ (0.15 *g*, 1.4 mmol), and HC≡CCO_2Me (0.096 cm^3, 1.2 mmol), and the system was left stirring in sunlight for 0.5 h. The solution was then taken to dyness *in vacuo*. Extraction with CH_2Cl_2 (5 cm^3) followed by filtration and addition of diethyl ether led to the precipitation of **1c** as a white solid, which was filtered off, washed with diethyl ether, and dried *in vacuo*. Further crops could be obtained from the mother liquor upon concentration and addition of diethyl ether (*ca.* 60% yield).

1a: Pale yellow, *ca.* 15% yield. ^{1}H NMR ($CDCl_3$): δ 7.6−6.9 (m, 40H, Ph−dppe), 2.9−2.5 (m, 8H, CH_2−dppe), 0.49 (s, br, 3H, CCH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −112.2 (d, $^2J_{PF}$ = 39 Hz). ^{19}F NMR ($CDCl_3$): δ −324.3 (qnt, $^2J_{PF}$ = 39 Hz). Anal. Calcd for $BC_{54}F_5H_{51}P_4Re\cdot0.5CH_2Cl_2$: C, 56.5; H, 4.5. Found: C, 56.5; H, 4.7.

1b: White, *ca.* 55% yield. ^{1}H NMR: δ 7.58−7.19 (m, 40 H, Ph−dppe), 3.87 (m, br, 4H, CH_2−dppe), 3.07 (m, br, 4H, CH_2−dppe), 1.69 (s, 2H, CCH_2Bu^t), 0.01 (s, 9H, CCH_2Bu^t). ^{31}P{^{1}H} NMR: δ −116.3 (d, $^2J_{PF}$ = 44 Hz). ^{19}F NMR: δ −324.3 (qnt, $^2J_{PF}$ = 44 Hz). ^{13}C{^{1}H} NMR: δ 135.9−128.7 (m, Ph−dppe), 65.28 (qnt, $^4J_{CP}$ = 10 Hz, CCH_2Bu^t), 33.06 (qnt, virtual J_{CP} = 10 Hz, CH_2−dppe), 31.85 (s, $C(CH_3)_3$), 30.05 (s, $C(CH_3)_3$). Anal. Calcd for $BC_{58}F_5H_{57}P_4Re$: C, 59.4; H, 5.1. Found: C, 59.6; H, 5.6.

1c: White, *ca.* 60% yield. IR (KBr pellet, cm^{-1}): 1726 (ν_{CO}). ^{1}H NMR ($CDCl_3$): 7.39−6.98 (m, 40H, Ph−dppe), 2.95 (s, 3H, CO_2CH_3), 3.1−2.9 (m, br, 4H, CH_2−dppe), 2.8−2.6 (m, br, 4H, CH_2−dppe), 1.85 (s, br, 2H, CCH_2CO_2Me).^{31}P{^{1}H} NMR ($CDCl_3$): δ −114.1 (d, $^2J_{PF}$ = 43 Hz). ^{19}F NMR ($CDCl_3$): δ −316.3 (qnt, $^2J_{PF}$ = 42 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 266.53 (m, CCH_2CO_2Me), 163.55 (s, CO_2Me), 134.3−127.9 (m, Ph−dppe), 52.20 (s, CCH_2CO_2Me), 51.93 (s, CO_2CH_3), 32.26 (qnt, virtual J_{CP} = 10 Hz, CH_2−dppe). Anal. Calcd for $BC_{56}F_5H_{53}O_2P_4Re\cdot2CH_2Cl_2$: C, 57.1; H, 4.7. Found: C, 56.9; H, 4.9.

1d: White, *ca.* 55% yield. IR (KBr pellet, cm^{-1}): 1470 (ν_{CO}). ^{1}H NMR ($CDCl_3$): δ 7.29−6.50 (m, 40H, Ph−dppe), 3.47 (q, 6.0 Hz, 2H, $CO_2CH_2CH_3$), 3.00 (m, br, 4H, CH_2−dppe), 2.65 (m, br, 4H, CH_2−dppe), 1.67 (s, 2H, CCH_2CO_2Et), 0.89 (t, J = 6.0 Hz, 3H, $CO_2CH_2CH_3$). ^{31}P{^{1}H} ($CDCl_3$): δ −114.3 (d, $^2J_{PF}$ = 43 Hz). ^{19}F NMR: δ −318.5 (qnt, $^2J_{PF}$ = 42 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 290.50 (qnt, $^2J_{CP}$ = 11 Hz, CCH_2CO_2Et), 163.45 (s, CO_2Et), 134.3−128.1 (m, Ph−dppe), 61.42 (s, $COCH_2CH_3$), 53.68 (s, CCH_2CO_2Et), 32.37 (qnt, virtual J_{CP} = 9.2 Hz, CH_2−dppe), 13.64 (s, $COCH_2CH_3$). ^{13}C NMR ($CDCl_3$): δ 290.50 (qnt), 163.45 (s), *ca.* 134−128 (m), 61.42 (t, J_{CH} = 146.5 Hz), 53.68 (t, J_{CH} = 129 Hz), 32.37 (tm, J_{CH} = 134.9 Hz), 13.64 (q, J_{CH} = 123.3 Hz). Anal. Calcd for $BC_{57}F_5H_{55}O_2P_4Re\cdot1.8CH_2Cl_2$: C, 58.2; H, 4.8. Found: C, 58.2; H, 5.3.

1e: Yellow, *ca.* 20% (not analytically pure). ^{1}H NMR ($CDCl_3$): δ 8.1−6.5 (m, 43H, Ph−dppe + CCH_2Ph (*m*, *p*)), 5.68 (d, J = 5.5 Hz, 2H, CCH_2Ph (o)), 3.1−2.6 (m, br, 8H, CH_2−dppe), 1.25 (m, 2H, CCH_2Ph). ^{31}P{^{1}H} ($CDCl_3$): δ −114.2 (d, $^2J_{PF}$ = 43 Hz) . ^{19}F NMR ($CDCl_3$): δ −322.1 (qnt, $^2J_{PF}$ = 43 Hz).

1f: Pale yellow, *ca.* 40% yield. ^{1}H NMR: δ 7.50−6.80 (m, 40H, Ph−dppe), 6.51(d, J = 6.0 Hz, 2H, C_6H_4Me), 5.64 (d, J = 6.0 Hz, 2H, C_6H_4Me), 2.65 (m, 8H, CH_2−dppe), 2.42 (s, br, 2H, $CCH_2C_6H_4$Me), 2.10 (s, 3H, $C_6H_4CH_3$). ^{31}P{^{1}H} NMR: δ −112.8 (d, $^2J_{PF}$ = 43 Hz). ^{19}F NMR: δ −321.4 (qnt, $^2J_{PF}$ = 42 Hz). ^{13}C{^{1}H} NMR: δ 279.60 (m, $CCH_2C_6H_4$Me), 135.0−127.1 (m, Ph−dppe), 55.84 (s, br, $CCH_2C_6H_4$Me), 32.46 (qnt, virtual J_{CP} = 10 Hz, CH_2−dppe), 20.62 (s, $C_6H_4CH_3$). ^{13}C NMR: δ 279.60 (m), *ca.* 135−127 (m), 55.84 (t, br, J_{CH} = 127 Hz), 32.46 (tqnt, J_{CH} = 132.4 Hz), 20.62 (q, J_{CH} = 112.3 Hz).

Preparation of *trans*-[ReF(=C=CHR)(dppe)$_2$] 3c (R = CO_2Me), 3d (R = CO_2Et), or 3f (R = C_6H_4Me-4). These fluoro−vinylidene complexes have been prepared by the deprotonation reaction, in CH_2Cl_2 and under dinitrogen, of the corresponding fluoro−carbyne compounds **1c**, **1d**, or **1f** by $[NBu_4]$OH in alcoholic solution (base added in a *ca.* stoichiometric amount). However, the less acidic carbyne **1b** did not appear to undergo deprotonation even under refluxing solvent conditions.

As a typical example, the preparation of *trans*-[ReF(=C=$CHCO_2$Et)(dppe)$_2$], **3d**, was carried out as follows: a CH_2Cl_2 solution (15 cm^3) of *trans*-[ReF(≡C−CH_2CO_2Et)(dppe)$_2$][BF_4] (0.12 *g*, 0.10 mmol) was treated with a 0.1 M solution of $[NBu_4]$OH in methanol (1.1 cm^3, 0.13 mmol). Addition of diethyl ether followed by concentration of the solution led to the precipitation of complex **3d** as a yellow solid, which was filtered off, washed with diethyl ether, and dried *in vacuo*. Further crops were obtained from the mother liquor upon concentration and addition of diethyl ether (*ca.* 60% yield).

3c: Yellow, *ca.* 50% yield. IR (KBr pellet, cm^{-1}): 1610, 1480 (ν_{CO} and $\nu_{C=C}$).^{1}H NMR ($CDCl_3$): δ 7.43−6.98 (m, 40 H, Ph−dppe), 3.10 (s, br, 3H, CO_2CH_3), 2.90 (m, br, 4H, CH_2−dppe), 2.54 (m, br, 4H, CH_2−dppe), 1.28 (m, br, 1H, CC$H$$CO_2$Me). ^{31}P{^{1}H} NMR ($CDCl_3$): δ −109.9 (d, $^2J_{PF}$ = 34 Hz). ^{19}F NMR ($CDCl_3$): δ −328.6 (m, br). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 298.20 (m, $CCHCO_2$Me), 168.27 (s, CO_2Me), 138.0−127.0 (m, Ph−dppe), 97.7 (m, br, $CCHCO_2$Me), 53.40 (s, CO_2CH_3), 32.80 (qnt, virtual J_{CP} = 12.2 Hz, CH_2−dppe). ^{13}C NMR ($CDCl_3$): δ 298.20 (m), 186.27 (s), *ca.* 138−127 (m, br), 53.40 (m), 32.80 (tqnt, J_{CH} = 132.8 Hz). Anal. Calcd for $C_{56}FH_{52}O_2P_4Re\cdot2CH_2Cl_2$: C, 59.8; H, 4.7. Found: C, 59.0; H, 4.8.

3d: Yellow, *ca.* 60% yield. IR (KBr pellet, cm^{-1}): 1610, 1485 (ν_{CO} and $\nu_{C=C}$). ^{1}H NMR: δ 7.33−7.02 (m, 40 H, Ph−dppe), 3.75 (m, 2H, CH_2CH_3), 2.82 (m, br, 4H, CH_2−dppe), 2.47 (m, br, 4H, CH_2−dppe), 1.4−0.6 (m, 4H, CC$H$$CO_2CH_2CH_3$). ^{31}P-{^{1}H} NMR: δ −109.8 (d, $^2J_{PF}$ = 34 Hz). ^{19}F NMR: δ −325.5 (qnt, $^2J_{PF}$ = 34 Hz). ^{13}C{^{1}H} NMR: δ 290.80 (m, $CCHCO_2$Et), 168.15 (s, CO_2Et), 137.6−127.5 (m, Ph−dppe), 97.40 (m, $CCHCO_2$Et), 58.72 (s, $CO_2CH_2CH_3$), 32.00 (s, CH_2−dppe), 15.24 (s, $CO_2CH_2CH_3$). ^{13}C NMR: δ 290.80 (m), 168.15 (s), *ca.* 138−127 (m), 97.40 (dm, J_{CH} = 156.3), 58.72 (t, J_{CH} = 144.5 Hz), 32.00 (t, J_{CH} = 133.4 Hz), 15.24 (q, J_{CH} = 126.5 Hz). Anal.

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Calcd for $C_{57}FH_{54}O_2P_4Re{\cdot}2CH_2Cl_2$: C, 60.1; H, 4.8. Found: C, 60.0; H, 5.2.

3f: Rose, *ca*. 45% yield: IR (KBr pellet, cm^{-1}): 1520 ($\nu_{C=C}$). ^1H NMR ($CDCl_3$): δ 7.58−6.94 (m, 40 H, Ph−dppe), 6.79 (d, J = 6.6Hz, 2H, C_6H_4Me), 5.90 (d, J = 6.6Hz, 2H, C_6H_4Me), 3.2−2.3 (m, 8H, CH_2−dppe), 2.00 (s, 3H, $C_6H_4CH_3$), 1.25 (m, br, 1H, $CCHC_6H_4Me$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −114.2 (d, $^2J_{PF}$ = 40 Hz). ^{19}F NMR ($CDCl_3$): δ −318.8 (qnt, $^2J_{PF}$ = 42 Hz). Anal. Calcd for $C_{61}FH_{56}P_4Re{\cdot}2CH_2Cl_2$: C 58.8; H, 4.7. Found: C, 58.7; H, 5.0.

Preparation of *trans*-[ReCl(=C=CHR)(dppe)$_2$] 4b (R = Bu^t), 4c (R = CO$_2$Me), 4d (R = CO$_2$Et), 4e (R = Ph) or 4f (R = C$_6$H$_4$Me-4). With the exception of **4f**, which was prepared for the first time in this work, the other chloro−vinylidene complexes **4b,c−e** have previously[15] been obtained from the slow reaction (for *ca*. 4 to 6 days) of *trans*-[ReCl(N_2)(dppe)$_2$] with the appropriate 1-alkyne (present in a 15−30-fold molar excess) in refluxing THF or under tungsten-filament bulb irradiation. We now report an improved synthetic method by exposure of the reaction solution to sunlight, a procedure that drastically reduces the reaction time to *ca*. 0.5−3 h (depending on the light intensity), even in the presence of a signicantly lower excess of the alkyne (4-fold stoichiometric excess, relative to the dinitrogen complex) than that required by the previous method (see above).

This general and new procedure consists of the preparation of a solution in toluene or THF (although with lower yields than when using toluene) of *trans*-[ReCl(N_2)(dppe)$_2$] and the appropriate 1-alkyne (4-fold stoichiometric excess), which is stirred under argon and in sunlight for *ca*. 0.5−3 h; the corresponding vinylidene product **4** precipitates out of the solution upon concentration and addition of pentane or diethyl ether, respectively. As a typical example, the detailed procedure for the novel complex *trans*-[ReCl(=C=CHC$_6$H$_4$Me-4)(dppe)$_2$], **4f**, is given as follows: the alkyne HC≡CC$_6$H$_4$Me-4 (0.145 cm^3, 1.15 mmol) was added to a solution of *trans*-[ReCl(N_2)(dppe)$_2$] (0.30 g, 0.29 mmol) in toluene (300 cm^3), prepared under argon, which was then stirred in sunlight. Its color turned from yellow to red, and after *ca*. 1 h no further changes were observed. The red solution (after *ca*. 2 h from the beginning) was concentrated *in vacuo* until a yellowish powder appeared which was filtered off. Upon further concentration *in vacuo* of the filtered solution and addition of pentane, complex **4f** precipitated as a red crystalline solid, which was filtered off, washed with pentane and dried *in vacuo*; further crops could be obtained from the mother liquor upon further concentration, addition of pentane, and/or cooling to *ca*. 0 °C (*ca*. 85% yield). Identical procedures were applied for the preparation of the other chloro−vinylidene complexes **4** and shorter reaction times could be used (*ca*. 0.5−1 h for **4b**, **4c**, or **4d**).

Complexes **4**, with the exception of **4b**, can also be prepared, although in a much less convenient and indirect way, upon deprotonation of the corresponding chloro−carbynes **2** (see below) by [NBu$_4$]OH, following a procedure identical to that described above for the analogous fluoro−vinylidene complexes **3**; however, the less acidic carbyne **2b** does not undergo such a deprotonation reaction.

4f: Red, *ca*. 85% yield. IR (KBr pellet, cm^{-1}): 1550, 1570 (sh) ($\nu_{C=C}$). ^1H NMR: δ 7.45−6.94 (m, 40H, Ph−dppe), 6.38 (d, J = 7.5 Hz, 2H, C_6H_4Me), 5.68 (d, J = 7.5 Hz, 2H, C_6H_4-Me), 2.71 (m, br, 4H, CH_2−dppe), 2.53 (m, br, 4H, CH_2−dppe), 2.31 (s, 3H, $C_6H_4CH_3$), 0.72 (m, br, 1H, $CCHC_6H_4Me$). $^{31}P\{^1H\}$ NMR: δ −126.4 (s).$^{13}C\{^1H\}$ NMR: δ 295.30 (s, $CCHC_6H_4$-Me), 137.6−123.6 (m, Ph−dppe, C_6H_4Me), 108.46 (s, $CCHC_6H_4$-Me), 31.89 (qnt, virtual J_{CP} = 11.3 Hz, CH_2−dppe), 21.48 (s, $C_6H_4CH_3$). ^{13}C NMR: δ 295.30 (s), *ca*. 138−123 (m), 108.46 (d, J_{CH} = 148.2 Hz), 31.89 (tm, J_{CH} = 126.7 Hz), 21.48 (q, J_{CH} = 124.7 Hz). Anal. Calcd for $C_{61}ClH_{56}P_4Re$: C, 64.8; H, 5.0. Found: C, 64.9; H, 5.3.

Preparation of *trans*-[ReCl(≡C−CH$_2$R)(dppe)$_2$] 2a (R = H), 2b (R = Bu^t), 2c (R = CO$_2$Me), 2d (R = CO$_2$Et), 2e (R = Ph), or 2f (R = C$_6$H$_4$Me-4). These chloro−carbyne complexes can be prepared (i) by treatment of a solution (in CH_2Cl_2 or in THF) of the appropriate chloro−vinylidene precursor *trans*-[ReCl(=C=CHR)(dppe)$_2$] **4** with acid (HBF_4, [NH_4][BF_4], or an alkylammonium salt such as [NHEt$_3$] [BPh$_4$]) or (ii) in a single-pot synthesis (although in a lower yield) from *trans*-[ReCl(N_2)(dppe)$_2$] by treating a THF solution of this complex with the appropriate 1-alkyne (RC≡CH) and [NH_4]-[BF_4], under sunlight, in an argon atmosphere. Complex **2a** was obtained, *via* route (ii), from HC≡CSiMe$_3$ which underwent desilylation. As a typical example, let us consider the preparation of *trans*-[ReCl(≡CCH$_2$Ph)(dppe)$_2$][BF_4] **2e**: *Route (i)*. To a stirred CH_2Cl_2 solution (25 cm^3) of *trans*-[ReCl(=C=CHPh)(dppe)$_2$], **4e** (0.36 g, 0.32 mmol), under dinitrogen, was added dropwise a diluted solution of [Et_2OH][BF_4] in diethyl ether (0.32 mmol of acid, *i.e*., 0.50 cm^3 of a 1:11 diluted solution of the commercially available 54% concentrated acid solution). Concentration of the solution was followed by slow addition of diethyl ether until the formation of a fine white powder, which was filtered off. Further addition of diethyl ether to the filtered solution and/or cooling to *ca*. 0 °C led to precipitation of complex **2e** as a pale yellow crystalline solid, which was filtered off, washed with a solutioon of diethyl ether/dichloromethane (3:1), and dried *in vacuo*. Further crops were obtained from the mother liquor upon concentration and addition of diethyl ether (*ca*. 70% yield). The use of an excess (3:1) of [Et_2OH][BF_4], as well as of an ammonium salt (the reaction was then carried out in THF) instead of this acid, resulted in the formation of the same complex.

Route (ii). A THF solution (250 cm^3) of *trans*-[ReCl(N_2)-(dppe)$_2$] (0.20 g, 0.19 mmol), under argon, was treated with [NH_4][BF_4] (0.10 g, 0.96 mmol) and HC≡CPh (0.084 cm^3, 0.77 mmol), and the system was left stirring in the sunlight for *ca*. 1 h and then overnight. The solvent was removed *in vacuo* nearly to dryness, CH_2Cl_2 (2 cm^3) added, and the solution filtered. Diethyl ether was added until a white powder started to be formed. It was filtered off, and complex **2e** precipitated from the filtered solution as a crystalline solid. It was isolated by filtration, washed with diethyl ether, and dried *in vacuo*. It could by recrystallized from CH_2Cl_2/diethyl ether. Further crops could be obtained from the mother liquor by a similar precipitation procedure (*ca*. 60% total yield).

2a: Pale yellow, *ca*. 15% yield. ^1H NMR ($CDCl_3$): δ 7.65−6.90 (m, 40H, Ph−dppe), 3.05−2.60 (m, br, 8H, CH_2−dppe), 0.45 (qt, $^4J_{HP}$ = 3.5Hz, 3H, CCH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −118.2(s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 273.60 (m, CCH_3), 135.1−127.4 (m, Ph−dppe), 36.30 (s, CCH_3), 31.20 (qnt, virtual J_{CP} = 10.9 Hz, CH_2−dppe). ^{13}C NMR ($CDCl_3$): δ 273.60 (m), *ca*. 135−127 (m), 36.30 (q, J_{CH} = 130.6 Hz), 31.20 (tqnt, J_{CH} = 130.6 Hz). Anal. Calcd for $BC_{54}ClF_4H_{51}P_4Re{\cdot}0.5CH_2Cl_2$: C, 55.7; H, 4.4. Found: C, 55.7; H, 4.5.

2b: White, *ca*. 65% yield. ^1H NMR: δ 7.65−6.80 (m, 40H, Ph−dppe), 3.2−2.4 (m, br, 8H, CH_2−dppe), 0.88 (qnt, br, $^4J_{HP}$ = 4.0 Hz, 2H, CCH_2Bu^t), 0.05 (s, 9H, CCH_2Bu^t). $^{31}P\{^1H\}$ NMR: δ −114.6 (s). $^{13}C\{^1H\}$ NMR: δ 280.21 (qnt, $^2J_{CP}$ = 10.5 Hz, CCH_2Bu^t), 134.0−128.3 (m, Ph−dppe), 64.89 (s, CCH_2Bu^t), 32.13 (s, $C(CH_3)_3$), 31.45 (qnt, virtual J_{CP} = 10.6 Hz, CH_2−dppe), 30.00 (s, $C(CH_3)_3$). ^{13}C NMR: δ 280.21 (qnt), *ca*. 134−128 (m), 64.89 (t, J_{CH} = 125.9 Hz), 32.13 (s), 31.45 (tm, J_{CH} = 133.3 Hz), 30.00 (q, J_{CH} = 126.0 Hz). Anal. Calcd for $BC_{58}ClP_4H_{57}P_4Re{\cdot}0.5CH_2Cl_2$: C, 57.1; H, 4.9. Found: C, 57.1; H, 5.1.

2c: Pale yellow, *ca*. 95% yield. IR (KBr pellet, cm^{-1}): 1740 (ν_{CO}). ^1H NMR: δ 7.45−7.06 (m, 40H, Ph−dppe), 3.02 (s, 3H, CO_2CH_3), 2.89 (m, br, 8H, CH_2−dppe), 1.62 (qnt, br, $^4J_{HP}$ = 3.5 Hz, CCH_2CO_2Me). $^{31}P\{^1H\}$ NMR: δ −117.2 (s). $^{13}C\{^1H\}$ NMR: δ 259.78 (qnt, $^2J_{CP}$ = 8.5 Hz, CCH_2CO_2Me), 162.70 (s, CO_2Me), 135.7−127.2 (m, Ph−dppe), 54.18 (s, CCH_2CO_2Me), 52.65 (s, CO_2CH_3), 31.00 (qnt, virtual J_{CP} = 10.9 Hz, CH_2−dppe). ^{13}C NMR: δ 259.78 (qnt), 162.70 (s), *ca*. 136−127 (m), 54.18 (t, J_{CH} = 129.3 Hz), 52.65 (q, J_{CH} = 148.5 Hz), 31.00

(tqnt, J_{CH} = 135.9 Hz). Anal. Calcd for $BC_{56}ClF_4H_{53}O_2P_4Re \cdot 0.25\ CH_2Cl_2$: C, 55.8; H, 4.2. Found: C, 55.9; H, 4.6.

2d: Pale yellow, *ca*. 75% yield. IR (KBr pellet, cm^{-1}): 1750 (ν_{CO}). ^1H NMR: δ 7.44−7.09 (m, 40H, Ph−dppe), 3.44 (q, J = 6.9 Hz, 2H, $CO_2CH_2CH_3$), 2.88 (m, br, 8H, CH_2−dppe), 1.60 (qnt, br, $^4J_{HP}$ = 2.9 Hz, 2H, CCH_2CO_2Et), 0.94 (t, J = 6.9 Hz, 3H, $CO_2CH_2CH_3$). $^{31}P\{^1H\}$ NMR: δ −117.0 (s). $^{13}C\{^1H\}$ NMR: δ 260.03 (s, CCH_2CO_2Et), 162.33 (s, CO_2Et), 135.2−127.2 (m, Ph−dppe), 62.22 (s, $CO_2CH_2CH_3$), 54.44 (s, CCH_2CO_2Et), 31.00 (qnt, virtual J_{CP} = 10.0 Hz, CH_2−dppe), 13.74 (s, $CO_2CH_2CH_3$). ^{13}C NMR: δ 260.03 (m), 162.33 (s), *ca*. 135−127 (m), 62.22 (t, J_{CH} = 148.4 Hz), 54.44 (t, J_{CH} = 130.9 Hz), 31.00 (tqnt, J_{CH} = 136.7 Hz), 13.74 (q, J_{CH} = 126.8 Hz). Anal. Calcd for $BC_{57}ClF_4H_{55}O_2P_4Re \cdot 0.75CH_2Cl_2$: C, 54.7; H, 4.7. Found: C, 54.6; H, 4.7.

2e: Pale yellow, *ca*. 70% yield. ^1H NMR: δ 7.60−6.95 (m, 43H, Ph−dppe + CCH_2Ph (*m*, *p*)), 6.07 (d, J = 5.5 Hz, 2H, CCH_2Ph (*o*)), 3.2−2.4 (m, br, 8H, CH_2−dppe), 2.23 (qnt, $^4J_{HP}$ = 3.5 Hz, CCH_2Ph). $^{31}P\{^1H\}$ NMR: δ −114.0 (s). $^{13}C\{^1H\}$ NMR: δ 269.89 (qnt, $^2J_{CP}$ = 12.4 Hz, CCH_2Ph), 134.0−127.9 (m, Ph−dppe), 56.75 (s, CCH_2Ph), 31.00 (qnt, virtual J_{CP} = 11.0 Hz, CH_2−dppe). ^{13}C NMR: δ 269.89 (qnt), *ca*. 134−127 (m), 56.75 (t, J_{CH} = 128.5 Hz), 31.00 (tqnt, J_{CH} = 130.7 Hz). Anal. Calcd for $BC_{60}ClF_4H_{55}P_4Re$: C, 59.6; H, 4.6. Found: C, 59.3; H, 4.6.

2f: Pale yellow, *ca*. 75% yield. ^1H NMR: δ 7.50−7.00 (m, 40H, Ph−dppe), 6.87 (d, J = 7.5 Hz, 2H, C_6H_4Me), 5.92 (d, J = 7.5 Hz, 2H, C_6H_4Me), 2.90 (m, br, 4H, CH_2−dppe), 2.60 (m, br, 4H, CH_2−dppe), 2.26 (s, 3H, $C_6H_4CH_3$), 2.14 (qnt, br, $^4J_{HP}$ = 3.4 Hz, 2H, $CCH_2C_6H_4Me$). $^{31}P\{^1H\}$ NMR: δ −115.8 (s). $^{13}C\{^1H\}$ NMR: δ 270.54 (m, $CCH_2C_6H_4Me$), 134.5−127.5 (m, Ph−dppe), 56.52 (s, $CCH_2C_6H_4Me$), 31.03 (qnt, virtual J_{CP} = 12.2 Hz, CH_2−dppe), 21.03 (s, $C_6H_4CH_3$). ^{13}C NMR: δ 270.54 (m), *ca*. 135−127 (m), 56.52 (t, J_{CH} = 129.2 Hz), 31.03 (tqnt, J_{CH} = 132.0 Hz), 21.03 (qt, J_{CH} = 126.5 Hz, $^3J_{CH}$ = 4.5 Hz). Anal. Calcd for $BC_{61}ClF_4H_{57}P_4Re \cdot {}^3/_2CH_2Cl_2$: C, 55.6; H, 4.3. Found: C, 55.5; H, 4.

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