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Preliminary Communication

Carbyne-fluoro complexes of rhenium. Single-pot synthesis of *trans*-[ReF($\equiv$CCH$_2$R)-(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$][BF$_4$]

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Abstract

Treatment of a THF solution of *trans*-[ReCl(N$_2$)(dppe)$_2$] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with a 1-alkyne HC$\equiv$CR (R = ^{t}Bu, CO$_2$Me, CO$_2$Et, or C$_6$H$_4$Me-4), in the presence of Tl[BF$_4$]/[NH$_4$][BF$_4$], under sunlight, affords the corresponding carbyne-fluoro complexes *trans*-[ReF($\equiv$CCH$_2$R)(dppe)$_2$][BF$_4$] in an unprecedented single-pot synthesis. Further reaction with [Bu$_4$N]OH leads to the vinylidene-fluoro compounds *trans*-[ReF(=C=CHR)(dppe)$_2$] (R = CO$_2$Me, CO$_2$Et, or C$_6$H$_4$Me-4).

Although the coordination chemistry of carbynes is of high current interest [1], routes to complexes of carbynes generally require difficult stepwise syntheses, involving as a final step, an α-abstraction or a β-addition, or a rearrangement of a carbyne-precursor ligand. Although *trans*-chloro-, bromo-, and iodo-carbyne complexes are well-known [1], analogous fluoro-carbyne compounds are rather rare [3–6]. For example, *trans*-[CrX(CNEt$_2$)(CO)$_4$], X = Cl, Br, or I, but not F [2]. In addition, few carbyne complexes of rhenium are known [1], compared to many for the related Group 6 transition metals.

The present work describes a convenient single-pot synthesis of *trans*-[ReF($\equiv$CCH$_2$R)(dppe)$_2$][BF$_4$] (**1**; R = ^{t}Bu, CO$_2$Me, CO$_2$Et, or C$_6$H$_4$Me-4; dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$), using readily available starting materials.

Complexes **1** are obtained directly from *trans*-[ReCl(N$_2$)(dppe)$_2$] (**2**), by treatment of a THF solution of this species with a 1-alkyne (HC$\equiv$CR) in the presence of Tl[BF$_4$]/[NH$_4$][BF$_4$], in sunlight under argon (eqn. (1)). They were isolated as rose (**1**, R = ^{t}Bu or COOEt) or yellow (**1**, R = COOMe or C$_6$H$_4$Me-4) solids in good yields (*ca.* 65–40%) with acceptable elemental (C and H) analyses. Their formation involves not only the displacement of N$_2$ followed by 1,2-hydrogen migration at the alkyne and protonation (by NH$_4^+$) of the metal-bonded vinylidene (C=CHR), but also the ready replacement of chloride by fluoride derived from BF$_4^-$. The thallium(I) is a chloride abstractor.

$$\textit{trans}\text{-}[\mathrm{ReCl(N_2)(dppe)_2}] + \mathrm{HC{\equiv}CR} \xrightarrow[-\mathrm{TlCl},\ -\mathrm{BF_3\cdot THF},\ -\mathrm{NH_3}]{\mathrm{Tl[BF_4],\ [NH_4][BF_4],\ THF}} \textit{trans}\text{-}[\mathrm{ReF({\equiv}CCH_2R)(dppe)_2}][\mathrm{BF_4}] \quad (1)$$

In earlier work [7], the preparation of the vinylidene-chloro-complexes *trans*-[ReCl(=C=CHR)(dppe)$_2$] (**3**, R = alkyl or aryl) by reaction of **2** with HC$\equiv$CR was described. These complexes undergo β-protonation to give the corresponding carbyne-chloro-compounds *trans*-[ReCl($\equiv$CCH$_2$R)(dppe)$_2$]$^+$. For R = ^{t}Bu using HBF$_4$ as the acid, the corresponding fluoro-carbyne-complex (**1**, R = ^{t}Bu) was also obtained [5], as a contamination of the chloro-carbyne main product, although in very low yield.

In the present work, the reaction has proceeded to the carbyne and metal fluoride has also formed. The fluoro-carbyne-compounds **1** are the convenient precursors for the corresponding fluoro-vinylidene-complexes *trans*-[ReF(=C=CHR)(dppe)$_2$] (**3**, R = CO$_2$Me, CO$_2$Et, or C$_6$H$_4$Me-4) which are obtained in high yield by treatment with [Bu$_4$N]OH.

The presence of fluoride *trans* to the carbyne (or the vinylidene) is unambiguously proved by a quintet [^2J(FP) = 42.0 Hz] and a doublet resonance (with identical coupling constant) in the ^{19}F (δ −321.4 ppm rel. CFCl$_3$) and ^{31}P [δ −112.8 ppm rel. P(OMe)$_3$] NMR spectra, respectively, of **1** (R = C$_6$H$_4$Me-4, CDCl$_3$, 298 K). Moreover, the ^{13}C NMR spectrum shows a carbyne resonance (*C*CH$_2$C$_6$H$_4$Me-4) as a low-field multiplet (δ −279.6 ppm rel. SiMe$_4$), whereas the methylene carbon resonance, in the ^{1}H-undecoupled ^{13}C spectrum, is the expected triplet [^1J(CH) = 128 Hz] at δ 55.84 ppm.

This work has established that fluoride can stabilize a *trans*-carbyne or -vinylidene, and the corresponding

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complexes can be readily prepared from easily available starting materials in single-pot syntheses.

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