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Preliminary Communication

Carbyne-fluoro complexes of rhenium. Single-pot synthesis of *trans*-[ReF(≡CCH₂R)- (Ph₂PCH₂CH₂PPh₂)₂][BF₄]

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Abstract

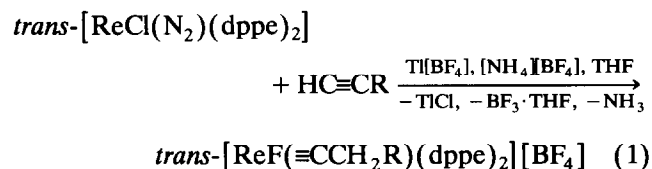
Treatment of a THF solution of *trans*-[ReCl(N₂(dppe)₂] (dppe = Ph₂PCH₂CH₂PPh₂) with a 1-alkyne HC≡CR (R = ^tBu, CO₂Me, CO₂Et, or C₆H₄Me-4), in the presence of Tl[BF₄]/[NH₄][BF₄], under sunlight, affords the corresponding carbyne-fluoro complexes *trans*-[ReF(≡CCH₂R)(dppe)₂][BF₄] in an unprecedented single-pot synthesis. Further reaction with [Bu₄N]OH leads to the vinylidene-fluoro compounds *trans*-[ReF(=C=CHR)(dppe)₂] (R = CO₂Me, CO₂Et, or C₆H₄Me-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(CNEt₂)(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(≡CCH₂R)(dppe)₂][BF₄] (1; R = ^tBu, CO₂Me, CO₂Et, or C₆H₄Me-4; dppe = Ph₂PCH₂CH₂PPh₂), using readily available starting materials.

Complexes 1 are obtained directly from *trans*-[ReCl(N₂(dppe)₂] (2), by treatment of a THF solution of this species with a 1-alkyne (HC≡CR) in the pres-

ence of Tl[BF₄]/[NH₄][BF₄], in sunlight under argon (eqn. (1)). They were isolated as rose (1, R = ^tBu or COOEt) or yellow (1, R = COOMe or C₆H₄Me-4) solids in good yields (ca. 65–40%) with acceptable elemental (C and H) analyses. Their formation involves not only the displacement of N₂ followed by 1,2-hydrogen migration at the alkyne and protonation (by NH₄⁺) of the metal-bonded vinylidene (C=CHR), but also the ready replacement of chloride by fluoride derived from BF₄⁻. The thallium(I) is a chloride abstractor.



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≡CR was described. These complexes undergo β -protonation to give the corresponding carbyne-chloro-compounds *trans*-[ReCl(≡CCH₂R)(dppe)₂]⁺. For R = ^tBu using HBF₄ as the acid, the corresponding fluoro-carbyne-complex (1, R = ^tBu) 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 = CO₂Me, CO₂Et, or C₆H₄Me-4) which are obtained in high yield by treatment with [Bu₄N]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 ¹⁹F (δ - 321.4 ppm rel. CFCI₃) and ³¹P (δ - 112.8 ppm rel. P(OMe)₃) NMR spectra, respectively, of 1 (R = C₆H₄Me-4, CDCl₃, 298 K). Moreover, the ¹³C NMR spectrum shows a carbyne resonance (CCH₂C₆H₄Me-4) as a low-field multiplet (δ - 279.6 ppm rel. SiMe₄), whereas the methylene carbon resonance, in the ¹H-undecoupled ¹³C 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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