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Preliminary communication

Synthesis of alkylidyne complexes of rhenium by protonation of the vinylidene complexes *trans*-[ReCl(=C=CHR)-($Ph_2PCH_2CH_2PPh_2$)$_2$] (R = alkyl or aryl): crystal structure of *trans*-[ReF(≡CH_2Bu^t)($Ph_2PCH_2CH_2PPh_2$)$_2$]BF_4

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Abstract

Treatment of *trans*-[ReCl(=C=CHR)(dppe)$_2$] (R = Bu^t or Ph; dppe = $Ph_2PCH_2CH_2PPh_2$) with [Et_2OH]BF_4 gives *trans*-[ReX(≡CCH_2R)(dppe)$_2$]BF_4 (X = Cl, R = Bu^t or Ph; X = F, R = Bu^t); the crystal structure of *trans*-[ReF(≡C-CH_2Bu^t)(dppe)$_2$]BF_4 is reported.

In contrast to the well-developed chemistry of alkylidyne complexes of the Group 15 (Nb and Ta) and 16 transition metals [1], a relatively limited number of well-defined alkylidyne complexes has been reported for rhenium [2–4]. Routes to these compounds involve nucleophilic attack at a carbonyl ligand or α-abstraction from a *C*-bonded ligand, e.g. ligating neopentylidene [3].

We have shown previously that β-electrophilic attack on unsaturated carbon species ligating electron-rich metal centres provides a versatile route to alkylidyne- and alkylidene-type ligands. Thus *trans*-[ReCl(CNR)(dppe)$_2$] is converted by β-protonation into *trans*-[ReCl(≐C≐NHR)(dppe)$_2$]$^+$ [5], and at the same rhenium centre a phenylallene ligand undergoes β-protonation to give the η^2-vinyl group in *trans*-[ReCl{=C(CH_2Ph)CH_2}(dppe)$_2$]BF_4 [6]. We have also shown that 1-alkynes undergo isomerization (1,2-hydrogen shift) to vinylidene ligands at the {ReCl(dppe)$_2$} site [7], and we now describe an extension of our studies of β-electrophilic attack to the conversion, at rhenium, of these vinylidene moieties into alkylidyne ligands. This route has been described for other systems [8].

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Thus treatment of a dichloromethane solution of *trans*-[ReCl(=C=CHR)(dppe)$_2$] (R = Bu^t or Ph) with [Et$_2$OH]BF$_4$, followed by addition of Et$_2$O, gives the alkylidyne complexes *trans*-[ReX(≡CCH$_2$R)(dppe)$_2$]BF$_4$ (**A**) (R = Bu^t, X = Cl or F, white crystals; R = Ph, X = Cl, yellow crystals), e.g. as in eq. 1.

$$trans\text{-}[\mathrm{ReCl({=}C{=}CHR)(dppe)_2}] + \mathrm{HBF_4} \rightarrow trans\text{-}[\mathrm{ReCl({\equiv}CCH_2R)(dppe)_2}]\mathrm{BF_4} \qquad (1)$$

The ^{13}C NMR spectra of complexes **A** (CD$_2$Cl$_2$, 298 K) show the alkylidyne resonance as a low-field quintet due to coupling to the four equivalent phosphorus nucleii in the *trans*-structure [**A**, X = Cl; R = Bu^t, δ 280.2 ppm, ^1J(CP) 10.5 Hz; R = Ph, δ 269.9 ppm, ^1J(CP) 12.4 Hz; rel. SiMe$_4$].

The formation of complex **A** (X = F, R = Bu^t) involves an unusual displacement of chloride by fluoride from BF$_4^-$; the molecular structure of this complex was determined by X-ray crystallography *, and is shown in Fig. 1.

The alkylidyne ligand is distorted from ideal geometry by the proximity of the dppe ligands; the "linear" arrangement at C(6) is reduced to an angle of 167.9(7)°, and the bond angle at C(7) is expanded to 125.6(9)°.

The rhenium–carbon distance [1.772(7) Å] is, as expected, considerably shorter than those in *trans*-[ReCl(=C=CHPh)(dppe)$_2$] [2.046(8) Å] [7] and *trans*-[ReCl(≕C≕NHR)-(dppe)$_2$]BF$_4$ [1.80(3) Å, R = Me; 1.80(2) Å, R = H] [5,9], where there is π-electron delocalisation within the ligand skeleton. The distance is, however, only just outside the range predicted (1.75–1.72 Å) from the sum of the triple-bonded covalent radii of Re and *sp*-C [5], although being slightly longer than for Re≕C in [Sn(TPP){Re(CO)$_3$C}$_2$] (1.75 Å, TPP = 5,10,15,20-tetraphenylporphinato) [4] or in [Re(≡CBu^t)(=CHBu^t)(C$_5$H$_5$N)$_2$I$_2$] [1.742(9) Å] [3]. In the latter case, the formally Re^{VII} metal might be expected to have a shorter radius than the formally Re^V metal of **A**.

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* *Crystal structure analysis of trans-[ReF(≡CCH$_2$Bu^t)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]BF$_4$.* Crystal data: C$_{58}$H$_{59}$FP$_4$Re, BF$_4$. M = 1172.0. Monoclinic, a 13.805(2), b 17.493(9), c 23.732(9) Å, β 96.47(2)°, V 5694.5 Å^3. Space group $P2_1/n$ (equivalent to no. 14). Z = 4, D_c 1.367 g cm^{-3}, $F(000)$ = 2368, μ(Mo-K_α) 23.2 cm^{-1}, λ(Mo-K_α) 0.71069 Å.

Crystals are clear, colourless rectangular prisms. One, ca. 0.45×0.25×0.20 mm, on a glass fibre and sealed in silicone grease, was examined photographically before measurement of cell parameters and diffraction intensities (7813 unique reflections to θ_{max} = 23°) on our Enraf–Nonius CAD4 diffractometer (with monochromator). Corrections were made for Lorentz-polarisation effects, absorption and statistically to ensure no negative intensities. Structure determination was by automated Patterson methods [10] and subsequent difference maps [11]. During refinement, hydrogen atoms were included in idealised positions, and geometrical restraints were applied in the disordered BF$_4^-$ anion; all other atoms were refined anisotropically by block-diagonal least-squares methods [12] to convergence at R = 0.054, R_w = 0.065 for all data, weighed $W = (\sigma_F^2 + 0.005F^2)^{-1}$.

Scattering factors for neutral atoms were from ref. 13. Computer programs used in this analysis have been listed above and in Table 4 of ref. 14, and were run on the VAX 11/750 at AFRC-IHR's Littlehampton Laboratory (G.C.R.I.).

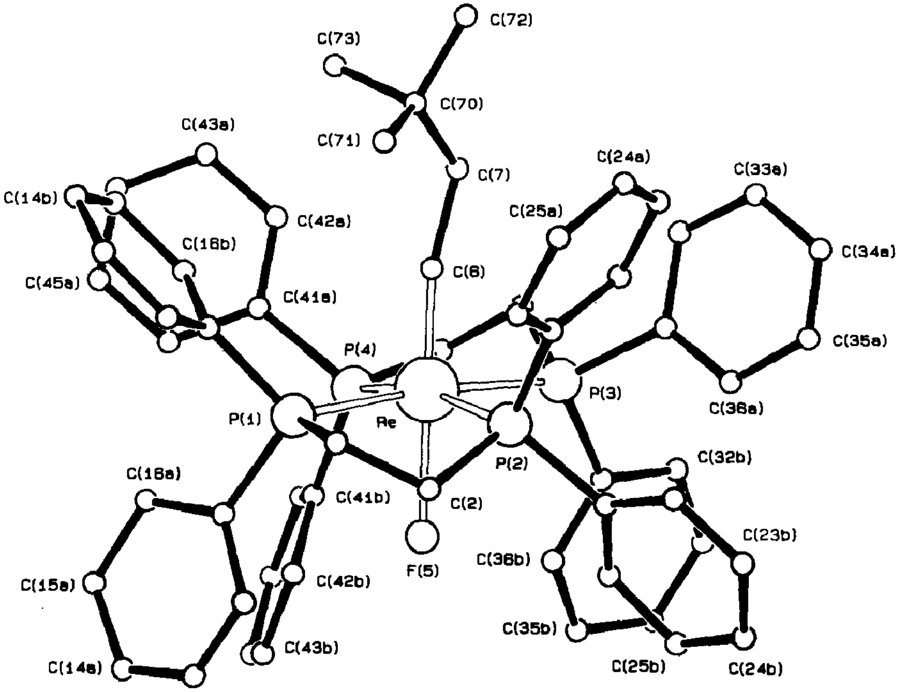

Fig. 1. View of the complex cation [ReF(≡CCH$_2$Bu^t)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$]$^+$. Principal dimensions (with e.s.d's in parantheses) include: Re–C(6) 1.772(7), C(6)–C(7) 1.505(13), Re–F(5) 2.134(4) Å, F(5)–Re–C(6) 174.6(3), Re–C(6)–C(7) 167.9(7), C(6)–C(7)–C(70) 125.6(9)°.

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