Journal of Organometallic Chemistry, 277 (1984) C7—C10
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF *trans*-[$ReCl(N_2)(Ph_2PCH_2CH_2PPh_2)_2$] WITH TERMINAL ACETYLENES. PREPARATION AND CRYSTAL STRUCTURE OF THE VINYLIDENE COMPLEX *trans*-[$ReCl(C{=}CHPh)(Ph_2PCH_2CH_2PPh_2)_2$]

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(Received September 3rd, 1984)

Summary

Terminal acetylenes ($HC{\equiv}CR$, R = Ph, Et or COOEt) react with *trans*-[$ReCl(N_2)(dppe)_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) in refluxing thf to afford the neutral vinylidene complexes *trans*-[$ReCl(C{=}CHR)(dppe)_2$]. The structure of the complex with R = Ph has been established by X-ray diffraction.

As part of our studies on the binding and activation of small unsaturated organic molecules by electron-rich, dinitrogen-binding transition metal centres, we have investigated [1] the reactions of isocyanides with *trans*-[$ReCl(N_2)(dppe)_2$] (A) (dppe = $Ph_2PCH_2CH_2PPh_2$) which can generate the unsaturated centre [$ReCl(dppe)_2$] by photolytic or thermal removal of N_2 [2].

In the complexes *trans*-[$ReCl(CNR)(dppe)_2$] (R = alkyl), prepared [1] by displacement of N_2 by CNR from A, the isocyanide ligand is activated towards attack by electrophilic reagents such as protic acids, leading to carbyne-type species, *trans*-[$ReCl(CNHR)(dppe)_2$]$^+$ [3]. Similar reactions were observed for complexes having the isocyanide bound to Mo^0- or W^0-d^6-sites {$M(dppe)_2$} (M = Mo or W) [4].

We have extended our studies to include investigation of the behaviour of alkynes at these electron-rich centres, and we have shown recently [5] that the η^2-phenylallene complex *trans*-[$\overline{ReCl(\eta^2\text{-}H_2C{-}C}{=}CHPh)(dppe)_2$] (B) is obtained on treatment of complex A with $PhC{\equiv}CCH_3$ by an apparent 1,3-

0022-328X/84/$03.00

migration of a proton from the methyl group of the parent alkyne. Here we report a further extension of our investigation to the reactions of terminal alkynes ($HC\equiv CR$) with the Re^I site, which leads to the formation of vinylidene complexes from these ligands.

The reaction of complex **A** with $PhC\equiv CH$ in refluxing THF occurs with evolution of N_2, and affords the phenyl vinylidene complex *trans*-[ReCl(C=CHPh)-(dppe)$_2$] (**C**, eq. 1) produced by a formal 1,2-proton shift. Other terminal acetylenes $RC\equiv CH$ (R = Et or COOEt) also react to give the corresponding vinylidene complexes.

$$trans\text{-}[ReCl(N_2)(dppe)_2] + PhC\equiv CH \rightarrow trans\text{-}[ReCl(C{=}CHPh)(dppe)_2] + N_2 \qquad (1)$$

A similar alkyne-to-vinylidene rearrangement at a metal d^6 centre has been observed by other authors in reactions of *fac*-[W(CO)$_3$(dppe)(THF)] with terminal acetylenes, which lead to [W(C=CHR)(CO)$_3$(dppe)] (**D**) [6].

Complex **C** was obtained as a red, diamagnetic crystalline solid; the vinylidene ligand has $\nu(C{=}C)$ at 1532 cm^{-1}, and in the ^1H NMR spectrum (CD_2Cl_2) the C*H*Ph resonance occurs as a somewhat broad quintet (^4J(PH) 4.6 Hz) centred at δ 0.87 ppm. Although low solubility in the usual solvents and decomposition in solution has precluded the detection of the expected [6,7] low-field ^{13}C α-carbon resonance of **C**, it was observed at 284 ppm down-field from $SiMe_4$-(CD_2Cl_2) for the C=CHCOOEt analogue.

The molecular structure of **C**, single crystal X-ray diffraction*, is shown in Fig. 1. The Re—C(carbene) distance (2.046(8) Å), although slightly longer than that observed for $[(\eta^5\text{-}C_5H_5)(CO)_2Re\{C{=}C(Ph)C(Ph){=}CH_2\}Re(CO)_2(\eta^5\text{-}C_5H_5)]$ (1.90(2) Å) [8] (where the Re—C π-density may be delocalised over the butadiene fragment), is nevertheless shorter than the expected Re—C single bond distance (2.297 Å) evaluated [9] as the sum of the single-bonded covalent radii of Re (1.53 Å) and sp^3C (0.767 Å). As might be expected, the Re—C (carbene) bond length is longer than that observed (1.80(3) Å) for the Re—C (carbyne) bond in *trans*-[ReCl(CNHMe)(dppe)$_2$][BF$_4$] [3].

The distance between the α- and β-carbon atoms (C(5)—C(6)) of the vinylidene ligand (1.308(16) Å) is close to that quoted for [MoBr(C=CHPh)-$\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)$] (1.327(7) Å) [10] and is typical for a C=C double bond; the angle at the C_β atom (C(6)) is 125.5(15)° in agreement with sp^2 hybridisation at this atom.

Although in the reactions of complex **A** with alkynes, η^2-alkyne complexes are conceivably formed as a first step, they were not isolated and only products from alkyne rearrangement (η^2-allene or vinylidene) were obtained. This paral-

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***For compound* **C**, *crystal data*: $C_{60}H_{54}ClP_4Re \cdot C_4H_8O$, M = 1192.7, triclinic, space group $P1$ (no. 1), a 9.901(2), b 13.569(4), c 13.132(4) Å, α 103.56(3), β 107.05(2), γ 114.86(2)°, U 1394.3(7) Å^3, Z = 1, D_C 1.42 g cm^{-3}, $F(000)$ = 606, μ(Mo-K_α) 21.2 cm^{-1}. Current R = 0.041 (R^{-} = 0.044) for 3887 absorption corrected intensities (293 K, ω scans, $2\theta \leqslant 45°$, $F \geqslant 4\sigma(F)$, Nicolet $P3m$ diffractometer, Mo-K_α X-radiation, λ 0.71069 Å).

The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain). Any request should be accompanied by the full literature citation for this communication.

lels observations of the above-mentioned alkyne-to-vinylidene conversion in the reactions of *fac*-[W(CO)$_3$(dppe)(THF)] with monosubstituted alkynes [6].

In view of the filled pseudo-t_{2g} set and electron-richness of the Re atom in the {ReCl(dppe)$_2$} fragment [1], we consider that the repulsive four-electron d_π(metal)-$\pi_\perp$(alkyne) interaction [11], thought to promote the alkyne-to-vinylidene rearrangements in W^0-d^6-complexes [6], also operates in the reactions reported here. An additional driving force for these reactions is the tendency for Mo, W, Re and related metals to form multiple bonds to ligand atoms with suitable π-orbitals, particularly nitrogen, oxygen and carbon [3,6,12]. In all the complex products **B**, **C** or **D**, the ligand derived from the alkyne rearrangement (allene or vinylidene) is *trans* to the strongest net electron-donor co-ligand (Cl in **B** and **C** or a phosphine in **D**), which reinforces its π-electron-acceptor character.

We are attempting to isolate the possible intermediate complexes in these reactions and are studying the chemical behaviour of the derived allene and vinylidene ligands. We are also extending this study to other substituted acetylenes and d^6-metal sites, namely {M(dppe)$_2$} (M = Mo or W).

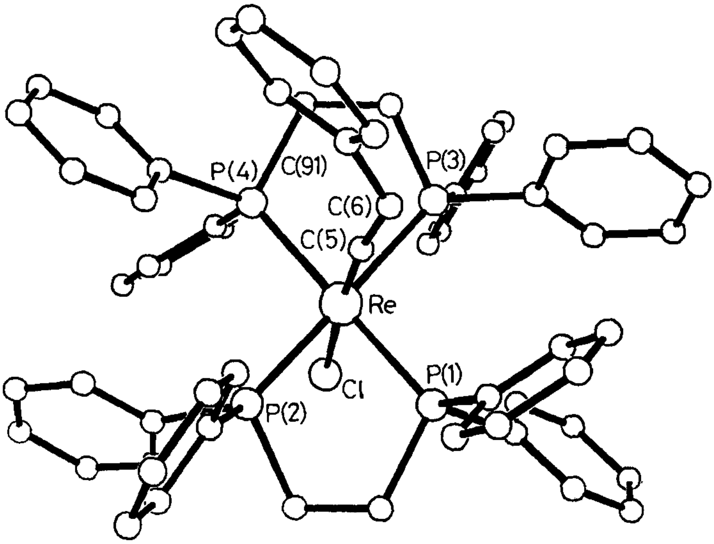

Fig. 1. The molecular structure of *trans*-[ReCl(C=CHPh)(Ph$_2$PCH$_2$CH$_2$PPh$_2$)$_2$] (**C**). Re—P(1) 2.389(8), Re—P(2) 2.402(9), Re—P(3) 2.440(8), Re—P(4) 2.441(9), Re—Cl 2.454(3), Re—C(5) 2.046(8), C(5)—C(6) 1.308(16) Å; P(1)—Re—P(2) 80.2(3), P(3)—Re—P(4) 78.7(3), P(1)—Re—P(4) 180.0(2), P(2)—Re—P(3) 177.7(2), C(5)—Re—Cl 176.8(4), Re—C(5)—C(6) 166.6(12), C(5)—C(6)—C(91) 125.5(15)°.

Acknowledgements

We thank the Calouste Gulbenkian Foundation, the Instituto Nacional de Investigação Científica, the Junta Nacional de Investigação Científica e Tecnológica and the British Council for financial support.

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