Journal of Organometallic Chemistry, 350 (1988) C4–C7
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Mononuclear alkynyl, alkenyl, alkylidyne and alkylidene complexes of molybdenum and tungsten from reactions of 1-alkynes with hydride complexes. Crystal structure of $[WH_2(C\equiv CCO_2Me)_2(Ph_2PCH_2CH_2PPh_2)_2]$

Adrian Hills, David L. Hughes, Neimat Kashef, Raymond L. Richards *

AFRC - IPSR Nitrogen Fixation Laboratory and School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9RQ (Great Britain)

M. Amelia N.D.A. Lemos and Armando J.L. Pombeiro

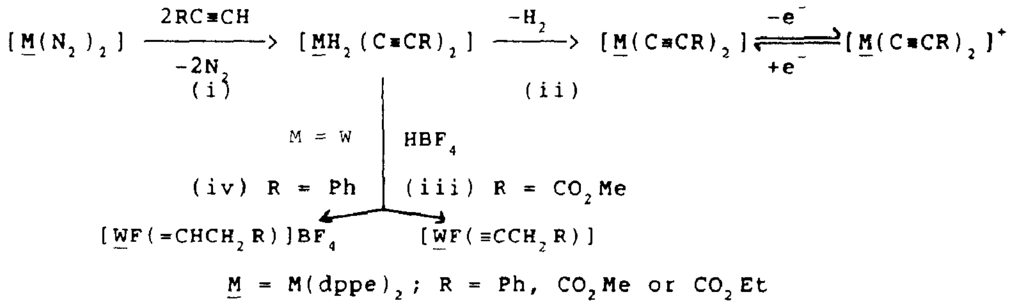
Centro de Quimica Estrutural, Complexo 1, Instituto Superior Tecnico, Av. Rovisco Pais, 1096 Lisboa Codex (Portugal)

(Received May 6th, 1988)

Abstract

$[WH_2(C\equiv CR)_2(dppe)_2]$ (R = Ph or CO_2Me; dppe = $Ph_2PCH_2CH_2PPh_2$) react with HBF_4 to give $[WF(\equiv CCH_2CO_2Me)(dppe)_2]$ and $[WF(=CHCH_2Ph)(dppe)_2]BF_4$; the X-ray structure of $[WH_2(C\equiv CCO_2Me)_2(dppe)_2]$ is reported. With HBF_4, $[MoH_4(dppe)_2]$ reacts with $R'CO_2C\equiv CH$ (R' = Me or Et) to give $[\overline{MoH_2\{CH{=}CC(O})OR'\}(dppe)_2]BF_4$, but with HBr, $[MoBrH_2(CH{=}CHR')(dppe)_2]$ are formed.

As part of our studies of the reactions of nitrogenase substrates at dinitrogen binding sites, we have investigated the behaviour of alkynes and have demonstrated the tendency for isomerisation to occur at the $\{ReCl(dppe)_2\}$ centre to give complexes of allene and vinylidene ligands [1]. In contrast, the dominant reaction which occurs at the $\{M(dppe)_2\}$ (M = Mo or W) centre is oxidative addition to form hydridoalkynyl and alkynyl complexes [2] (reactions i and ii of Scheme 1). We



Scheme 1

0022-328X/88/$03.50

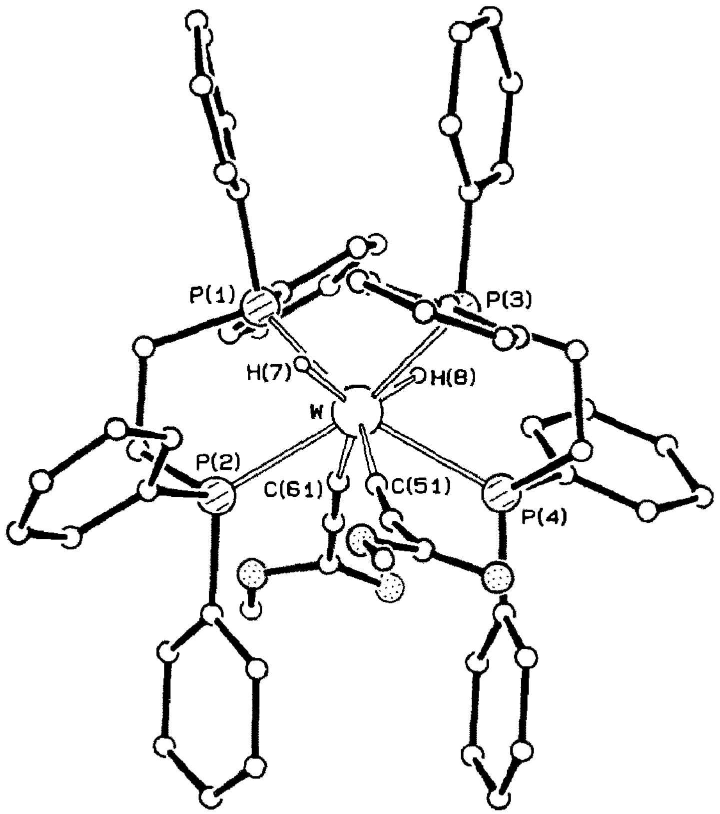


Fig. 1. Molecular structure of $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$. Selected molecular dimensions (with e.s.d. in parentheses) are: W–P(1) 2.448(6), W–P(2) 2.488(5), W–P(3) 2.470(5), W–P(4) 2.504(6), W–C(51) 2.04(2), W–C(61) 2.04(3), W–H(7) 1.52(12), W–H(8) 1.56(15), C(51)–C(52) 1.22(3), C(61)–C(62) 1.24(4) Å; H(7)–W–C(51) 77(4), H(8)–W–C(61) 70(4), W–C(51)–C(52) 172.8(16), W–C(61)–C(62) 174.5(20)°.

report preliminary results of an X-ray study * of one member of the hydride series, $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$. The rapid deterioration of the crystal during data collection limited the overall accuracy of the final structure, but it clearly has square antiprismatic coordination geometry, as shown in Fig. 1, the legend to which includes selected bond angles and distances.

---

* Crystal data for $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]\cdot$thf. $C_{60}H_{56}O_4P_4W \cdot C_4H_8O$, $M = 1221.0$. Triclinic, space group $P\bar{1}$ (no. 2), a 11.751(4), b 20.737(4), c 12.216(2) Å, α 90.63(2), β 102.46(2), γ 102.74(2)°, V 2829.5 Å^3. $Z = 2$, D_c 1.433 g cm^{-3}, $F(000) = 1244$, μ(Mo-K_α) 22.4 cm^{-1}, λ(Mo-K_α) 0.71069 Å. Crystals were small, bright red plates. After photographic examination one was mounted on an Enraf–Nonius CAD4 diffractometer (with monochromator) for accurate cell dimensions and intensity data: 2279 unique reflections were measured to θ_{max} 15° before crystal deteriorated.

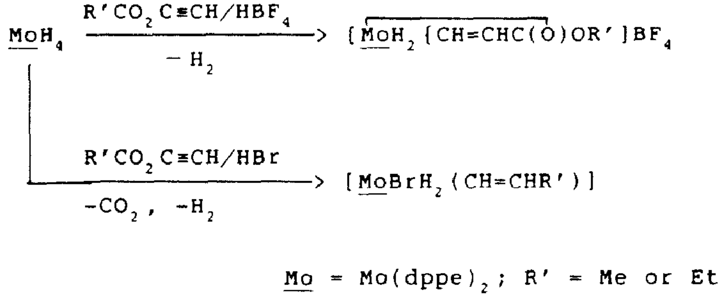
Structure was determined by heavy atom method in SHELX [9]; hydride atoms located in difference map. Refinement by large-block least-squares methods; W, P and ligand O atoms allowed anisotropic thermal parameters. Other H atoms included are in idealised positions. Two thf molecules, each disordered, were included with geometrical restraints.

At completion of refinement, $R = 0.045$, $R_w = 0.046$ [9] for the 1927 reflections with $I > 2\sigma(I)$, each weighted $w = (\sigma^2(F) + 0.00134F^2)^{-1}$. Principal peaks (ca. 0.7 eÅ^{-3}) in a final difference map were in the region of the thf molecules.

We have shown that N_2, RNC and RCN bound at these electron-rich centres are susceptible to β-electrophilic attack, which can lead to reductive cleavage, e.g. of N_2 to NH_3 [3] and RNC to RNH_2 and CH_4 [4]. We now report that similar β-electrophilic attack on alkynyl complexes gives alkylidene and alkylidyne complexes (reactions iii and iv of Scheme 1). Thus e.g. treatment of $[WH_2(C{\equiv}CPh)_2(dppe)_2]$ with HBF_4 in thf (tetrahydrofuran) gives, in good yield, $[WF({=}CHCH_2Ph)(dppe)_2]BF_4$ *, and treatment of $[WH_2(C{\equiv}CCO_2Me)_2(dppe)_2]$ with HBF_4 gives, also in good yield $[WF({\equiv}CCH_2CO_2Me)(dppe)_2]$ **. The mechanisms of these reactions are complicated, and are under investigation.

The alkynyl complexes $[M(C{\equiv}CR)_2(dppe)_2]$ are derived from $[MH_2(C{\equiv}CR)_2(dppe)_2]$ and can be reversibly oxidised electrochemically (Scheme 1); e.g., $E^{ox}_{1/2}$ for $[W(C{\equiv}CPh)_2(dppe)_2]$ is at -0.29 V (rel. calomel, Pt electrode in 0.2 *M* $[Bu_4N][BF_4]$/thf). This value is close to that for $[WCl_2(dppe)_2]$ (-0.24 V) [5] and thus the electronic behaviour of the $C{\equiv}CPh^-$ and Cl^- ligands appears to be similar towards this metal centre.

We have also investigated the reactions of $[MoH_4(dppe)_2]$ with the activated 1-alkynes $R'CO_2C{\equiv}CH$ (R' = Me or Et) in presence of acids. Henderson [6] has recently shown that such a reaction with $PhC{\equiv}CH$ and HBF_4 gives the alkyne complex $[MoF(HC{\equiv}CPh)(dppe)_2]BF_4$. In contrast, $R'CO_2C{\equiv}CH$ gives the cyclic alkenyl [7] complexes shown in Scheme 2 for HBF_4, but decarboxylation occurs if HBr is used, presumably because Br^- is able to ligate the molybdenum, destabilising any cyclic ligand which would be resistant to decarboxylation.



Scheme 2

The β-electrophilic attack on the alkynyl complexes investigated here stops at the alkylidene stage. In principle it could proceed further, perhaps under the influence of more electron-releasing co-ligands, to the alkyl stage, and thence give alkenes by β-elimination.

In view of the production of alkenes from alkynes by molybdenum nitrogenase [8], further protonation reactions of these and analogous complexes will be investigated.

Acknowledgement. We thank Mr. C. Macdonald and Dr. A. Avent for NMR spectra, the I.N.I.C. and the J.N.I.C.T., Portugal (M.A.N.D.A.L. and A.J.L.P.) for support.

---

* NMR data in CD_2Cl_2: $\delta(WF)$ -97.3 ppm rel. $CFCl_3$, quintet, $^2J(PF)$ 34.0 Hz; $\delta(WCH)$ 251.8 ppm rel. $SiMe_4$, doublet, $^1J(CH)$ 155 Hz; $\delta(WCHCH_2Ph)$ 58.3 ppm, triplet, $^1J(CH)$ ca. 145 Hz.

** NMR data in CD_2Cl_2: $\delta(WF)$ -141.0 ppm, quintet, $^2J(PF)$ 35.0 Hz; $\delta(W{\equiv}C)$ 291 ppm; $\delta(WCCH_2CO_2Me)$ 44.7, triplet, $^1J(CH)$ 120 Hz.

References

1 A.J.L. Pombeiro, D.L. Hughes, R.L. Richards, J. Silvestre, and R. Hoffmann, J. Chem. Soc. Chem. Commun., (1986) 1125 and ref. therein.

2 N.A. Buang, D.L. Hughes, N. Kashef, R.L. Richards, and A.J.L. Pombeiro, J. Organomet. Chem., 323 (1987) C47.

3 J. Chatt and R.L. Richards, J. Organomet. Chem., 239 (1982) 65; R.A. Henderson, G.J. Leigh and C.J. Pickett, Adv. Inorg. Radiochem., 27 (1983) 197.

4 M.F.N.N. Carvalho, O. Orama, C.J. Pickett, A.J.L. Pombeiro, R.L. Richards, and U. Schubert, J. Chem. Soc. Dalton Trans, (1985) 2079; A.J.L. Pombeiro and R.L. Richards, Trans. Met. Chem., 5 (1980) 281.

5 T.I. Salih and C.J. Pickett, J. Chem. Soc., Dalton Trans., (1985) 1255.

6 R. Ellis, R.A. Henderson, A. Hills, and D.L. Hughes, J. Organomet. Chem. 333 (1987) C6.

7 T. Ito, H. Tosaka, S. Yoshida, K. Mita, and A. Yamamoto, Organometallics, 5 (1986) 735.

8 M.J. Dilworth, Biochim. Biophys. Acta, 127 (1966) 283; C.E. McKenna, M.-C. McKenna, C.N. Huang, Proc. Natl. Acad. Sci. U.S.A., 76 (1979) 4773.

9 G.M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.