www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 587 (1999) 191–194

Is the unconventional H···H bond more common than expected? Synthesis and X-ray structure of monomeric $[Ru(CO)H_2(PPh_3)_3]$

Peter C. Junk [a,*], Jonathan W. Steed [b]

[a] *Department of Chemistry, James Cook University of North Queensland, Townsville Qld, 4811, Australia*
[b] *Department of Chemistry, Kings College London, Strand, London WC2R 2LS, UK*

Received 19 April 1999

Abstract

The X-ray crystal structure of $[Ru(CO)H_2(PPh_3)_3]\cdot CH_2Cl_2$ adopts a distorted octahedral geometry and displays an intriguing intramolecular unconventional Ru–H···H–C hydrogen bond. A Cambridge Crystallographic Database search indicates these types of hydrogen bonds may be commonplace in transition metal hydride complexes which have triphenylphosphine ligands.

Keywords: Hydrogen bond; Hydride; Triphenylphosphine; Ruthenium

1. Introduction

Supramolecular interactions such as O–H···π-arene, C–H···π-arene and edge to face π-stacking of aromatic moieties have been actively studied during recent years due to their importance in biological systems, crystal engineering and self assembly [1]. Such weak interactions assume particular importance where large numbers of them are present, synergically enhancing their organizational ability. More recently, these studies have been extended to unconventional hydrogen bonds involving hydrogen atoms of opposite polarity where there are unusually short H···H contacts typically in the range from 2.0 to 2.4 Å [2–9]. Several examples are known involving transition metal hydrides, e.g. $[ReH_5(PPh_3)_3]$, [4] B–H···H–N interactions [5] and one recent example of Ga–H···H–N bonding [7]. While investigating the structures of some ruthenium hydride complexes, we have looked at both the typical bonding arrangements and the *inter*- and *intramolecular* interactions. These results show that, in these systems, there are also unconventional interactions between transition metal hydrido species and adjacent C–H protons. Thus, we report herein, an example of an intramolecular transition metal hydride to H–C hydrogen bond in $[Ru(CO)H_2(PPh_3)_3]$.

2. Experimental

2.1. Synthesis of $[Ru(CO)H_2(PPh_3)_3]\cdot CH_2Cl_2$

$[Ru(CO)ClH(PPh_3)_3]$ (0.3g, 0.31 mmol), 2-methoxyethanol (10 cm^3), triphenylphosphine (0.3g, 1.1 mmol) and KOH (one pellet) were heated to reflux for 10 min with stirring. The mixture was allowed to cool, and the product was collected on a filter frit and washed with ethanol (10 cm^3). The colourless material was recrystallised from dichloromethane/ethanol and dried in a vacuum desiccator (yield 0.20 g, 65%), m.p. 158–60°C ([10] 160–162°C). Found: C, 66.96; H, 4.96; Anal. Calc. for $C_{56}H_{49}Cl_2P_3ORu$; C, 67.07; H, 4.92%. IR (nujol, ν): 1960m, 1941vs, 1898m, 1157w, 1088m, 743m, 696s, 527s cm^{-1}.

2.2. X-ray crystallography

2.2.1. Structure determination

Crystals were mounted on a thin glass fibre using a fast-setting epoxy resin and cooled on the diffractometer to 173 K using an Oxford Cryostream low-tempera-

---

* Corresponding author. Fax: +61-7-4781-4523.
E-mail address: peter.junk@jcu.edu.au (P.C. Junk)

PII: S0022-328X(99)00317-4

ture attachment. A total of 90 oscillation frames each of width 2° in ϕ and of 30 s exposure time were recorded using a Nonius $^{\text{Kappa}}$CCD diffractometer, with a detector to crystal distance of 25 mm. Crystals were indexed from the first ten frames using the DENZO-SMN package [11] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO, Scalepack [11]) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. The structures was solved using SHELXS-97 [12] and developed via alternating least squares cycles and difference Fourier synthesis (SHELXL-97 [12]) with the aid of the program RES2INS [13]. All non-hydrogen atoms were modelled anisotropically, while hydrogen atoms were assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. All calculations were carried out with either a Silicon Graphics Indy R5000 workstation or an IBM-compatible PC. A summary of data collection parameters is presented in Table 1. Selected bond lengths and angles are shown in Table 2. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 118490 for $[Ru(CO)H_2(PPh_3)_3]\cdot CH_2Cl_2$. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033, or e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

Table 1
Crystal data and summary of data collection

Compound	$Ru(CO)H_2(PPh_3)_3\cdot CH_2Cl_2$
Molecular formula	$C_{56}H_{49}Cl_2OP_3Ru$
Molecular weight	1002.83
Crystal system, space group	Orthorhombic, *Pcab*
a (Å)	18.3140(4)
b (Å)	19.1832(4)
c (Å)	28.8074(4)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	9418.0(3)
Molecules/unit cell	8
$D_{\text{calc.}}$ (g cm^{-3})	1.415
μ (mm^{-1})	0.589
F(000)	4128
Crystal dimensions (mm)	$0.30\times0.20\times0.20$
Radiation	Mo–K$_\alpha$
2θ range (°)	6.72–52.00
Max/min transmission	0.8913/0.8431
No. reflections collected	80264
No. of unique reflections	9224
No. of parameters varied	577
Sigma cutoff	None
Temperature of data collection (K)	173(2)
R (data with $I>2\sigma(I)$)	0.036
wR_2 (all data)	0.086

Table 2
Selected bond lengths (Å), and angles (°) for $[Ru(CO)H_2(PPh_3)_3]\cdot CH_2Cl_2$

Bond length (Å)			
Ru(1)–C(1)	1.893(3)	Ru(1)–P(2)	2.4010(6)
Ru(1)–P(1)	2.3241(6)	Ru(1)–P(3)	2.3111(7)
Ru(1)–H(1)	1.59(3)	Ru(1)–H(2)	1.65(3)
C(1)–O(1)	1.155(3)	H(1)···H(55)	2.027
H(2)···H(49)	2.25 *	H(2)···H(27)	2.27 *
Bond angle (°)			
C(1)–Ru(1)–P(1)	104.20(8)	P(1)–Ru(1)–P(2)	101.35(2)
C(1)–Ru(1)–P(2)	91.21(8)	P(1)–Ru(1)–P(3)	147.86(2)
C(1)–Ru(1)–P(3)	96.20(8)	P(2)–Ru(1)–P(3)	102.78(2)
H(1)–Ru(1)–H(2)	87(2)		
Ru(1)–H(1)···H(55)	139.1		

* Outside the 2.2 Å cutoff considered as significantly shorter than the sum of the van der Waals radii of d_{HH} of 2.4 Å, but the interaction is considered as significant.

3. Results and discussion

$[Ru(CO)H_2(PPh_3)_3]$ was prepared according to the route shown in Scheme 1. This preparation varies slightly from the literature preparation [10], where the complex is made directly from $RuCl_3$ by treatment with PPh_3 and formaldehyde/KOH. Colourless crystals were isolated in good yield after recrystallisation from dichloromethane/ethanol. The infrared spectrum shows a very strong band at 1941 cm^{-1} attributed to ν(CO) and weaker bands at 1960 and 1898 cm^{-1} attributed to ν(RuH).

$$[Ru(CO)ClH(PPh_3)_3] \xrightarrow[\text{2. } CH_2Cl_2/EtOH]{\text{1. } PPh_3\text{, KOH, 2-methoxyethanol}} [Ru(CO)H_2(PPh_3)_3]$$

Scheme 1. Synthesis of $[Ru(CO)H_2(PPh_3)_3]$.

The X-ray crystal structure of $[Ru(CO)H_2(PPh_3)_3]$ at 173 K demonstrates that the complex is, as expected, an octahedral monomer Fig. 1. The low-temperature data collection enabled the hydrido ligands to be located from the Fourier difference map and their positional and thermal parameters refined freely to give Ru–H distances of 1.59(3) and 1.65(3) Å and an H–Ru–H angle of 87°. Close inspection of *intra*- and *intermolecular* contacts reveals some very interesting features. First, there is an intramolecular H···H interaction between the hydrido ligand H(1) and an adjacent *o*-C–H proton (idealised position) of a phenyl group of one of the phosphine ligands. This H···H distance of 2.02 Å is significantly shorter than the sum of the van der Waals radii (2.4 Å), and it has been suggested [5] that a d_{HH} cutoff of 2.2 Å be considered for significant attractive interactions and therefore must be considered as real. The Ru–H···H and H···H–C angles of 139° and 128°, respectively are not linear as a consequence of the steric demands of the coordination complex as a whole, however the aryl ring C(50)–C(55) is clearly orientated in such a way as to bring about the relatively short H···H contact. In other complexes where H···H interactions have been noted, these are all intermolecular interactions, except in the tetramethylpiperidine adduct of AlH_3 where the H···H bond is responsible for the observed eclipsed geometry [3]. The second hydrido ligand, H(2), does not form a single extremely short H···H interaction, apparently because of the interlocked nature of the aryl rings which precludes the formation of two such interactions. In fact, H(2) engages in a bifurcated pair of H···H_{phenyl} contacts of length 2.25 and 2.27 Å.

Within the present system, the H···H contacts are all intramolecular and do not account for crystal packing. However, there is a long intermolecular Ar–H···OC hydrogen bond between the hydrogen on C(48) and a carbonyl oxygen on an adjacent molecule (C···O, 3.85 Å). From a crystal assembly point of view, this interaction appears to be partially responsible for the packing of the molecules within the crystal.

The observation of these interactions prompted us to investigate other ruthenium hydrido-triphenylphosphine species to determine if this is a common feature of such systems. Indeed a survey of the Cambridge Crystallographic Database [37] revealed that there are many such cases in (Table 3). Crystallographically determined H···H distances range from 1.71–2.16 Å with the majority clustering around 1.95–2.05 Å. The realisation is that the $H_{(\mathrm{hydrido})}\cdots H_{(\mathrm{protic})}$ interactions are in fact more commonplace than may have been expected. In fact, within this data set it seems likely that the unconventional may indeed be conventional. It is highly likely that in other related systems where transition metal hydride complexes also have ligands with δ^+ H atoms present, these unconventional interactions are to be expected.

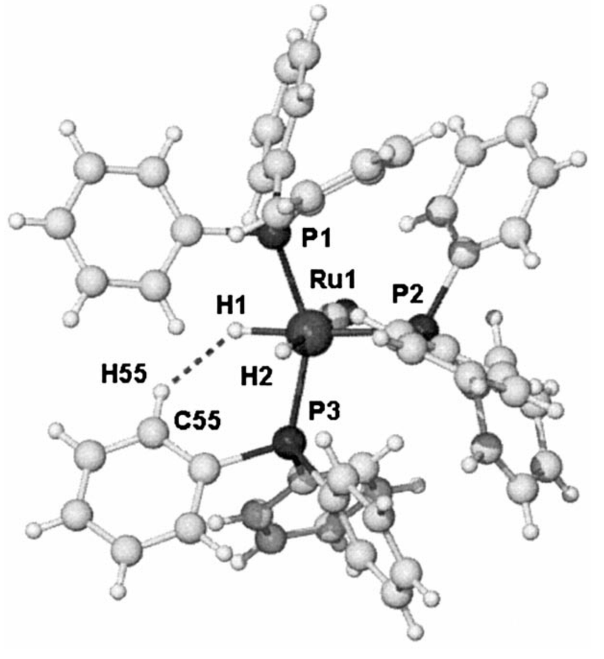

Fig. 1. Molecular structure of octahedral monomeric [Ru(CO)-$H_2(PPh_3)_3$] showing H···H interaction.

Table 3
H···H distances in ruthenium hydrido triphenylphosphine complexes [a]

Complex	Å	Reference
$[18\text{-crown-6}\cdot K][H_3Ru(PPh_3)_3]\cdot thf$	2.004	[14]
$[1,1,1\text{-}(PPh_3)HCl\text{-}1\text{-}RuB_9H_7\text{-}3,5\text{-}(PPh_3)_2]$	2.084	[15]
$[(\eta^6\text{-}C_7H_8)RuH(PPh_3)_2][BPh_4]$	2.044	[16]
$[Ru(CO)HCl(Hdmpz)(PPh_3)_2]$	2.159	[17]
$[\{(PPh_3)_2Ru\}(\mu\text{-}MeCOO)_2(\mu\text{-}H)_2\text{-}\{RuB_{10}H_7(OCOMe)\}]$	2.151 1.856	[18]
$[H(CO)(PPh_3)_2Ru(bim)Rh(cod)]$	2.107	[19]
$[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2]$	1.713	[20]
$[RuH(CO_2Me)(PPh_3)_3]$	2.161	[21]
$[RuClH(CO)(PPh_3)_2(SN_2C_6H_4)]$	2.107	[22]
$[RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\}\text{-}C_2B_9H_{10}]$	2.079 2.190	[23]
$[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}ampy)(CO_2Me)(CO)_6(PPh_3)_2]\cdot MeOH$	1.958	[24]
$[RuH(terpy)(PPh_3)_2](salicylate)$	1.947	[25]
$[RuH(NCO)(CO)_2(PPh_3)_2]\cdot thf$	1.934 2.158	[26]
$[Cp^*TaS_3\{RuH(PPh_3)_2\}_2]$	1.929 1.991 1.984	[27]
$[(\mu_2\text{-}H)_3(\mu_2\text{-}CO)Cr(CO)_2Ru(PPh_3)_3\text{-}K\{(CH_3(OCH_2CH_2)_2)_3N\}]$	2.069	[28]
$[(CO)Ru(PPh_3)_2H(\mu\text{-}H)_2B_3H_6]$	2.159	[29]
$[NEt_4][HRu_3(CO)_8(PPh_3)(PPhC_6H_4)]$	2.125	[30]
$[Ru_3H(CO)_9(PPh_3)(\mu\text{-}COMe)]$	2.034	[31]
$[Ru_3(CO)_6(PPh_3)_3BH_5]\cdot CH_2Cl_2$	2.114	[32]
$[Ru\{NHC(CF_3)NC(CF_3)NH\}H(CO)(PPh_3)_2]$	2.150	[33]
$[(PPh_3)_3Ru(\mu_2\text{-}H)_3Re(CO)(PPh_2Me)_2]$	2.050	[34]
$[(\mu\text{-}H)_2Ru_3(\mu_3\text{-}\eta^2\text{-}EtCCEt)(CO)_6(PPh_3)_3]\cdot 3CH_2Cl_2$	2.162	[35]
$[(\mu_2\text{-}H)Ru_3(CO)_8(PPh_3)(\mu_3\text{-}\eta^2\text{-}SCNHPhNPh)]$	2.060	[36]

[a] The d_{HH} cutoff of 2.2 Å is adopted. According to Crabtree et al. [6], this value, which is markedly shorter than the sum of the van der Waals radii (2.4 Å) represents a significant attractive interaction. Hdmpz, 3,5-dimethylpyrazole; bim, 2,2′-bi-imidazalato; cod, cycloocta-1,5-diene; ampy, 2-amido-6-methylpyridine; terpy, 2,2′:6′,2″-terpyridine; Cp*, pentamethylcyclopentadienyl.

In summary, we have shown that the unconventional H···H bond may not be as uncommon as expected within many crystal systems. With stronger emphasis being placed on supramolecular chemistry, where *intra*- and *intermolecular* interactions are now being routinely investigated, it may be expected that the H···H bond may become almost commonplace in hydrido systems.

Acknowledgements

We thank the EPSRC and King's College London for funding the diffractometer system and the Nuffield Foundation for the provision of computing equipment. We are also grateful to the EPSRC Daresbury Laboratory Chemical Database Service.

References

[1] (a) B.V. Cheney, M.W. Schulz, J. Cheney, W.G. Richards, J. Am. Chem. Soc. 110 (1988) 4195. (b) W.L. Jorgensen, D.L. Severance, J. Am. Chem. Soc. 112 (1990) 4768. (c) C.A. Hunter, J.K.M. Sanders, J. Am. Chem. Soc. 112 (1990) 5525. (d) J.L. Atwood, F. Hamada, K.D. Robinson, G.W. Orr, R.L. Vincent, Nature 349 (1991) 683.

[2] I. Alkorta, I. Rozas, J. Elguero, Chem. Rev. 27 (1998) 163.

[3] J.L. Atwood, G.A. Koutsantonis, F.-C. Lee, C.L. Raston, J. Chem. Soc. Chem. Commun. (1994) 91.

[4] J. Wessel, J.C. Lee, E. Peris, G.P.A. Yap, J.B. Fortin, J.S. Ricci, G. Sini, A. Albinati, T.F. Koetzle, O. Eisenstein, A.L. Rheingold, R.H. Crabtree, Angew. Chem. Int. Ed. Engl. 34 (1995) 2507.

[5] T.B. Richardson, S. de Gala, R.H. Crabtree, J. Am. Chem. Soc. 117 (1995) 12875.

[6] R.H. Crabtree, R.E.M. Siegbahn, O. Eisenstein, A.L. Rheingold, T.F. Koetzle, Acc. Chem. Res. 29 (1996) 348.

[7] J.P. Campbell, J.-W. Hwang, V.G. Young, R.B. Von Dreele, C.J. Cramer, W.L. Gladfelter, J. Am. Chem. Soc. 120 (1998) 521.

[8] G. Sini, O. Eisenstein, W. Yao, R.H. Crabtree, Inorg. Chim. Acta 280 (1998) 26.

[9] D. Braga, P. De Leonardis, F. Grepioni, E. Tedesco, M.J. Calhorda, Inorg. Chem. 37 (1998) 3337.

[10] N. Ahmad, J.J. Levison, S.D. Robinson, M.F. Uttley, Inorg. Synth. 15 (1974) 48.

[11] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1996).

[12] G.M. Sheldrick, SHELXL-97, University of Göttingen, 1997.

[13] L.J. Barbour, RES2INS, University of Missouri, Columbia, 1995.

[14] A.S.C. Chan, H.-S. Shieh, J. Chem. Soc. Chem. Commun. (1985) 1379.

[15] J.E. Crook, M. Elrington, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, J.D. Woollins, J. Chem. Soc. Dalton Trans. (1985) 2407.

[16] A.R. Siedle, R.A. Newmark, L.H. Pignolet, D.X. Wang, T.A. Albright, Organometallics 5 (1986) 38.

[17] A. Romero, A. Vegas, A. Santos, A.M. Cuadro, J. Chem. Soc. Dalton Trans. (1987) 183.

[18] X.L.R. Fontaine, N.N. Greenwood, J.D. Kennedy, M. Thornton-Pett, Z. Peiju, J. Chem. Soc. Chem. Commun. (1987) 1717.

[19] M.P. Garcia, A.M. Lopez, M.A. Esteruelas, F.J. Lahoz, L.A. Oro, J. Chem. Soc. Chem. Commun. (1988) 793.

[20] Z. He, S. Nefedov, N. Lugan, D. Neibecker, R. Mathieu, Organometallics 12 (1993) 3837.

[21] A.C. Skapski, F.A. Stephens, J. Chem. Soc. Dalton Trans. (1974) 390.

[22] N.W. Alcock, A.F. Hill, M.S. Roe, J. Chem. Soc. Dalton Trans. (1990) 1737.

[23] F. Teixidor, J.A. Ayllon, C. Vinas, R. Kivekas, R. Sillanpaa, J. Casabo, J. Chem. Soc. Chem. Commun. (1992) 1281.

[24] P.L. Andreu, J.A. Cabeza, M.A. Pellinghelli, V. Riera, A. Tiripicchio, Inorg. Chem. 30 (1991) 4611.

[25] A. Pramanik, N. Bag, A. Chakravorty, J. Chem. Soc. Dalton Trans. (1992) 97.

[26] F. Ragaini, T. Longo, S. Cenini, F. Demartin, J. Chem. Soc. Dalton Trans. (1996) 3221.

[27] K. Tatsumi, H. Kawaguchi, Y. Inoue, A. Nakamura, R.E. Cramer, J.A. Golen, Angew. Chem. Int. Engl. 32 (1993) 763.

[28] W. Weng, A.M. Arif, R.D. Ernst, J. Clust. Sci. 7 (1996) 629.

[29] I.D. Burns, A.F. Hill, A.R. Thompsett, N.W. Alcock, K.S. Claire, J. Organomet. Chem. 425 (1992) C8.

[30] H. Jungbluth, G. Suss-Fink, M.A. Pellinghelli, A. Tiripicchio, Organometallics 8 (1989) 925.

[31] J. Evans, P.M. Stroud, M. Webster, Acta Crystallogr. Sect. C 46 (1990) 2334.

[32] C.E. Housecroft, D.M. Matthews, A.J. Edwards, A.L. Rheingold, J. Chem. Soc. Dalton Trans. (1993) 2727.

[33] M.B. Hursthouse, M.A. Mazid, S.D. Robinson, A. Sahajpal, J. Chem. Soc. Dalton Trans. (1994) 3615.

[34] I. Moldes, S. Nefedov, N. Lugan, R. Methieu, J. Organomet. Chem. 490 (1995) 11.

[35] W. Paw, C.H. Lake, M.R. Churchill, J.B. Keister, Organometallics 14 (1995) 3768.

[36] L.A. Hoferkamp, G. Rheinwald, H. Stoeckli-Evans, G. Suss-Fink, Organometallics 15 (1996) 704.

[37] April 1998 update, 181 309 entries: F.H. Allen, O. Kennard, Chem. Des. Autom. News 8 (1993) 31.