Cite this: New J. Chem., 2011, 35, 2018-2021

Vinylidene and pentatetraenediyl rhodium complexes obtained from a bulky rhodium(1) dimer and a functionalized 1,3-diyne[†]

Ivan Kovacik and Helmut Werner*

Received (in Victoria, Australia) 5th May 2011, Accepted 9th May 2011 DOI: 10.1039/c1nj20392d

The vinylidene complex *trans*-[RhCl(=C=CHC=CCPh₂O-SiMe₃)(PiPr₃)₂] (5), prepared from [RhCl(PiPr₃)₂]₂ (1) and HC=CC=CCPh₂OSiMe₃ (2), is in equilibrium with the pentatetraenediyl isomer *trans*-[RhCl(=C=C=C=C=CHCPh₂OSiMe₃)(PiPr₃)₂] (6) in benzene solution. The reaction of the diynyl(hydrido) compound [RhH(Cl)(C=CC=C=CPh₂OSiMe₃)(PiPr₃)₂(py)] (7) with triffic acid in THF/water afforded the functionalized rhodium(1) vinylidene *trans*-[RhCl(=C=CHC(O)CH=CPh₂)(PiPr₃)₂] (9), which was also obtained from the metallacumulene *trans*-[RhCl(=C=C=C=C=C=C=C=C=C=C=CPh₂)(PiPr₃)₂] (8) under analogous conditions.

Following our work on the chemistry of vinylidene rhodium(1) and iridium(I) complexes of the general composition trans- $[MCl(=C=CRR')(PiPr_3)_2]$ and their allenylidene analogues trans-[MCl(=C=C=CRR')(PiPr_3)₂] (M = Rh, Ir; R, R' = H, alkyl, aryl),^{1,2} we recently reported the synthesis and molecular structure of the pentatetraenediyl and hexapentaenediyl iridium(I) compounds trans-[IrCl(=C=C=CPh₂)(PiPr₃)₂] and trans-[IrCl($=C=C=C=C=CPh_2$)(PiPr_3)2], respectively.^{3,4} While the hexapentaenediyl rhodium(1) complex trans-[RhCl(=C=C=C=C=CPh₂)(PiPr₃)₂] could also be generated and trapped with diazomethane to give two isomers of the metal hexapentaene trans-[RhCl(H₂C=C=C=C=CPh₂)(PiPr₃)₂],⁵ previous attempts to obtain a RhC₄ cumulene, related to trans-[IrCl(=C=C=CPh₂)(PiPr₃)₂], remained unsuccessful. In this letter we disclose the spectroscopic data of the RhC₄ cumulene trans-[RhCl(=C=C=CHR)(PiPr₃)₂] $(R = CPh_2OSiMe_3)$ and report about the reactivity of the RhC₅ counterpart trans-[RhCl(=C=C=C=CPh₂)(PiPr₃)₂] towards phenyl azide and triflic acid in the presence of water.

The rhodium(I) dimer **1**, which had already been used to prepare the above-mentioned vinylidene and allenylidene rhodium(I) compounds,¹ reacts with the diyne **2** to give the square-planar complex **3**, in which the terminal triple bond is linked to the metal atom.⁵ Compound **3** rearranges stepwise

E-mail: helmut.werner@mail.uni-wuerzburg.de

Published on 10 June 2011. Downloaded by University of Windsor on 28/10/2014 14:10:27

in benzene or toluene at room temperature to give the diynyl(hydrido) and vinylidene isomers 4 and 5 (Scheme 1). The ³¹P NMR spectrum of the labile intermediate 4 displays a doublet at δ 50.2 with *J*(Rh,P) 97.4 Hz, which is in excellent agreement with the data for *trans*-[RhH(Cl)(C \equiv CC \equiv CPh)(P*i*Pr₃)₂] (δ 49.9, *J*(Rh,P) 96.0 Hz).⁶

The vinylidene complex 5, which had been isolated under carefully controlled conditions,⁵ is significantly more labile than the related iridium(I) compound trans-[IrCl(=C=CHC= CCPh₂OH)(P*i*Pr₃)₂],³ and in benzene or toluene partly isomerizes to the RhC₄ cumulene 6. After 12 h at 22 °C in C_6D_6 , about equal amounts of 5 and 6 are formed. Changing the reaction conditions (solvent, temperature, time of reaction) has almost no effect on the equilibrium. Typical spectroscopic features of **6** are the singlet at δ 5.73 for the =CH proton in the ¹H NMR spectrum and the four distinct signals for the carbon atoms of the RhC₄ chain in the ¹³C NMR spectrum. These signals exhibit quite different ¹³C-¹⁰³Rh and ¹³C-³¹P coupling constants. It is worth mentioning that the chemical shifts of the resonances for the cumulene carbon atoms in α -, β - and γ -position (δ 237.3, 161.1 and 173.1) are rather similar to those of the IrC₄ counterpart trans-[IrCl(=C=C= $C = CPh_2(PiPr_3)_2 (\delta 225.7, 164.1 \text{ and } 174.6)^3$ Moreover, we note that prior to the synthesis of trans-[IrCl(=C=C= $C \equiv CPh_2)(PiPr_3)_2]$,³ Selegue and Lomprey,⁷ Bruce *et al.*,⁸ Winter and Hornung,9 and Dixneuf et al.10 reported the in situ formation of cationic ruthenium(II) complexes containing the fragment Ru=C=C=C=CH₂, and they supported the presence of those species in solution by trapping experiments with nucleophiles such as NHPh₂, PPh₃, water and imines. Berke et al. described a different approach to the generation of the pentatetraenediyl ligand $C = C = CH_2$ at manganese(1) as the metal atom using the stannyl-substituted derivatives $[(C_5H_4R)Mn\{=C=C=C(SnPh_3)_2\}(R'_2PCH_2CH_2PR'_2)]$ (R = H, Me; R' = Me, Et) as the precursors.¹¹ While the latter were stable under ambient conditions, the MnC_4H_2 compounds $[(C_5H_4R)Mn(=C=C=C=CH_2) (R'_2PCH_2CH_2PR'_2)]$ decomposed above -5 °C and were characterized by NMR spectroscopy. Most recently, a similar synthetic protocol to that used for the MnC₄(SnPh₃)₂ derivatives was disclosed also by Berke's group for the tungsten(0) compounds $[W(CO){=C=C=C(R)C_6H_4tBu}$ - $(Ph_2PCH_2CH_2PPh_2)_2] (R = H, SnMe_3).^{12}$

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany.

[†] Dedicated to Professor Didier Astruc in recognition of his important contributions to inorganic and organometallic chemistry.



Scheme 1 L: PiPr₃, 2: HC = CC = CCPh₂OSiMe₃, Tf: CF₃SO₂.

The reaction of the five-coordinate diynyl(hydrido) complex 4 with pyridine leads to the octahedral 1:1 adduct 7, which on treatment with triflic acid anhydride and triethylamine gives the RhC₅ cumulene 8.⁵ Whereas diazomethane reacts with 8 to furnish two isomers of the hexapentaene complex trans-[RhCl(H₂C=C=C=C=C=CPh₂)(PiPr₃)₂],⁵ treatment of 8 with phenylazide under the same conditions affords a mixture of products, among which trans-[RhCl(N₂)(PiPr₃)₂] is the dominating species. It has been characterized by the mass spectrum and by reference to the IR and NMR spectroscopic data.¹³ Reaction of either 7 or 8 with triflic acid in the presence of an equimolar amount of water gives the rhodium(I) vinylidene complex 9 (Scheme 2) as an orange solid, which for short periods of time can be handled in air. The IR spectrum of 9 shows a strong band at 1640 cm⁻¹, assigned to the C=O stretching mode of the ketone unit. Typical NMR spectroscopic features of 9 are the broadened triplet for Rh=C=CH proton at



 δ 1.78 and the doublets-of-triplets resonances for the vinylidene carbon atoms at δ 288.5 (α-C) and δ 117.8 (β-C). A functionalized vinylidene ligand of the composition C=CHC(O)CHPh₂, related to that found in **9**, was recently generated at iridium(I) and ruthenium(II) from HC=CC(O)-CHPh₂ as the precursor.^{3,10}

As confirmed by X-ray diffraction analysis,¹⁴ in compound 9 the rhodium atom is coordinated in a slightly distorted square-planar fashion, with the two phosphine ligands trans to each other and the chloride trans-disposed to the metalbound carbon atom. The Rh=C distance is 1.784(6) Å, which is almost identical with the rhodium-carbon bond lengths in the related complexes trans-[RhCl(=C=CHCH₃)(PiPr₃)₂] $[1.775(6) \text{ Å}]^{15}$ and *trans*-[RhCl(=C=CHC(CH₃)=CH₂)- $(PiPr_3)_2$ [1.78(1) Å].¹⁶ The carbon atoms of the vinylidene fragment Rh=C=C and the ketonic unit C-C(O)-CH=C lie essentially in the same plane, indicating that in the crystal this conformation is preferred. The lengths of the two formal CH-C(O) single bonds [1.456(6) and 1.471(6) Å] are shorter than expected, which is presumably due to conjugative effects. With regard to the formation of 9 from 8, we propose a stepwise mechanism with the initial step being either the protonation at the β-carbon of the RhC₅ chain or the attack of the water molecule to the γ -carbon atom. Theoretical studies revealed that metallacumulenes of the general composition $[M = C(=C)_n R_2(L)_x]$ with n = 1 to 4 react preferentially with *electrophiles* at C_2 or C_4 and with *nucleophiles* at C_1 , C_3 or C_5 .¹⁷ The reactivities of the square-planar rhodium(I) and iridium(I) complexes trans- $[MCl{=C(=C)_nR_2}(PiPr_3)_2]$ (M = Rh, n = 1, 2; M = Ir, n = 1, 2, 3) are in perfect agreement with these results.

All experiments were carried out under an atmosphere of argon using Schlenk techniques. The starting materials 1^{18} and 2^{19} were prepared as described in the literature. The preparative protocol for **3**, **7** and **8** was already described.⁵ NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 spectrometer. Melting points were determined by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants J and N [N = ${}^{3}J(P,H) + {}^{5}J(P,H)$ or ${}^{1}J(P,C) + {}^{3}J(P,C)$ or ${}^{2}J(P,C) + {}^{4}J(P,C)$] in Hz.

Syntheses

Generation of [Rh(H)Cl(C=CC=CCPh₂OSiMe₃)-(*PiPr*₃)₂], **4**. A sample of **3** (54 mg, 0.07 mmol) was dissolved in d₈-toluene (0.5 cm³) at room temperature. The solution was stirred for *ca*. 5 min and then cooled to -20 °C. The ¹H and ³¹P NMR spectra indicated the formation of the alkynyl(hydrido) isomer **4** as well as of small amounts of the vinylidene complex **5**. Typical NMR data of **4**: $\delta_{\rm H}$ (C₆D₅CD₃, 200 MHz, 253 K) -16.42 [dt, *J*(Rh,H) 44.0, *J*(P,H) 13.0, RhH]; $\delta_{\rm P}$ (C₆D₅CD₃, 81.0 MHz, 253 K) 50.2 [d, *J*(Rh,P) 97.4].

trans-[RhCl(=C=CHC=CCPh₂OSiMe₃)(PiPr₃)₂], 5. A solution of 3 (110 mg, 0.14 mmol) in C_6D_6 (2 cm³) was stirred at room temperature and the course of the reaction was carefully monitored by ³¹P NMR spectroscopy. After 30 min the spectrum revealed the presence of approximately 90% of the vinylidene isomer. The solvent was quickly removed *in vacuo*, and pentane (1 cm^3) was added to the viscous residue. After the mixture was stored for 1 h at -20 °C, a red-violet solid was formed. It was separated from the mother liquor, washed twice with 1 cm³ portions of pentane (-20 °C) and dried in vacuo: yield 63 mg (57%); mp 71 °C (decomp). Anal. found: C, 58.68; H, 8.22%. C38H62ClOP2RhSi requires: C, 59.79; H, 8.19%. IR (KBr): ν (C \equiv C) 2195, ν (C \equiv C) 1605 cm⁻¹. NMR (C₆D₆): $\delta_{\rm H}$ (200 MHz, 295 K) 7.77 [4 H, d, J(H,H) 7.2, ortho-H of C₆H₅], 7.22-6.95 (6 H, br m, meta- and para-H of C₆H₅), 2.75 (6 H, m, PCHCH₃), 1.28 [36 H, dvt, N 13.8, J(H,H) 6.9, PCHCH₃], 0.83 [1 H, dt, J(Rh,H) 0.6, J(P,H) 2.9, Rh=C=CH, 0.23 (9 H, s, OSiMe₃); δ_C (100.6 MHz, 295 K) 291.3 [dt, J(Rh,C) 62.3, J(P,C) 15.9, Rh=C=CH], 147.9 (s, ipso-C of C₆H₅), 127.9, 127.3, 126.7 (all s, C_6H_5), 101.5 (s, $C \equiv CCPh_2$), 90.4 [dt, J(Rh,C) 17.8, J(P,C) 6.4, Rh=C=CH], 77.0 (s, C=CCPh₂), 66.3 [t, J(P,C)3.5, $C \equiv CCPh_2$], 23.7 (vt, N 20.3, PCHCH₃), 20.3 (s, PCHCH₃), 1.8 (s, SiCH₃); δ_P (162.0 Hz, 295 K) 43.1 [d, J(Rh,P) 132.3]. Note: it is important to measure the NMR spectra immediately after the solid sample is dissolved in C₆D₆.

Isomerization of 5 to *trans*-[RhCl(=C=C=C=CHCPh₂-OSiMe₃)(PiPr₃)₂], 6. A sample of 5 (38 mg, 0.05 mmol) was dissolved in C_6D_6 (0.5 cm³) and the NMR spectra of the solution were carefully monitored in time intervals of 30 min at room temperature. After 12 h, the spectra revealed the presence of approximately equal amounts of the isomers 5 and 6. Attempts to separate the isomers by column chromatography or fractional crystallization failed. Spectroscopic data of **6**: NMR (C₆D₆): $\delta_{\rm H}$ (200 MHz, 295 K) 7.52 [4 H, d, J(H,H) 8.0, ortho-H of C₆H₅], 7.22–6.95 (6 H, br m, meta- and para-H of C₆H₅), 5.73 (1 H, s, =CH), 2.75 (6 H, m, PCHCH₃), 1.29 [36 H, dvt, N 13.8, J(H,H) 6.9, PCHCH₃], 0.11 (9 H, s, OSiMe₃); $\delta_{\rm C}$ (100.6 MHz, 295 K) 237.3 [dt, J(Rh,C) 66.1, J(P,C) 16.9, Rh=C], 173.1 [dt, J(Rh,C) 3.8, J(P,C) 3.2, Rh=C=C=C], 161.1 [dt, J(Rh,C) 19.1, J(P,C) 6.7, Rh=C=C], 148.7, 148.5 (both s, *ipso*-C of C₆H₅), 128.1, 127.2, 127.0 (all s, C₆H₅), 88.0 [t, J(P,C) 3.5, Rh=C=C=C=CH], 72.3 [t, J(P,C) 3.5, CPh₂], 24.0 (vt, N 20.3, PCHCH₃), 20.7 (s, PCHCH₃), 2.0 (s, SiCH₃); $\delta_{\rm P}$ (162.0 Hz, 295 K) 41.1 [d, J(Rh,P) 128.9].

Reaction of compound 8 with phenyl azide. A solution of **8** (80 mg, 0.12 mmol) in toluene (10 cm³) was treated with an equimolar amount of PhN₃ and stirred for 30 min at room temperature. A change of color from deep violet to orange occurred. The solution was concentrated *in vacuo* to *ca.* 2 cm³ and pentane (5 cm³) was added. After the mixture was stored for 4 h at -20 °C, an orange solid precipitated. Based on the ³¹P NMR spectrum, it contained a mixture of two rhodium-containing compounds in the ratio of *ca.* 6:1. Attempts to separate the two compounds failed. The major product was identified as *trans*-[RhCl(N₂)(PiPr₃)₂] by mass spectrometry (*m*/*z* 486), and IR and NMR spectroscopic data.

trans-[RhCl(=C=CHC(O)CH=CPh₂)(PiPr₃)₂], 9. Α solution of either 7 (300 mg, 0.36 mmol) or 8 (242 mg, 0.36 mmol) in tetrahydrofurane (3 cm³) was treated at -78 °C first with an equimolar amount of water and then with trifluoromethanesulfonic acid $(0.64 \text{ cm}^3, 0.72 \text{ mmol})$. Under continuous stirring the solution was slowly warmed to room temperature, which led to a change of color from off-white to orange. The solution was concentrated in vacuo to ca. 2 cm³ and the concentrate was chromatographed on Al_2O_3 (acidic, activity grade I). With chilled toluene (-50 °C) an orange fraction was eluted from which the solvent was removed *in vacuo*. To the viscous residue pentane (1 cm^3) was added, and the mixture was stored for 6 h. An orange solid precipitated, which was separated from the mother liquor, washed twice with 1 cm³ portions of pentane (-20 °C) and dried in vacuo: yield 120 mg (49%); mp 84 °C (decomp). Anal. found: C, 59.83; H, 7.71%. C₃₅H₅₄ClOP₂Rh requires: C, 60.83; H, 7.88%. IR (KBr): ν (C=O) 1640 cm⁻¹. NMR (C₆D₆, 295 K): $\delta_{\rm H}$ (200 MHz) 7.35–6.95 (11 H, br m, C₆H₅ and CH=CPh₂), 2.65 (6 H, m, PCHCH₃), 1.78 [1 H, t, J(P,H) 2.6, Rh=C=CH], 1.29 [36 H, dvt, N 13.2, J(H,H) 6.8, PCHCH₃]; $\delta_{\rm C}$ (100.6 MHz) 288.5 [dt, J(Rh,C) 61.0, J(P,C) 14.0, Rh=C=CH], 180.1 (s, C=O), 150.8 (s, CH=CPh2), 142.2, 140.1 (both s, *ipso*-C of C_6H_5), 130.1 (s, CH=CPh₂), 129.1, 128.9, 128.5, 128.2 (all s, C₆H₅), 117.8 [dt, J(Rh,C) 15.3, J(P,C) 5.1, Rh=C=CH], 24.2 (vt, N 20.3, PCHCH₃), 20.3 (s, PCHCH₃); δ_P (162.0 Hz) 43.8 [d, J(Rh,P) 132.3].

Acknowledgements

We gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Humboldt Foundation. We also thank Mrs R. Schedl and Mr C. P. Kneis (DTA and elemental analyses) and Dr G. Lange and Mr F. Dadrich (mass spectra).

References

- Reviews for M = Rh: H. Werner, Nachr. Chem., Tech. Lab., 1992, 40, 435; H. Werner, Organomet. Chem., 1994, 475, 45; H. Werner, J. Chem. Soc., Chem. Commun., 1997, 903; H. Werner, Coord. Chem. Rev., 2004, 248, 1693.
- 2 Review for M = Ir: H. Werner, K. Ilg, R. Lass and J. Wolf, J. Organomet. Chem., 2002, 661, 137.
- 3 K. Ilg and H. Werner, Angew. Chem., Int. Ed., 2000, 39, 1632;
 K. Ilg and H. Werner, Chem.-Eur. J., 2002, 8, 2812.
- 4 R. W. Lass, P. Steinert, J. Wolf and H. Werner, *Chem.-Eur. J.*, 1996, **2**, 19.
- 5 I. Kovacik, M. Laubender and H. Werner, *Organometallics*, 1997, **16**, 5607.
- 6 H. Werner, O. Gevert, P. Steinert and J. Wolf, Organometallics, 1995, 14, 1786.
- 7 J. R. Lomprey and J. P. Selegue, Organometallics, 1993, 12, 616;
 J. P. Selegue, Coord. Chem. Rev., 2004, 248, 1543.
- M. I. Bruce, P. Hinterding, E. R. T. Tiekink, B. W. Skelton and A. H. White, J. Organomet. Chem., 1993, 450, 209; M. I. Bruce, P. Hinterding, P. J. Low, B. W. Skelton and A. H. White, J. Chem. Soc., Dalton Trans., 1998, 467; M. I. Bruce, M. Ke, B. D. Kelly, P. J. Low, B. W. Skelton and A. H. White, J. Organomet. Chem., 1999, 590, 184; P. J. Low and M. I. Bruce, Adv. Organomet. Chem., 2001, 48, 71; M. I. Bruce, Coord. Chem. Rev., 2004, 248, 1603.
- 9 R. F. Winter and F. M. Hornung, *Organometallics*, 1997, 16, 4248;
 R. F. Winter, *Chem. Commun.*, 1998, 2209;
 R. F. Winter and

F. M. Hornung, Organometallics, 1999, **18**, 4005; R. F. Winter, *Eur. J. Inorg. Chem.*, 1999, 2121; R. F. Winter and S. Zalis, *Coord. Chem. Rev.*, 2004, **248**, 1565.

- 10 P. Haquette, D. Touchard, L. Toupet and P. Dixneuf, J. Organomet. Chem., 1998, 565, 63; S. Rigaut, J. Massue, D. Touchard, J.-L. Fillaut, S. Golhen and P. H. Dixneuf, Angew. Chem., Int. Ed., 2002, 41, 4513.
- 11 O. Gevert, Dissertation, Universität Würzburg, 1998.
- K. Venkatesan, F. J. Fernandez, O. Blacque, T. Fox, M. Alfonso, H. W. Schmalle and H. Berke, *Chem. Commun.*, 2003, 2006; K. Venkatesan, O. Blacque, T. Fox, M. Alfonso, H. W. Schmalle and H. Berke, *Organometallics*, 2004, 23, 4661; K. Venkatesan, O. Blacque and H. Berke, *Organometallics*, 2006, 25, 5190.
- 13 S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan and H. Berke, *Angew. Chem., Int. Ed.*, 2009, **48**, 5203; S. N. Semenov, O. Blacque, T. Fox, K. Venkatesan and H. Berke, *Organometallics*, 2010, **29**, 6321.
- 14 C. Busetto, A. D'Alfonso, F. Maspero, G. Perego and A. Zazzetta, J. Chem. Soc., Dalton Trans., 1977, 1828.
- 15 H. Werner, F. J. Garcia Alonso, H. Otto and J. Wolf, Z. Naturforsch., B: Chem. Sci., 1988, 43, 722.
- 16 T. Rappert, O. Nürnberg, N. Mahr, J. Wolf and H. Werner, Organometallics, 1992, 11, 4156.
- 17 B. E. R. Schilling, R. Hoffmann and D. L. Lichtenberger, J. Am. Chem. Soc., 1979, 101, 585; N. M. Kostic and R. F. Fenske, Organometallics, 1982, 1, 974; F. Delbecq, J. Organomet. Chem., 1991, 406, 171.
- 18 H. Werner, J. Wolf and A. Höhn, J. Organomet. Chem., 1985, 287, 395.
- 19 J. B. Armitage, E. R. H. Jones and M. C. Whiting, J. Chem. Soc., 1952, 1993.