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Hydrodimetalation of *tert*-Butylphosphaethyne by a Diruthenium Complex: Crystal and Molecular Structure of $[Ru_2(CO)_4(\mu\text{-}PBu^t{}_2)(\mu\text{-}Ph_2PCH_2PPh_2)\{\mu\text{-}PC(H)Bu^t\}]$

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The reaction of $[Ru_2(CO)_3(PBu^n{}_3)(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ (**1a**) with *tert*-butylphosphaethyne leads under hydrodimetalation to the novel phosphaethenyl complex $[Ru_2(CO)_4(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (**2**), which has been characterized by spectroscopic methods as well as by X-ray diffraction. Compound **2** represents the first structurally characterized complex with a phosphaalkenyl ligand of the type μ-PC(H)R bridging two metal centers.

Within our studies on the reactivity of the coordinatively unsaturated complexes $[M_2(CO)_4(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ (M = Fe, Ru; dppm = $Ph_2PCH_2PPh_2$)[1] we observed a facile insertion of carbon disulfide into the dimetal hydrido core of $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ (**1**), resulting in the dithioformato compound $[Ru_2(CO)_4(\mu\text{-}S_2CH)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$.[2] Terminal alkynes such as $PhC\equiv CH$ did not insert into the $Ru_2(\mu\text{-}H)$ core of **1**, because the starting complex is a strong base and on the other hand the alkyne is too acidic; therefore the acetylide-bridged species $[Ru_2(CO)_4(\mu,\eta^1{:}\eta^2\text{-}C\equiv CPh)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ was obtained.[3] In light of more insertion reactions we were interested in the reaction behavior of **1** toward phosphaalkynes. Since the development of preparative pathways to stable phosphaalkynes,[4] several types of reactions involving these compounds have been observed in the coordination sphere of transition metals such as oligomerizations, cyclizations, and insertions.[5] Therefore phosphaalkynes show a complex coordination behavior dominated by bonding modes involving mainly the phosphorus carbon triple bond. An analogous reaction pattern to the alkynes has been observed in several cases. Thus, we could show that a kind of heteroalkyne metathesis can be realized, wherein the alkoxide complexes $[(RO)_3W\equiv W(OR)_3]$ reacted with phosphaalkynes in the presence of $[W(CO)_5THF]$, yielding the products $[(RO)_3W\equiv CR]$ and $[(RO)_3W\equiv P\rightarrow W(CO)_5]$.[6] Furthermore, two interesting transformations on $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}dppm)]$ in the presence of $P\equiv CBu^t$ were reported: UV irradiation in toluene for 9 h yielded $[Fe_2(CO)_5(\mu\text{-}dppm)\{\mu,\eta^2\text{-}PC(CO)Bu^t\}]$, whereas under prolonged UV irradiation (12−30 h) a mixture of products was obtained containing $[Fe_2(\mu\text{-}CO)(CO)_4(\mu,\eta^2\text{-}PCBu^t)]$.[7] Moreover, a few hydrometalation reactions of phosphaalkynes induced by transition metal complexes were reported.[8,9] Thus, the reaction of $[RuH(CO)Cl(PPh_3)_3]$ with $P\equiv CBu^t$ results in insertion of the phosphaalkyne into the M−H bond to give the phosphaalkenyl complex $[Ru(CO)Cl(PPh_3)_2\{P{=}C(H)Bu^t\}]$.[8] To our knowledge for dinuclear complexes and metal clusters, respectively, this kind of hydrodimetalation of $P\equiv CR$ resulting in a bridging phosphaalkenyl ligand, μ-PC(H)R, has not been reported until now. An "indirect" hydrodimetalation was described during the reaction of $[HIr_4(CO)_{10}(\mu\text{-}PPh_2)]$ with $[Pt(dppe)(\eta^2\text{-}PCBu^t)]$, yielding the clusters $[Ir_4Pt(dppe)(CO)_n(\mu\text{-}PPh_2)\{\mu\text{-}PC(H)Bu^t\}]$ (n = 9, 10; dppe = $Ph_2PC_2H_4PPh_2$).[9] The structures of these compounds, isolated as a mixture only, were proposed on the basis of NMR and mass spectrometry experiments. Herein we describe reactions of the complexes $[Ru_2(CO)_3L(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ (L = CO, **1**; L = $PBu^n{}_3$, **1a**) with $P\equiv CBu^t$ resulting in the synthesis and structural characterization of the novel complex $[Ru_2(CO)_4(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (**2**).

Treatment of the coordinatively unsaturated $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}PBu^t{}_2)(\mu\text{-}dppm)]$ (**1**) with an excess of $P\equiv CBu^t$ in DME solution under reflux for 8 h does not result in any conversion. As described for the reaction of **1** with phenylethyne, long reaction times in refluxing

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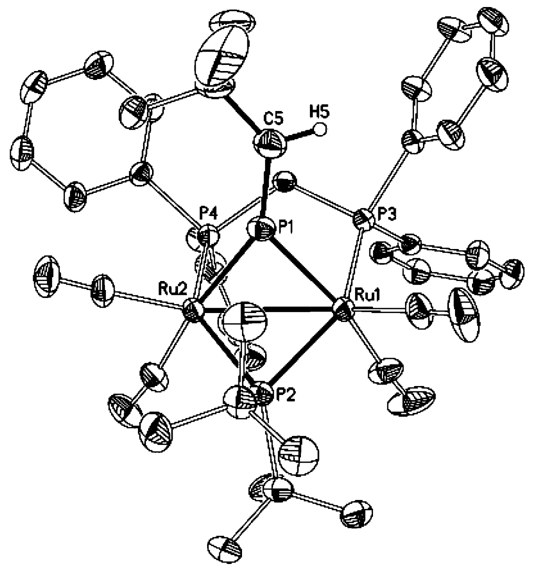
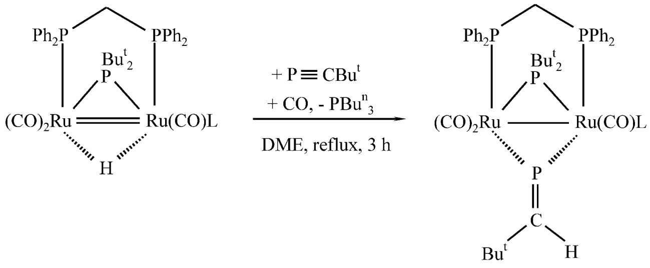


Figure 1. Molecular structure of $[Ru_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (**2**) showing 30% thermal displacement ellipsoids. Selected bond distances (Å) and angles (deg): Ru(1)−Ru(2) 2.854(1), Ru(1)−P(1) 2.286(2), Ru(1)−P(2) 2.362(1), Ru(1)−P(3) 2.361(1), Ru(2)−P(1) 2.311(2), Ru(2)−P(2) 2.376(2), Ru(2)−P(4) 2.350(1), P(1)−C(5) 1.662(7); Ru(1)−P(1)−Ru(2) 76.77(5), Ru(1)−P(1)−C(5) 132.0(2), Ru(2)−P(1)−C(5) 148.8(3), Ru(1)−Ru(2)−P(1) 51.21(4), Ru(2)−Ru(1)−P(1) 52.02(4).

Scheme 1



$L = PBu^n_3$, **1a** $L = CO$, **2**

toluene were necessary to afford a noticeable transformation of the reactants.[3] However due to the labile phosphine ligand, the complex $[Ru_2(CO)_3(PBu^n_3)(\mu\text{-}H)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]$ (**1a**) is much more reactive, which resulted in a drastic decrease in reaction time and in a remarkable increase in the yield of the main product in the course of this reaction. Thus, treatment of **1a** with an excess of $P{\equiv}CBu^t$ in refluxing DME afforded a complete conversion after 3 h. Workup of the reaction mixture gave yellow crystals, which were subjected to X-ray structure analysis, revealing the dinuclear complex $[Ru_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (**2**). Figure 1 shows an ORTEP view of the molecule. The molecule consists of a diruthenium core bridged by a phosphido group, the dppm, and a phosphaethenyl group as a $3e^-$ ligand. The coordination sphere of the two ruthenium atoms is completed by four carbonyl ligands, and therefore by electron counting **2** exhibits 34 cluster valence electrons. The result of the X-ray structure analysis showed that no direct insertion of the phosphaethyne in **1a** occurred, because four carbonyl ligands were found in the product **2** (Scheme 1). Although there is no experimental evidence for a possible formation pathway of **2**, the following two pathways can be considered: (i) the dimetal complexes **1** and **1a** exhibit formal Ru−Ru double bonds; therefore an addition of the triple bond of the phosphaethyne to the Ru−Ru double bond could be taken into account. The LUMO of the Ru=Ru bond exhibits π^* character and could interact with the HOMO π orbital of the phosphaethyne. Thus, by this way the "clean" addition product $[Ru_2(CO)_3(PBu^n_3)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ should be obtained, which is however not the case. Therefore we have to assume that due to the steric hindrance of the tributylphosphine a simultaneous dissociation occurs that is followed by a CO addition. The CO must be produced in side reactions of this thermolysis, which occur with certainty because the formation of the complexes $[Ru(CO)_4(PBu^n_3)]$ and $[Ru(CO)_3(PBu^n_3)_2]$ was indicated by ^{31}P NMR. Since these speculations about a possible reaction pathway are not very convincing, the following pathway seems to us to be the more realistic one. (ii) Here, in a first step the dissociation of the phosphine occurs followed by an "end-on" coordination of the phosphaethyne via the phosphorus lone pair. Furthermore, the phosphaethyne undergoes a bridging of the Ru−Ru bond with a simultaneous migration of the hydride to the phosphaethyne carbon to form the phosphaethenyl ligand. Finally, the remaining free coordination site is occupied by the sterically less demanding and better π acceptor ligand CO (compared to PBu^n_3). Obviously, the free phosphine leads to a degradation of the dinuclear core of the starting material under the employed thermolytic conditions. Thus, $^{31}P\{^1H\}$ NMR investigations of crude reaction mixtures indicate additionally the presence of free PBu^n_3 as well as mononuclear complexes such as $[Ru(CO)_4(PBu^n_3)]$ and $[Ru(CO)_3(PBu^n_3)_2]$ to some extent. Similar degradation reactions were described during the thermal treatment of the complexes $[Ru_2(CO)_4(PBu^n_3)_2(\mu\text{-}O_2CMe)_2]$ in heptane solution for example.[10]

The $^{31}P\{^1H\}$ NMR spectrum of **2** reveals an AMXY spectrum due to the chemical inequivalence of the two phosphorus nuclei of the bridging dppm ligand. These groups appear as two signals that couple with the P nucleus of the phosphido bridge and the phosphorus of the bridging phosphaethenyl ligand. For **2** the signal at δ 255.9 can be assigned with certainty to the phosphido bridge $\mu\text{-}PBu^t_2$.[1,11] Therefore, the downfield signal at δ 378.4 is attributable to the P atom of the $\mu\text{-}P{=}C(H)Bu^t$ group and correlates with observations for, for example, $[Ru(CO)Cl(PPh_3)_2\{P{=}C(H)Bu^t\}]$ (δ 450.4).[8] The assignment of this signal was confirmed additionally by a selective phosphorus decoupled proton NMR experiment: irradiation at δ 378.4 resulted in the disappearance of the doublet at δ 3.34 in the proton spectrum to give a singlet instead. Furthermore, the proton coupled ^{31}P NMR spectrum of **2** showed a doublet at δ 379.5 ($^2J_{PH}$ = 40.0 Hz), confirming the correct assignment of the signal. The ^1H NMR spectrum of **2** exhibits, in addition to the other signals for $\mu\text{-}PBu^t_2$ and dppm, a resonance at δ 3.34 (d) attributable to the proton of the phosphaethenyl ligand (H5) with a large coupling to the phosphaethenyl phosphorus (40 Hz). No

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further coupling of this H to the other P nuclei is found. For $[Ir_4Pt(dppe)(CO)_{10}(\mu\text{-}PPh_2)\{\mu\text{-}PC(H)Bu^t\}]$ a resonance at δ 4.2 (dd) is reported with corresponding couplings $^2J_{PH} = 12$ Hz and $^4J_{PH} = 3$ Hz, respectively.[9] The H atoms of the Bu^t substituent of the latter compound resonate at δ 0.50 as a multiplet, and in accordance with this we assign the signal at δ 0.57 (d, $^4J_{PH} = 1.1$ Hz) to the *tert*-butyl substituent of the phosphaethenyl group.

The bonding characteristics of the bridging phosphaethenyl ligand in the structure of **2** have no precedent. Therefore a comparison with some bonding parameters found for the related compounds $[Fe_2(CO)_6\{\mu\text{-}P{=}C(SiMe_3)_2\}_2]$ (**3**)[12] and $[Fe_2(CO)_6(\mu\text{-}SBu^t)\{\mu\text{-}P{=}C(SiMe_3)_2\}]$ (**4**)[13] should be given. In this light the most interesting feature refers to the P−C distance exhibiting these species as phosphaalkenyl complexes. For **3** and **4** the corresponding P−C bond lengths were found to be 1.650(4) and 1.621(9) Å and are in good accordance with the distance P(1)−C(5) found for **2** (Figure 1). In a similar context the corresponding distance in $[Ru\{P(Me){=}C(H)Bu^t\}Cl(I)(CO)(PPh_3)_2]$ was reported to be 1.657(8) Å and discussed clearly as multiple in nature.[14] Furthermore, the angles M−P−M of compounds **2**−**4** are in good agreement: **3**, 75.0°; **4**, 73.0° (for **2** see Figure 1). Moreover, the angle between the planes of Ru(1)−P(1)−Ru(2) and Ru(1)−P(2)−Ru(2) is 70.05(5)°, and the planes between the almost planar arrangement of the phosphaethenyl ligand (av deviation from the idealized plane: 0.0374 Å) and the Ru(1)−P(1)−Ru(2) plane is 8.7°. The Ru−Ru distance in **2** corresponds to a single bond, and the other structural parameters agree well with those found for similarly constituted diruthenium complexes reported by us.[1]

In conclusion, these results stimulate further studies of the general type of reaction of polynuclear hydridometal complexes with phosphaalkynes.

Experimental Section

General Comments. All reactions were performed under an atmosphere of dry argon using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves and were distilled under argon prior to use. The phosphaethyne $P{\equiv}CBu^t$ [15] as well as the complexes $[Ru_2(CO)_3L(\mu\text{-}H)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]$ (L = CO, **1**; L = PBu^n_3, **1a**)[3] were prepared according to the reported procedures. IR spectra were recorded as KBr pellets on a Bruker FT-IR spectrometer IFS 28. Mass spectra were obtained on a Varian MAT 711 spectrometer (70 eV). NMR spectra were recorded on Bruker AC 250 equipment (^{1}H, 250.133 MHz; ^{31}P, 101.256 MHz). Chemical shifts are given in ppm relative to $SiMe_4$ (^{1}H) or 85% H_3PO_4 (^{31}P).

Synthesis of $[Ru_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (2). A solution of $[Ru_2(CO)_3(PBu^n_3)(\mu\text{-}H)(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)]$ (**1a**) (306 mg, 0.3 mmol) in DME (25 mL) was treated with a 0.4 M solution of $P{\equiv}CBu^t$ in hexane (0.5 mmol) and refluxed with stirring for 3 h. During this time the color of the solution changed from deep violet to orange brown. After cooling to room temperature the solvent was removed in vacuo and the remaining residue extracted three times with 10 mL portions of hexane. The combined extracts were reduced to 5 mL in vacuo and stored at −28 °C overnight to obtain **2** as yellow crystals (156 mg, 55% yield based on **1a**). Anal. Calcd for $C_{42}H_{50}O_4P_4Ru_2$: C, 53.39; H, 5.33. Found: C, 53.05; H, 4.97. IR (KBr, cm^{-1}): ν(CO) 1983s, 1965vs, 1924vs. ^{1}H NMR (THF-d_8): δ 8.02−6.77 (m, 20H, PC_6H_5), 4.27−3.80 (m, 2H, P-CH_2-P), 3.34 (d, 1H, $^2J_{PH} = 40.2$ Hz, P=C*H*), 1.67 (d, 9H, $^3J_{PH} =$ 13.6 Hz, PC_4H_9), 1.42 (d, 9H, $^3J_{P,H} = 13.0$ Hz, PC_4H_9), 0.57 (d, $^4J_{P,H} = 1.1$ Hz, P=C-*Bu^t*). ^{31}P{^{1}H} NMR (THF-d_8): δ 378.4 (ddd, $^2J_{P1,P2} = 95$ Hz, $^2J_{P1,P3} = 49$ Hz, $^2J_{P1,P4} = 56$ Hz, *P1*), 255.9 (ddd, $^2J_{P2,P1} = 95$ Hz, $^2J_{P2,P3} = 124$ Hz, $^2J_{P2,P4} = 134$ Hz, *P2*), 34.9 (ddd, $^2J_{P3,P1} = 49$ Hz, $^2J_{P3,P2} = 124$ Hz, $^2J_{P3,P4} = 79$ Hz, *P3*), 29.5 (ddd, $^2J_{P4,P1} = 56$ Hz, $^2J_{P4,P2} = 134$ Hz, $^2J_{P4,P3} = 79$ Hz, *P4*). EI MS: *m/z* (%) 946 (2.1) M$^+$, 918 (3.1) [M − CO]$^+$, 890 (36.8) [M − 2CO]$^+$.

X-ray Structure Determination and Details of Refinement. Crystals of **2** were obtained from hexane by cooling to −28 °C. X-ray data were collected on a Stoe IPDS diffractometer using graphite-monochromated Ag Kα radiation (λ = 0.56087 Å). Corrections for Lorentz and polarization effects, for crystal decay, and for absorption were applied. The structure was solved by direct methods using the program SHELXS-97.[16a] Structure solution by full-matrix least-squares refinement on F^2 was carried out with the program SHELXL-97[16b] with anisotropic displacement for non-hydrogen atoms. Hydrogen atoms were placed in idealized positions and refined isotropically according to the riding model. Residue electron density for H5 was found, for which the distance was fixed and freely refined. The methyl groups of the Bu^t substituent at C5 were found to be disordered over two different positions.

$[Ru_2(CO)_4(\mu\text{-}PBu^t_2)(\mu\text{-}dppm)\{\mu\text{-}PC(H)Bu^t\}]$ (2): $C_{42}H_{50}O_4P_4Ru_2$, $M = 944.84$, crystal dimensions 0.30 × 0.16 × 0.04 mm, monoclinic, space group $C2/c$, unit cell parameters a = 35.639(7) Å, b = 16.820(2) Å, c = 16.730(2) Å, β = 97.11(2)°, Z = 8, V = 9952(3) Å^3, T = 210(2) K, D_c = 1.261 mg m^{-3}, μ(Ag Kα) = 0.408 mm^{-1}, 25 753 independent reflections, θ range for data collection 1.66−20.00°, 9097 unique reflections (R_{int} = 0.0613), goodness-of-fit on F^2 = 1.055, R_1 = 0.0550, wR_2 = 0.1481 ($I > 2\sigma(I)$), R_1 = 0.0878, wR_2 = 0.1671 (all data).

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Supporting Information Available: Listings of atomic coordinates, H atom parameters, anisotropic temperature factors, and bond lengths and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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