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Note

Convenient access to an alkenyl(biscarbene)-bridged heterobinuclear (Ru–W) complex. X-ray structure of $[(\eta^6\text{-}C_6Me_4H_2)Ru{=}C(OMe)(CH{=}CHC_6H_4CH{=}CH{-}CO_2Me)\text{-}(Cl)(PMe_3)][PF_6]$

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Abstract

Treatment of $(CO)_5W{=}C(OMe){-}CH{=}CH{-}C_6H_4{-}(OH)(H)C{\equiv}CH$ (**2a**) with the neutral tetramethylbenzene ruthenium precursor $[(\eta^6\text{-}C_6Me_4H_2)Ru(Cl)_2(PMe_3)]$ (**3**), in the presence of one equivalent of $NaPF_6$ (CH_2Cl_2–MeOH) affords, after work-up, the monometallic ester compound $[(\eta^6\text{-}C_6Me_4H_2)Ru(Cl)(PMe_3)\{{=}C(OMe)CH{=}CH{-}C_6H_4{-}CH{=}CH{-}CO_2Me\}][PF_6]$ (**5a**), whereas, the expected bimetallic ruthenium–tungsten complex $[(\eta^6\text{-}C_6Me_4H_2)Ru(Cl)(PMe_3){=}C(OMe)CH{=}CH{-}C_6H_4{-}CH{=}CH{-}(NMe_2)C{=}W(CO)_5][PF_6]$ (**4b**) is formed starting from the aminocarbene derivative **2b**. Crystal structure analysis of **5a** has been determined.

Keywords: Ruthenium; Tungsten; Carbene complex; Bridging ligand

1. Introduction

Although, homobimetallic bis(carbene) complexes with unsaturated bridging spacers have received an increasing amount of attention during the last decade, examples of heterodinuclear complexes featuring π-conjugated-bridged bis(carbene) ligands remain relatively rare [1]. A bis(methoxycarbene) chromium–tungsten complex containing a 2,2′-bithienylene spacer has been obtained by the classical Fischer route [2]. The formation of a bis(aminocarbene) chromium–iron complex, has been achieved by reaction of an aryl bis-amide with $Cr(CO)_5^{2-}$ and $Fe(CO)_4^{2-}$ [3]. Heterobinuclear chromium–iron and chromium–nickel cyclobutenylidene complexes have been recently prepared by [2 + 2] cycloaddition of alkynyl complexes to vinylidene complexes [4]. We have previously shown that activation of 2-alkyn-1-ols by Group 6 and 8 metals opens a route to α,β-unsaturated carbene complexes [5–7]. With the use of dialkynol derivatives this procedure was more recently applied to the synthesis of a series of new dinuclear alkenyl-bridged carbene chromium(0) and tungsten(0) complexes [8]. With the goal of designing new 'push–pull' complexes, which could be of interest in non-linear optics [9], we thought to apply this methodology for the preparation of heterobimetallic bis(carbene) compounds with Groups 6 and 8 metals. Herein, we wish to report on the intermolecular coupling of a ruthenium–arene complex and methoxy- and aminocarbene-tungsten derivatives.

2. Results and discussion

In our first attempt to prepare heterobimetallic bis(alkenylcarbene)complexes, we explored the reaction between a methanol solution of the cationic (methoxy)-alkenylcarbene ruthenium(II) complex **1** (Scheme 1)

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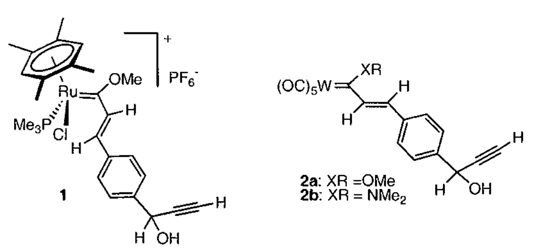
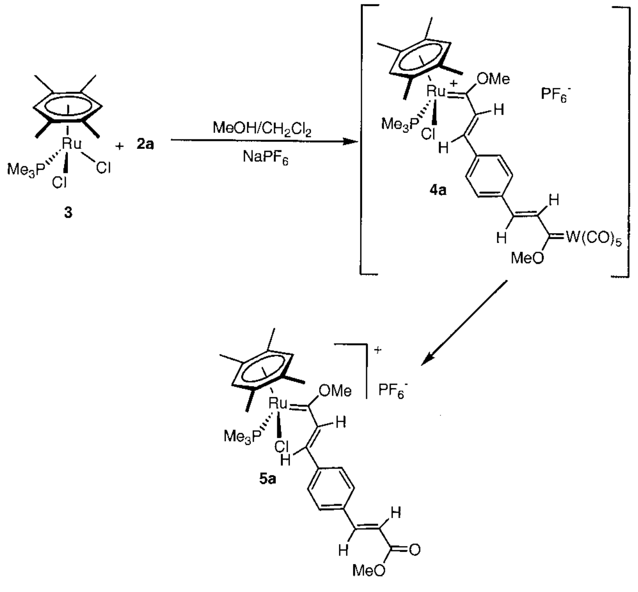


Scheme 1.



Scheme 2.

[10], containing a free propargyl alcohol substituent, and the photogenerated $W(CO)_5 \cdot THF$ adduct. However, the reaction gave a mixture of untractable cationic species including **1**.

An alternative approach consisted of, the treatment of (methoxy)alkenylcarbene tungsten(0) (**2a**) with the neutral tetramethylbenzene ruthenium precursor **3** in a methanol–dichloromethane solution, in the presence of one equivalent of $NaPF_6$ (Scheme 2). The reaction was very slow and afforded, after 24 h at room temperature, the monometallic compound **5a** in 47% yield, instead of the expected bimetallic ruthenium–tungsten complex **4a**. In contrast to the first attempt, this second way starting from neutral species allows a good separation of the reaction product by a simple crystallization in CH_2Cl_2–ether mixture. The carbene–ester complex **5a**, is suggested to be produced by rapid air oxidation of **4a** in solution during the process. Such transformation has already been observed in other binuclear bis(-methoxy)carbene complexes of Groups 6 and 7 metals [11–13]. Spectroscopic data (IR, ^{1}H-, ^{31}P- and ^{13}C-NMR) are in agreement with the proposed structure [14]. The ^{1}H-NMR spectrum exhibits two singlets for the two non-equivalent methoxy groups, and two AB systems for the alkenyl protons with $^{3}J_{HH}$ coupling constants of 15 and 16 Hz, which are indicative of *E* configurations. In the ^{13}C-NMR spectrum, we note in particular the presence of one low-field doublet at $\delta = 300.1$ ppm ($J_{CP} = 18.8$ Hz) for the carbene(ruthenium) resonance, whereas, the ester group gives rise to a characteristic signal at $\delta = 167.1$ ppm.

The structure of **5a** was confirmed by single X-ray crystallography (Fig. 1) [15]. The *trans* geometry of the two C–C double bonds is in agreement with the observed ^{3}J(H–H) coupling constant. The dienyl substituent of the carbene ligand adopts an *s-cis* conformation. This result is in agreement with the NOE studies previously performed on different α,β-unsaturated carbene-(arene)ruthenium complexes [5]. The second dienyl moiety adopts an *s-trans* conformation. The Ru–$C_{carbene}$ [1.973(4) Å] and C–O [1.342(5) Å] bond distances are comparable to that of the mononuclear complex $[(\eta^6\text{-}C_6Me_6)Ru(Cl)(PMe_3)\{C(OMe)CH{=}CPh_2\}]$ [1.98(1), 1.30(2) Å] [5,16]. The bond distances C(13)–C(12), C(12)–C(11) and C(10)–C(11) are indicative of alternate single and double C–C bonds. Moreover, the dihedral angle between the arene centroid-Ru–$C_{carbene}$ and O–$C_{carbene}$–Ru planes of 92.2° shows

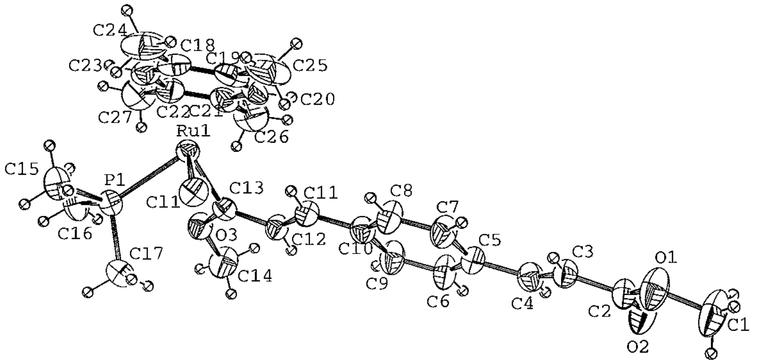
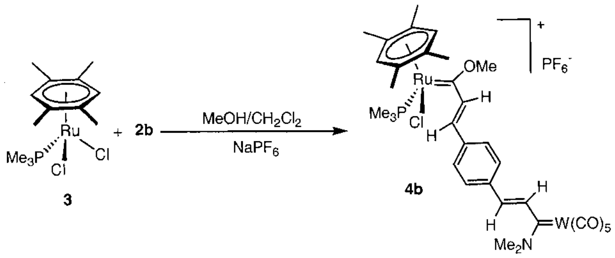


Fig. 1. Crystal structure of **5a**. Significant bond distances (Å) and angles (°). Ru–C(13) 1.973(4), Ru–Cl(1) 2.403(15), C(13)–C(12) 1.420(6), C(12)–C(11) 1.332(6), C(11)–C(10) 1.455(7), C(4)–C(5) 1.458(6), C(3)–C(4) 1.302(6), C(2)–C(3) 1.469(6), C(13)–O(3) 1.342(5), C(2)–O(2) 1.195(5); C(13)–Ru–Cl(1) 94.89(12), C(11)–C(12)–C(13) 123.3(4), C(3)–C(4)–C(5) 129.7(5), C(10)–C(11)–C(12) 127.2(4), C(2)–C(3)–C(4) 121.3(5), O(2)–C(2)–C(3) 124.6(4).



Scheme 3.

that the carbene ligand is parallel to the plane of the $C_6Me_4H_2$ ring [17]. This contrasts with the generally observed 'upright conformation' of half-sandwich CpRu or TpRu derivatives [16].

In order to isolate the target heterobimetallic (Ru–W) complex we sought to use the (dimethylamino)alkenylcarbene tungsten complex **2b**, which is more stable than the corresponding (methoxy)carbene complex **2a** due to the better stabilizing effect of the amino substituent. In a procedure, analogous to that employed for **5a**, the stable black bimetallic complex **4b** was obtained in 60% (Scheme 3). The structure of **4b** could easily be inferred from spectroscopic data [18]. The presence of the $W(CO)_5$ moiety is evidenced in IR by the typical A_1 (*trans*) and E ν(CO) absorptions. The resonance signals for the two carbene carbon atoms in the ^{13}C-NMR spectrum ($\delta_{Ru=C} = 298.6$; $\delta_{W=C} = 250.1$) compare well with those usually observed for (methoxy)carbene and (amino)carbene complexes, respectively. This unsymmetrical alkenyl-bridged complex also exhibits two distinct sets of proton and carbon resonances for the α,β- and α',β'-alkenyl protons and carbons, respectively. This preliminary result represents a new entry to bridged bis(carbene) heterodinuclear complexes, and could be extended to other organometallic fragments capable of activating propargyl alcohol derivatives. This opens an access to π-conjugated 'push–pull' molecules featuring donor and acceptor organometallic end groups.

3. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 165697 for compound **5a**. Copies of this information can be obtained free of charge from The Director CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[14] Selected data for **5a**: IR (CH_2Cl_2) ν(CO) 1751 cm^{-1}. ^{1}H-NMR (CD_2Cl_2) δ 8.54 (d, $J_{HH} = 15.0$ Hz, 1H, C*H*=), 7.82 (d, 2H, $J_{HH} = 8.4$ Hz, C_6H_4–), 7.67 (d, $J_{HH} = 16.0$ Hz, 1H, C*H*=), 7.66 (d, $J_{HH} = 8.4$ Hz, 2H, C_6H_4–), 7.42 (d, $J_{HH} = 15.0$ Hz, 1H, C*H*=), 6.57 (d, $J_{HH} = 16.0$ Hz, 1H, C*H*=), 5.80 (s, 2H, $C_6H_2Me_4$), 4.47 (s, 3H, O*Me*), 3.77 (s, 3H, O*Me*), 2.05 (s, 6H, $C_6H_2Me_4$), 1.89 (s, 6H, $C_6H_2Me_4$), 1.48 (d, $J_{PH} = 10.9$ Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H}-NMR (CD_2Cl_2) δ 300.1 (d, $J_{PC} = 18.8$ Hz, Ru=*C*), 167.1 (s, *C*O$_2$Me), 143.2 (s, *C*H=), 139.7, 136.2, 131.2 (s, C_6H_4–), 129.5 (s, *C*H=), 128.0 (s, C_6H_4–), 121.2 (s, *C*H=), 107.7, 106.0, 99.0 (s, $C_6H_2Me_4$), 65.4 (s, O*Me*), 51.7 (s, O*Me*), 17.1 (s, $C_6H_2Me_4$), 17.0 (d, $J_{PC} = 28$ Hz, P*Me*$_3$). ^{31}P-NMR (CD_2Cl_2) 13.9 (s, *P*Me$_3$). HMRS (FAB$^+$) Calc. for $C_{27}H_{37}ClF_6O_3P_2Ru$ [M–PF$_6$]$^+$: 577.1213. Found: 577.1217.

[15] Crystal data for **5a**: $C_{28}H_{39}Cl_3F_6O_3P_2Ru$, $M = 806.95$ monoclinic space group $P2_1/c$, $a = 12.652(5)$, $b = 9.127(5)$, $c = 31.005(5)$ Å, $\beta = 91.758(5)°$, $V = 3579(2)$ Å^{-3}, $Z = 4$, $\rho_{calcd} = 1.498$ g cm^{-3}, CAD4 NONIUS diffractomer, Mo–K$_\alpha$, refinement method: full-matrix least-squares on F^2, $F(000) = 1640$, $T = 293$ K, 8404 reflections, 4684 with $I > 2\sigma(I)$ observed, $R = 0.1228$, $R_w = 0.1775$ (residual $\Delta\rho < 0.53$ eÅ^{-3}).

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(c) M.A.J. Tenorio, M.J. Tenorio, M.C. Puerta, P. Valerga, Organometallics 16 (1997) 5528.

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[18] Selected data for **4b**: IR (CH_2Cl_2) ν(CO) 2061 (m), 1925 (s) cm^{-1}. UV–vis (CH_2Cl_2) λ_{max} 435, 360 nm. ^{1}H-NMR (CD_2Cl_2) δ 8.58 (d, $J_{HH} = 14.8$ Hz, 1H, C*H*=), 7.80 (d, 2H, $J_{HH} = 8.2$ Hz, C_6H_4–), 7.55 (d, $J_{HH} = 8.2$ Hz, 2H, C_6H_4–), 7.40 (d, $J_{HH} = 14.8$ Hz, 1H, C*H*=), 7.22 (d, $J_{HH} = 16.6$ Hz, 1H, C*H*=), 5.92 (d, $J_{HH} = 16.6$ Hz, 1H, C*H*=), 5.77 (s, 2H, $C_6H_2Me_4$), 4.44 (s, 3H, O*Me*), 3.82 (s, 3H, N*Me*$_2$), 3.40 (s, 3H, N*Me*$_2$), 2.05 (s, 6H, $C_6H_2Me_4$), 1.89 (s, 6H, $C_6H_2Me_4$), 1.48 (d, $J_{PH} = 10.9$ Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H}-NMR (CD_2Cl_2) δ 298.6 (d, $J_{PC} = 18.8$ Hz, Ru=*C*), 250.1 (s, W=*C*), 204.0 (s, *C*O), 199.0 (s, *C*O), 168.1 (s, *C*H=), 142.2 (s, C_6H_4–), 141.3 (s, *C*H=), 134.3, 131.5 (s, C_6H_4–), 128.3 (s, *C*H=), 128.0 (s, C_6H_4–), 121.4 (s, *C*H=), 107.7, 106.0, 99.0 (s, $C_6H_2Me_4$), 66.1 (s, O*Me*), 54.4 (s, N*Me*), 45.2 (s, N*Me*), 17.1 (s, $C_6H_2Me_4$), 17.0 (d, $J_{PC} = 28$ Hz, P*Me*$_3$). ^{31}P-NMR (CD_2Cl_2) 19.5 (s, *P*Me$_3$). HMRS (FAB$^+$) Calc. for $C_{33}H_{40}ClF_6NO_6P_2Ru^{184}W$ [M–PF$_6$]$^+$: 898.0852. Found: 898.0840.