Synthesis of a bimetallic platinum–tungsten complex with a bridging μ-diboranyl–oxycarbyne moiety†‡

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The novel bimetallic μ-diboranyl–oxycarbyne bridged platinum–tungsten complex [W{η^1,μ-CO-B(NMe_2)-B(NMe_2)-(η^5-C_5H_4)}$(CO)_2${Pt$(PPh_3)_2$}] (*W–Pt*) (3) has been synthesised by a two-step reaction, starting from the dilithiated half-sandwich compound Li[W(η^5-C_5H_4Li)$(CO)_3$] (1) *via* the *ansa*-diboranyl–oxycarbyne tungsten complex [W{η^1-CO-B(NMe_2)B(NMe_2)(η^5-C_5H_4)}$(OC)_2$] (2) by use of stoichiometric amounts of $B_2(NMe_2)_2Br_2$ and [Pt(η^2-C_2H_4)$(PPh_3)_2$], respectively.

Since 1980, Stone and co-workers proved that metal–carbon triple bonds can be complexed by zero-valent platinum, thus synthesising *e.g.* the bimetallic platinum–tungsten species [W(μ-C-C_6H_4Me-*p*)-(η^5-C_5H_5)$(CO)_2${Pt$(PR_3)_2$}] (*W–Pt*) (R_3 = Me_2Ph, Me_3) with a μ-bridging carbyne ligand (Fig. 1).[1]

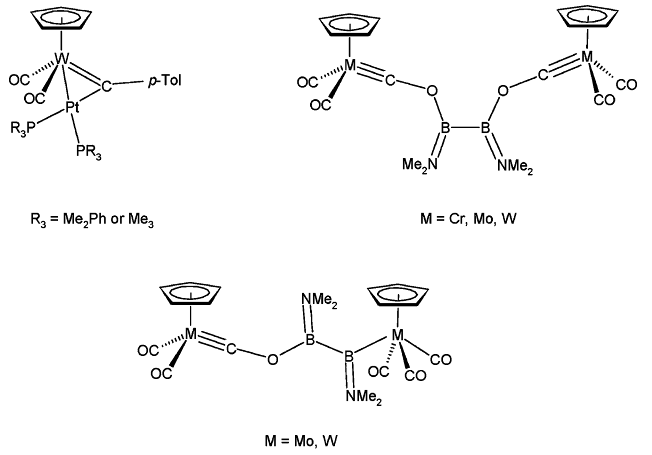


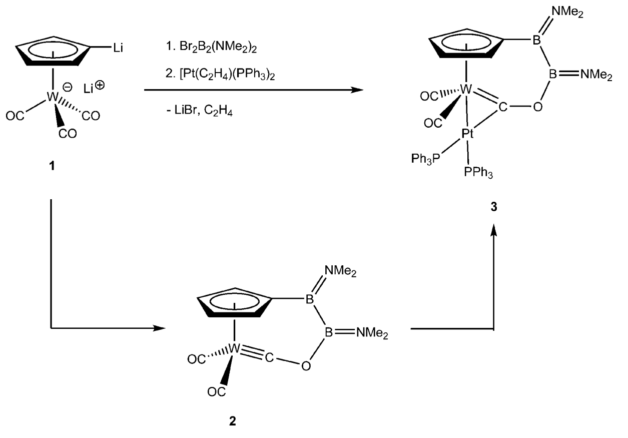
Fig. 1 Complexes specifically mentioned in the introductory paragraph.

Recently, we obtained a series of novel oxycarbyne complexes, namely [{(η^5-C_5H_5)$(OC)_2$M≡CO}$_2$-$B_2(NMe_2)_2$] (M = Cr, Mo, W), from reaction of the diborane(4) $B_2(NMe_2)_2I_2$ with Group 6 metal carbonylates. The Mo and W complexes underwent a quantitative rearrangement to give the thermodynamically favoured complexes [{(η^5-C_5H_5)$(OC)_2$M≡CO}-B(NMe_2)B(NMe_2)-{M$(CO)_3$(η^5-C_5H_5)] (M = Mo, W), characterized by one metal–boron linkage (Fig. 1).[2]

Over the course of our studies on diborane(4)yl complexes of tungsten, we now have succeeded in combining these two topics, thus revealing a new reactivity pattern of the boryl–oxycarbyne triple bond.

In this communication we report the synthesis of the first half-sandwich *ansa*-complex bearing a diboranyl–oxycarbyne bridge between the cyclopentadienyl ligand and the tungsten centre (**2**) and its stabilisation by complexation to a Pt^0 centre to yield the bimetallic *ansa*-platinum–tungsten complex **3**.§ Furthermore, a single-crystal X-ray diffraction study was carried out to establish unequivocally the structure of **3** in the solid state.¶

Reaction of the lithiated tungsten complex Li[W(C_5H_4Li)$(CO)_3$] (**1**) with one equivalent of $B_2(NMe_2)_2Br_2$ in benzene at room temperature leads to the generation of **2** by alkali salt elimination, according to Scheme 1. However, the poor thermal stability of this strained *ansa*-compound prevents its work-up and isolation as well as obtaining satisfactory ^{13}C NMR data. A crucial characteristic feature in the ^{1}H NMR spectrum of **2** is the splitting of the cyclopentadienyl resonances into four sets of multiplets (δ = 5.91, 5.63, 5.47 and 5.40 ppm), indicating C_1 symmetry in solution. Such geometry would appear to arise from the existence of a $B_2(NMe_2)_2$ *ansa*-bridge and torsion of the $N(Me_2)_2$ fragments, thus imposing slow equilibration with respect to the NMR time scale. A corresponding spectroscopic phenomenon was already observed in our group in context with boron-bridged constrained geometry complexes of titanium, namely for [Ti{η^1-NPh-(BNSiMe$_3$)(η^5-C_5H_4)Cl_2].[3] Owing to chemical inequivalence and hindered



Scheme 1 Synthesis of the μ-diboranyl–oxycarbyne bridged platinum—tungsten complex **3**, *via* the strained *ansa*-diboranyl–oxycarbyne tungsten complex **2**.

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rotation, four resonances are detected for the aminomethyl groups in the ^{1}H NMR spectrum (δ = 3.07, 3.00, 2.80 and 2.73 ppm). Spectroscopic proof for the formation of the highly unusual C–O–B–B *ansa*-bridge with nucleophilic attack of the carbonyl oxygen atom at boron[2] is provided by the ^{11}B NMR resonances at 44.3 and 35.7 ppm. The former resonance is indicative of metallocenophanes with bis(dimethylamino)diborane bridges (*e.g.* [Fe{(η^5-C_5H_4)$_2$($BNMe_2$)$_2$}], δ = 44.4 ppm),[4] while the latter falls in the typical range of boryloxycarbyne complexes (*e.g.* [{(η^5-C_5H_5)(OC)$_2$W≡CO}$_2$-$B_2(NMe_2)_2$], δ = 30.8 ppm),[2] thus indicating the presence of a B–O bond.

The formation of a metal–boron bond, which is usually observed for the reaction of anionic half-sandwich complexes with $B_2(NMe_2)_2Hal_2$ (Hal = Cl, Br), would result in a characteristically deshielded signal at $\delta_B > 60$.[2,5] The preference of B–O over W–B bond formation observed here, may be ascribed either to an enhanced nucleophilicity of the anionic (OC)$_3$W fragment as a result of the attachment of the diborane moiety to the Cp ligand or is just the result of a better accessibility of the linear W–CO unit. In any case, attempts to convert **2** into a possibly thermodynamically favoured compound bearing a W–B bond failed and led to decomposition.

When treated consecutively with $B_2(NMe_2)_2Br_2$ and [Pt(η^2-C_2H_4)(PPh_3)$_2$] in benzene at room temperature, respectively, **1** converts to the novel bimetallic μ-diboranyl–oxycarbyne bridged platinum–tungsten complex [W{η^1,μ-CO-B(NMe_2)-B(NMe_2)-(η^5-C_5H_4)}(CO)$_2${Pt(PPh_3)$_2$}] (*W–Pt*) (**3**) (Fig. 2). After work-up, **3** was obtained as a yellow powder in 35% yield. The complexation of the Pt(PPh_3)$_2$ moiety leads to a release of the molecular strain due to change of the hybridisation of the carbyne C atom from sp to sp^2, and hence, an increased thermal stability compared to its precursor **2** may be assumed for the *ansa*-complex **3**, thus allowing its facile isolation. Moreover, **3** can be stored under Ar atmosphere at +5 °C for several months without decomposition. The NMR spectroscopic data are in full agreement with the formation of a C_1-symmetric compound. As already observed for **2**, the ^{1}H NMR spectrum of **3** shows four multiplets (δ = 5.41, 5.37, 5.11 and 4.89 ppm). Consequently, four singlets were detected for the aminomethyl groups (δ = 2.75, 2.62, 2.34 and 1.74 ppm). The complexation of the platinum fragment to the W≡C triple bond does not lead to any significant shift of the ^{11}B NMR resonances which are found at δ = 43.41 (BC) and 34.77 (BO) ppm. The ^{31}P NMR spectrum exhibits two singlets at δ = 41.51 and 31.61 ppm which are flanked by characteristic ^{31}P–^{195}Pt satellites with coupling constants of $^1J_{Pt-P}$ = 4293 and $^1J_{Pt-P}$ = 2825 Hz, respectively. The two PPh_3 ligands in **3** are thus non-equivalent, and the small value of $^1J_{Pt-P}$ (2825 Hz) is characteristic for a *cis*-Pt(PPh_3)$_2$ arrangement and the larger ^{195}Pt–^{31}P coupling associated with the resonance at 41.51 ppm can be assigned to the phosphine ligand *trans* to the Pt–W bond.[1,6] **3** displays carbonyl stretching bands in the IR spectrum at 1939 and 1920 cm^{-1} which are blue-shifted when compared with [W(μ-C-C_6H_4Me-*p*)-(η^5-C_5H_5)(CO)$_2${Pt(PMe_2Ph)$_2$}] (*W–Pt*) (1898 and 1818 cm^{-1}).

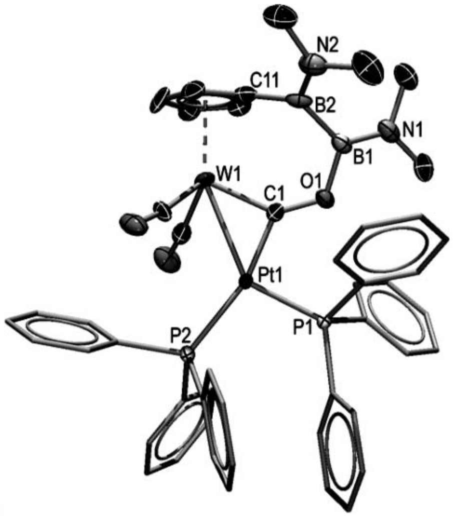

Fig. 2 View of the molecular structure of [W{η^1,μ-CO-B(NMe_2)-B(NMe_2)-(η^5-C_5H_4)}(CO)$_2${Pt(PPh_3)$_2$}] (*W–Pt*) (**3**) with the atom labelling scheme. Ellipsoids are drawn at the 50% probability level, and the hydrogen atoms have been omitted. Selected bond lengths [Å], angles [°]: W1–Pt1 2.7718(9), W1–C1 1.98(1), Pt1–C1 1.99(1), Pt1–P1 2.2540(18), Pt1–P2 2.3361(18), C1–O1 1.337(10), O1–B1, 1.432(12), B1–B2 1.702(17); C11–B2–B1 115.3(8), O1–B1–B2 117.2(8), W1–Pt1–C1 45.4(4) and P1–Pt1–P2 103.22(6).

Boron–boron bonds are prone to undergo facile oxidative addition towards a variety of low-valent transition metal complexes[7] with concomitant formation of bis(boryl)–metal complexes [$L_xM(BR_2)_2$],[8] thus effectively enabling the transition-metal-catalysed diboration of alkenes, alkynes and 1,3-dienes.[7] Interestingly, the reaction of complex **2** which is characterised by two reactive centres (B–B and W≡C) with [Pt(η^2-C_2H_4)(PPh_3)$_2$] leads to complexation of the Pt^0 centre to the W≡C triple bond rather than oxidative addition of the B–B bond. This result may be ascribed to the decreased steric demand of the environment at the carbyne unit in comparison to the boron–boron bond.

The constitution of **3** was confirmed by single crystal X-ray diffraction. Suitable crystals were grown from slow evaporation of a saturated solution of **3** in d$_6$-benzene at ambient temperature. The result of this analysis is depicted in Fig. 2. The complex crystallises in the monoclinic space group $P2_1/n$. The entire C–O–B–B *ansa*-bridge is disordered and its metric parameters have to be regarded carefully (see CIF for further details).

An important structural element of **3** is the C–O–B–B *ansa*-bridge, which imposes moderate molecular ring strain, which is best reflected by the C–B–B [C11–B2–B1 115.3(8)°] and the B–B–O [O1–B1–B2 117.2(8)°] angles that are slightly smaller than expected for an ideally sp^2-hybridised boron atom. The boron–boron bond itself [B1–B2 1.702(17) Å] is neither affected by ring formation nor by Pt^0 complexation and is almost identical to that found in [(η^5-C_5H_5)(OC)$_3$W-{B(NMe_2)-B(NMe_2)Cl}] [1.690(1) Å][5a] or [{(η^5-C_5H_5)(OC)$_2$Mo≡CO}-B(NMe_2)B(NMe_2)-{Mo(CO)$_3$(η^5-C_5H_5)] [1.704(6) Å].[2b] Another characteristic structural feature is the three-membered ring consisting of tungsten, carbon and platinum, showing parameters [W1–Pt1 2.7748(4), W1–C1 1.98(1) or Pt1–C1 1.99(1) Å] very similar to those of [W(μ-C-C_6H_4Me-*p*)-(η^5-C_5H_5)(CO)$_2${Pt(PMe_2Ph)$_2$}] (*W–Pt*).[1] The W–C1 distance is significantly longer (est. 0.16 Å) than the M–C(carbyne) separations in [W(≡CC_6H_4Me-*p*)(CO)$_2$(η^5-C_5H_5)] and [{(η^5-C_5H_5)(OC)$_2$Mo≡CO}-B(NMe_2)B(NMe_2)-{Mo(CO)$_3$(η^5-C_5H_5)] [1.82(2)[9] and 1.825(4) Å], respectively, and hence, can be classified as a W=C double bond interaction, although delocalisation within the W–C–Pt three-membered ring is probable, too.[1] Notable pertinent metric parameters around the platinum centre, which displays a distorted square-planar environment, include the Pt–W [Pt1–W1 2.7718(9) Å], the Pt–C [Pt1–C1 1.99(1) Å] bond lengths, the Pt–P distances [Pt1–P1 2.2540(18), Pt1–P2 2.3361(18) Å], the W–Pt–C angle [45.4(4)°], and the P–Pt–P bond angle [103.22(6)°] all of which lie within previously reported ranges.[1,10] The carbon–oxygen and oxygen–boron distances of 1.337(10) and 1.432(12) Å resemble those in $[\{(\eta^5\text{-}C_5H_5)(OC)_2Mo{\equiv}CO\}\text{-}B(NMe_2)\text{-}B(NMe_2)\{Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ and suggest that the bonding situation should be described in terms of a carbonyl–oxygen double and a oxygen–boron single bond.

Notes and references

§ All manipulations were conducted either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glove box techniques. Solvents (benzene and pentane) were purified by distillation from appropriate drying agents (sodium and sodium wire) under dry argon, immediately prior to use. C_6D_6 was degassed by three freeze–pump–thaw cycles and stored over molecular sieves. IR spectra were recorded as solutions between KBr plates on a Bruker Vector 22 FT-IR-spectrometer. NMR spectra were recorded on either a Bruker 200 Avance spectrometer at 200.1 (^{1}H, internal standard TMS) and 64.2 MHz (^{11}B, $BF_3{\cdot}OEt_2$ in C_6D_6 as external standard), a Bruker 400 Avance spectrometer at 400.13 (^{1}H, internal standard TMS) and 100.61 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS) or a Bruker Avance 500 at 500.13 MHz (^{1}H, internal standard TMS), 125.77 MHz ($^{13}C\{^1H\}$, APT, internal standard TMS) and 160.46 MHz (^{11}B, $BF_3{\cdot}OEt_2$ as external standard). Elemental analyses (C, H, N) were obtained from a Vario Micro (Elementar Analysensysteme). Starting materials were prepared according to literature procedures: $Li[W(\eta^5\text{-}C_5H_4Li)(CO)_3]$ (**1**), [11] $B_2(NMe_2)_2Br_2$[12] and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$.[13] $[W\{\eta^1\text{-}CO\text{-}B(NMe_2)\text{-}B(NMe_2)\text{-}(\eta^5\text{-}C_5H_4)\}(CO)_2]$ (**2**): A suspension of 0.52 g (0.82 mmol) of $Li[W(\eta^5\text{-}LiC_5H_4)(CO)_3]$ (**1**) in 5 mL benzene was treated with 0.84 mL (0.22 g, 0.82 mmol, 0.97 M solution in toluene) of $B_2(NMe_2)_2Br_2$ at ambient temperature. The solvent was removed *in vacuo* and the residue was extracted with C_6D_6 for NMR spectroscopy. Further isolation was not possible due to poor stability of the product. ^{1}H NMR (200.0 MHz, C_6D_6): δ = 5.91 (m, 1 H, C_5H_4), 5.63 (m, 1 H, C_5H_4), 5.47 (m, 1 H, C_5H_4), 5.40 (m, 1 H, C_5H_4), 3.07 (s, 3 H, Me), 3.00 (s, 3 H, Me), 2.80 (s, 3 H, Me), 2.73 (s, 3 H, Me) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): δ = 44.32 (br, B–C), 35.7 (br, B–O) ppm. $[W\{\eta^1,\mu\text{-}CO\text{-}B(NMe_2)\text{-}B(NMe_2)\text{-}(\eta^5\text{-}C_5H_4)\}(CO)_2\{Pt(PPh_3)_2\}]$ (*W–Pt*) (**3**): Similar to above, 350 mg (0.55 mmol) of $Li[W(\eta^5\text{-}LiC_5H_4)(CO)_3]$ (**1**) in 10 mL benzene and 570 µL (148 mg, 0.55 mmol, 0.97 M solution in toluene) of $B_2(NMe_2)_2Br_2$ were added at ambient temperature. After 5 min of stirring 412 mg (0.55 mmol) $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ were added and the mixture was stirred for another 2 h. The benzene was removed under reduced pressure and the brown residue was dried *in vacuo* thoroughly. After extraction with cyclohexane (6 × 15 mL) the combined extracts were filtered through Celite and the solvent was removed under reduced pressure. The residue was washed with cyclohexane (1 × 3 mL), pentane (3 × 5 mL) and finally dried *in vacuo*. Yield 224 mg (0.19 mol, 35%). Yellow powder. ^{1}H NMR (500.0 MHz, C_6D_6): δ = 7.90–6.80 (m, 30 H, Ph), 5.41 (m, 1 H, C_5H_4), 5.37 (m, 1 H, C_5H_4), 5.11 (m, 1 H, C_5H_4), 4.89 (m, 1 H, C_5H_4), 2.75 (s, 3 H, Me), 2.62 (s, 3 H, Me), 2.34 (s, 3 H, Me), 1.74 (s, 3 H, Me) ppm. $^{11}B\{^1H\}$ NMR (160.5 MHz, C_6D_6): δ = 43.41 (br, BC), 34.77 (br, BO) ppm. $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$): δ = 216.40 (s, CO), 216.30 (s, CO), 134.42–127.53 (m, Ph), 101.76 (s, C_5H_4), 100.72 (s, C_5H_4), 96.28 (s, C_5H_4), 94.77 (s, C_5H_4), 45.01 (s, Me), 42.19 (s, Me), 40.45 (s, Me), 37.49 (s, Me) ppm. $^{31}P\{^1H\}$ NMR (202.5 MHz, C_6D_6): $\delta = 41.51$ [d, $^2J_{P\text{–}P} = 33.2$ Hz, $^1J_{Pt\text{–}P} = 4293$ Hz, PPh_3], 31.61 [d, $^2J_{P\text{–}P} = 33.2$ Hz, $^1J_{Pt\text{–}P} = 2825$ Hz, PPh_3] ppm. IR (hexane) $\nu(C{=}O) = 1939$ (vs), 1920 (vs) cm^{-1}.

¶ The crystal data of **3** were collected on a Bruker X8APEX diffractometer with CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using direct methods, refined with SHELX software package[14] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealised positions and were included in structure factors calculations. $C_{48}H_{46}B_2N_2O_3P_2PtW$, $M_r = 1161.37$, orange block, 0.18 × 0.10 × 0.09 mm, monoclinic, space group $P2_1/n$, $a = 10.4940(2)$ Å, $b = 24.5737(6)$ Å, $c = 17.0162(4)$ Å, $\beta = 93.4940(10)°$, $V = 4379.92(17)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.761$ g cm^{-3}, $\mu = 5.932$ mm^{-1}, $F(000) = 2256$, $T = 100(2)$ K, $R_1 = 0.0523$, $wR^2 = 0.1114$, $R_{int} = 0.058$, 8742 independent reflections [$2\theta \leq 52.46$] and 586 parameters.

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