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COMMUNICATION

C–X bond formation and cleavage in the reactions of the ditungsten hydride complex $[W_2(\eta^5-C_5H_5)_2(H)(\mu-PCy_2)(CO)_2]$ with small molecules having multiple C–X bonds (X = C, N, O)[†]

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Two molecules of $C_2(CO_2Me)_2$ or isocyanides could be added to the title hydride complex under mild conditions to give dienyl- $[W_2Cp_2\{\mu-\eta^1,\kappa;\eta^2-C(CO_2Me)=$ $C(CO_2Me)C(CO_2Me)=CH(CO_2Me)\}(\mu-PCy_2)(CO)_2]$ (Cp = $\eta^5-C_5H_5$), diazadienyl- $[W_2Cp_2\{\mu-\kappa,\eta;\kappa,\eta-C\{CHN(4-MeO-C_6H_4)\}N(4-MeO-C_6H_4)\}(\mu-PCy_2)(CO)_2]$ or aminocarbynebridged derivatives $[W_2Cp_2\{\mu-CNH(2,6-Me_2C_6H_3)\}(\mu-PCy_2)\{CN(2,6-Me_2C_6H_3)\}(CO)]$. In contrast, its reaction with excess (4-Me-C_6H_4)C(O)H gave the C-O bond cleavage products $[W_2Cp_2\{CH_2(4-Me-C_6H_4)\}(O)(\mu-PCy_2)(CO)_2]$ and $[W_2Cp_2\{\mu-\eta;\eta,\kappa-C(O)CH_2(4-Me-C_6H_4)\}(O)(\mu-PCy_2)(CO)]$.

Recently we reported the preparation of the unsaturated ditungsten hydride $[W_2Cp_2(H)(\mu-PCy_2)(CO)_2](1)$,¹ a new member of the scarce family of 30-electron binuclear complexes having bridging hydride ligands, a circumstance providing these electron-deficient molecules with a high reactivity towards many different reagents under mild conditions, and hence with a substantial synthetic potential, as illustrated by the wide chemistry developed around the polyhydrides $[M_2Cp^*_2(\mu-H)_4]$ (M = Fe, Ru),² and $[M_2(\eta^6-C_6Me_6)_2(\mu-H)_3]^+$ (M = Ru, Os),³ and the molybdenum analogue of 1, the monohydride $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$ (2).⁴ Unlike the latter species, which displays solely an H-bridged structure,^{4a,f} the ditungsten complex 1 exists in solution as a mixture of two isomers in equilibrium (Chart 1): the expected one with a bridging hydride ligand (**B**, major isomer) and a second one having a terminal



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hydride and a semi-bridging carbonyl (**T**, minor isomer).¹ It was thus thought that, in addition to the differences originated from the change in the metal (W instead of Mo), the presence of the isomer **T** in the solutions of **1** might imply a significant modification in the reactivity of this ditungsten complex, compared to the behaviour observed for $[Mo_2Cp_2(\mu-H)(\mu-PCy_2)(CO)_2]$. We thus initiated a systematic study on the reactivity of **1** aimed at examining these differences. In this paper we report our preliminary studies on the reactions of **1** with different unsaturated organic molecules such as alkynes, isocyanides and aldehydes (Scheme 1). From this we conclude that the reactivity of the ditungsten complex indeed exhibits features unparalleled by its dimolybdenum analogue, notably its ability to incorporate two, rather than one, molecules of reagent, then promoting C–C coupling processes at room



Scheme 1 Reactions of complex 1 with small unsaturated molecules ($R^1 = CO_2Me$: $R^2 = 2,6-Me_2C_6H_3$; $R^3 = 4-MeO-C_6H_4$; $R^4 = 4-Me-C_6H_4$).

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temperature, and its unusual ability to cleave the C–O bond of an aldehyde under moderate thermal activation.

Compound 1 is able to add two molecules of alkyne under the right conditions, a circumstance not met by its molybdenum analogue 2.4e For instance, the reaction with excess dimethyl acetylenedicarboxylate at 273 K gives a mixture of the alkenyl complex cis-[W₂Cp₂{ μ - η ¹: η ²-C(CO₂Me)=CH(CO₂Me)}(μ - $PCy_2(CO)_2$ (3), and the 1,3-dienvl derivative $[W_2Cp_2\{\mu$ - $\eta^1, \kappa; \eta^2 - C(CO_2Me) = C(CO_2Me)C(CO_2Me) = CH(CO_2Me) \{\mu - \mu^2, \kappa; \eta^2 - C(CO_2Me)\} = CH(CO_2Me) \}$ $PCy_2)(CO)_2$ (4) (Scheme 1). Spectroscopic data for 3 (see the ESI[†]) indicate a cisoid arrangement of the carbonyl ligands and are not very different from those of *cis*-[Mo₂Cp₂{ μ - η^1 , κ : η^2 - $C(CO_2Me) = CH(CO_2Me) \{(\mu - PCy_2)(CO)_2\}, a minor isomer$ formed in the reactions of the dimolybdenum hydride 2 with $C_2(CO_2Me)_2$ and exhibiting coordination of the O atom of a carboxylate group to one of the Mo atoms, as determined crystallographically.4e However, the relatively high value of the ³¹P-¹⁸³W couplings in 3 (av. 303 Hz) are characteristic of coordinatively unsaturated complexes, so we trust that the alkenyl ligand in this complex is exclusively bound to the ditungsten centre via the C atoms.

The spectroscopic data for **4** clearly establish the presence of two $C_2(CO_2Me)_2$ units in this complex, and the migration of the former hydride ligand to one of the C atoms of the added alkyne. An X-ray analysis of this compound confirmed the presence of a dienyl chain σ -bound to one of the W atoms through the alkenyl carbon (W1–C3 = 2.17(1) Å) and one of the carboxylate groups (W1–O7 = 2.24(1) Å), while π -bound to the other W atom through the second double C=C bond (W–C lengths *ca.* 2.25 Å) (Fig. 1).‡



Fig. 1 ORTEP drawing (30% probability) of compound 4, with H atoms (except H12) and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): W1–W2 = 3.0273(6), W1–P1 = 2.433(3), W1–C1 = 1.99(1), W1–C3 = 2.17(1), W1–O7 = 2.24(1), W2–P1 = 2.475(3), W2–C2 = 1.94(1), W2–C9 = 2.24(1), W2–C12 = 2.26(1), C3–C6 = 1.35(1), C6–C9 = 1.50(1), C9–C12 = 1.44(1), C9–C10 = 1.46(1), C10–O7 = 1.24(1); W2–W1–C1 = 73.2(3), W1–W2–C2 = 118.4(3).

The formation of **4** can be viewed as resulting from the insertion of a $C_2(CO_2Me)_2$ molecule into the W–C σ -bond in an alkenyl intermediate following from the insertion of the first $C_2(CO_2Me)_2$ molecule into the W–H bond of the hydride **1**. A separate experiment, however, revealed that the alkenyl complex **3** is not such an intermediate. Although the reactions of complexes having unsaturated $M_2(\mu-H)_x$ centres with alkynes typically give

alkenyl products,^{2,4e,5,6} apparently none of these previous reactions involved an alkenyl–alkyne coupling as observed in the formation of **4**, and further studies on the reactivity of **1** towards different alkynes are now under way. We note, however, that the dihydride $[Os_3(\mu-H)_2(CO)_{10}]$ has been shown to induce alkyne–alkyne coupling of C_2Ph_2 and C_2H_2 ,^{5,7} and that a comparable C–C coupling has been previously observed in the reactions of anionic diiron alkenyl complexes of the type $[Fe_2(\mu-\eta^1:\eta^2-CRCHR')(CO)_6]^-$ with alkynes.⁸

The reactivity of the hydride 1 towards isocyanides CNR was found to be strongly dependent both on the nature of R and on the experimental conditions, and it again involved products which cannot be afforded using the molybdenum hydride 2. For instance, the reaction of 1 with excess $CN(4-MeO-C_6H_4)$ at room temperature gives, with good yield, the C-C coupled diazadienyl complex $[W_2Cp_2\{\mu-\kappa,\eta:\kappa,\eta-C\{CHN(4-MeO-C_6H_4)\}N(4-MeO-C_6H_4)\}$ C_6H_4 (μ -PCy₂)(CO)₂ (5), whereas the analogous reaction with $CN(2,6-Me_2C_6H_3)$ gives the aminocarbyne-isocyanide derivative $[W_2Cp_2\{\mu$ -CNH(2,6-Me_2C_6H_3)\}(\mu-PCy₂){CN(2,6- $Me_2C_6H_3$ (CO)] (6). Spectroscopic and microanalytical data for 5 (see the ESI[†]) confirmed the incorporation of two isocyanide molecules into the complex and the migration of the former hydride ligand to a carbon atom, but otherwise are comparable $CHNR)(\mu$ -PCy₂)(CO)₂] formed in the reactions of **2** with CNR $(R = {}^{t}Bu, 4-Me-C_{6}H_{4}).{}^{4a,d}$ Moreover, the low ${}^{31}P-{}^{183}W$ couplings in 5 (av. 193 Hz) are fully consistent with the proposed μ - κ , η : κ , η coordination of the diazadienvl ligand, this leading to the full saturation of the dimetal centre.

The spectroscopic data for **6** denoted the presence of two isomers in solution, and were for both clearly indicative of the incorporation of two molecules of isocyanide, migration of the former hydride ligand to a nitrogen atom, and formation of an aminocarbyne ligand (δ_c *ca.* 335 ppm, see the ESI†). However, these data could not define the actual binding of the second CNR molecule. An X-ray study on this complex[‡] (Fig. 2) revealed that the latter molecule was coordinated in a relatively unusual terminal-bent mode (C3–N2–C12 139(2)°), surely due to steric crowding, thus explaining the absence in solution of C–N stretches in the usual (linear) terminal region (around 2100 cm⁻¹). The intermetallic length in **6** is quite short (2.677(2) Å), as expected for carbyne-bridged 32-electron complexes of the type [M₂Cp₂(μ -CX)(μ -PR₂)L₂], for which a double metal–metal bond should be formulated.⁹

It is well established that reactions of complexes having unsaturated $M_2(\mu-H)_x$ centres with isocyanides can lead either to formimidoyl or to aminocarbyne derivatives, depending on whether the hydride ligand is transferred to the carbon or to the nitrogen atoms of the incoming ligand.^{44,5,10} The formation of **5** requires, however, the additional insertion of a second isocyanide molecule into the W–C bond of the formimidoyl intermediate that would follow from insertion of the first isocyanide molecule into the W–H bond of the hydride **1**, with concomitant C–C coupling. This coupling process is rather unusual. Actually, the first example of such a process involving a binuclear hydride complex has just been described while our work was in progress,^{11a} and the related reductive coupling of two isocyanide ligands at a dimetal centre is also a rare event.^{11b} Interestingly, the monitoring by ³¹P NMR spectroscopy of the reactions leading to compounds



Fig. 2 ORTEP drawing (30% probability) of compound **6**, with H atoms (except H1) and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): W1–W2 = 2.677(2), W1–P1 = 2.403(6), W1–C1 = 1.93(3), W1–C2 = 1.97(3), W2–P1 = 2.356(7), W2–C2 = 2.06(2), W2–C3 = 1.94(2), C2–N1 = 1.31(3), N1–C4 = 1.46(3), C3–N2 = 1.23(3), N2–C12 = 1.42(3), W2–W1–C1 = 79.6(8), W1–W2–C3 = 95.9(7). C2–N1–C4 = 127(2), C3–N2–C12 = 139(2).

5 and **6** revealed the presence of at least an unstable intermediate characterized in both cases by a similar resonance at ca. 30 ppm, and further work is now in progress to fully elucidate the complex pathways under operation in these reactions.

Compound 1 did not react with the aldehyde (4-Me– C_5H_4)C(O)H at room temperature even using a large excess of reagent, but does react slowly above *ca.* 303 K. This reaction can be more conveniently completed (*ca.* 1 h) in refluxing toluene solutions and by using *ca.* 3 equiv of reagent or above, to give a mixture containing as major products the oxo–alkyl complex [W₂Cp₂{CH₂(4-Me–C₆H₄)}(O)(μ -PCy₂)(CO)₂] (7) and its oxo–acyl isomer [W₂Cp₂{ μ - η : η , κ -C(O)CH₂(4-Me–C₆H₄)}(O)(μ -PCy₂)(CO)] (8), along with small amounts of other products as yet uncharacterized. Fortunately, the isomers 7 and 8 could be separated chromatographically and fully characterized (Fig. 3



Fig. 3 ORTEP drawing (30% probability) of compound 7, with H atoms (except the methylenic ones), CH_3 group and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): W1–W2 = 2.9532(6), W1–P1 = 2.385(3), W1–C1 = 1.97(1), W1–C2 = 1.94(1), W2–P1 = 2.469(3), W2–O3 = 1.723(7), W2–C3 = 2.23(1); W2–W1–C2 = 90.5(3), C1–W1–P1 = 77.8(3), C3–W2–P1 = 80.0(3), O3–W2–W1 = 94.9(2).



Fig. 4 ORTEP drawing (30% probability) of compound **8**, with H atoms (except the methylenic ones), CH₃ group and cyclohexyl rings (except the C¹ atoms) omitted for clarity. Selected bond lengths (Å) and angles (deg): W1–W2 = 2.8510(8), W1–P1 = 2.364(3), W1–C1 = 1.96(1), W1–C2 = 2.16(1), W1–O3 = 2.166(7), W2–P1 = 2.422(3), W2–O2 = 1.729(7), W2–C2 = 2.102(9); W2–W1–C1 = 93.0(3), O2–W2–W1 = 110.6(2).

and 4). The structures of these compounds are comparable to those recently determined by us for the isomeric pair of dinitrosyl complexes $[Mo_2Cp_2(\mu - PCy_2)R(CO)(NO)_2]$ (R = Me, CH₂Ph) and $[Mo_2Cp_2\{\mu-\eta:\eta,\kappa-C(O)Me\}(\mu-PCy_2)(NO)_2]^{12}$ although there are differences in the corresponding metric parameters, and in the fact that the ditungsten isomers do not interconvert in refluxing toluene solutions, as shown by independent experiments. The formation of compounds 7 and 8 requires a C-O bond cleavage in the hypothetical alkoxide complex that would follow from the initial insertion of the aldehyde into the W-H bond of 1. The latter reaction is a process reported previously for some unsaturated hydride-bridged complexes.13 Indeed a 31 P NMR monitoring of the above reaction allowed the detection of an unstable intermediate identified by a resonance at 58.8 ppm (J_{PW} 300 Hz) that could well correspond to a complex of formula $[W_2Cp_2\{\mu$ -OCH₂(4-Me-C₆H₄) $(\mu$ -PCy₂)(CO)₂] (cf. $\delta_{\rm P}$ 89.3 ppm, with $J_{\rm PW} = 292$ Hz for $[W_2Cp_2(\mu-I)(\mu-PCy_2)(CO)_2])$.¹ The subsequent oxidative addition of the C-O bond of the alkoxide group to yield oxo and alkyl ligands is a rather unusual event,14 although we can quote at least one example presumably involving a bridging alkoxide ligand.15

In summary, we have shown that the replacement of molybdenum with tungsten in the 30-electron hydrides $[M_2Cp_2(H)(\mu-PCy_2)(CO)_2]$ has significant effects not only on the structure but also on the reactivity and nature of the corresponding derivatives. The ditungsten hydride **1** exhibits enhanced reactivity towards small unsaturated organic molecules such as alkynes, isocyanides and aldehydes under mild conditions. Up to two molecules of the organic molecule can be easily incorporated into the unsaturated ditungsten centre, therefore enabling different C–C coupling processes to take place under mild conditions. At the same time, the unsaturated nature of the dimetal centre seems also to be critical to induce a rare C–O bond cleavage process in the reaction with (4-Me–C₆H₄)C(O)H. Further studies are now in progress to fully explore the synthetic potential of this 30-electron ditungsten hydride.

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‡ Crystal data for 4: dark green crystals, C₃₇H₄₇Cl₂O₁₀PW₂ (4·CH₂Cl₂), M = 1121.32, triclinic ($P\overline{1}$), a = 9.8445(4), b = 9.9405(5), c = 20.4221(9)Å, $\alpha = 76.143(3)$, $\beta = 84.799(3)$, $\gamma = 76.694(3)^{\circ}$, V = 1886.9(2) Å³, T =100 K, Z = 2, 60960 reflections measured, 8399 unique ($R_{int} = 0.1597$). Final R = 0.0585 (observed data with $I > 2\sigma(I)$), GOF = 1.000. *Crystal data for* **6**: dark green crystals, C₄₁H₅₁N₂OPW₂, M = 986.51, tricline ($P\bar{1}$), a = 10.806(3), b = 11.238(3), c = 16.928(6), a = 99.745(18), $\beta = 105.192(10)$, B = 105.202(10), B =105.113(18), $\gamma = 105.295(13)^\circ$, V = 1850.8(10) Å³, T = 100 K, Z = 2, 21272 reflections measured, 4486 unique ($R_{int} = 0.1572$). Final R = 0.0674(observed data with $I > 2\sigma(I)$), GOF = 1.022. Crystal data for 7: orange crystals, $C_{32}H_{41}O_3PW_2$, M = 872.32, monoclinic $(P2_1/c)$, a = 13.9983(6), $b = 12.3286(6), c = 17.0691(9) \text{ Å}, \beta = 92.294(2)^{\circ}, V = 2943.4(2) \text{ Å}^3, T = 100$ K, Z = 4, 43580 reflections measured, 5784 unique ($R_{int} = 0.1242$). Final R = 0.0513 (observed data with $I > 2\sigma(I)$), GOF = 1.040. Crystal data for 8: orange crystals, $C_{33}H_{43}Cl_2O_3PW_2$ (8·CH₂Cl₂), M = 957.22, monoclinic $(P2_1/c), a = 11.693(4), b = 12.758(5), c = 22.391(8) \text{ Å}, \beta = 102.867(5)^{\circ}, V =$ 3256(2) Å³, T = 100 K, Z = 4, 36132 reflections measured, 6420 unique $(R_{int} = 0.0680)$. Final R = 0.0483 (observed data with $I > 2\sigma(I)$), GOF =1.105.

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