

# Stepwise oxidation of a $\mu$ -alkylidene palladium–tungsten compound

Philippus F. Engel,<sup>a</sup> Michel Pfeffer,<sup>\*a</sup> André De Cian<sup>b</sup> and Jean Fischer<sup>b</sup>

<sup>a</sup> Laboratoire de Synthèses Métallo-induites, Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France

<sup>b</sup> Laboratoire de Cristalochimie (URA 424 du CNRS), Université Louis Pasteur, 4, rue Blaise Pascal, F-67070 Strasbourg Cedex, France

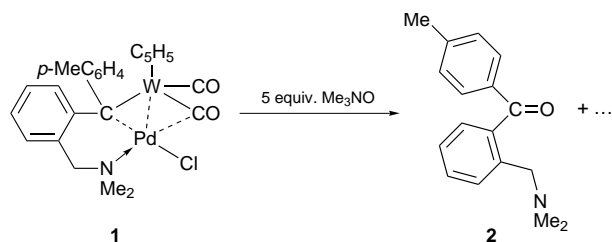
**The  $\mu$ -alkylidene unit of a tungsten–palladium compound is oxidized to the corresponding ketone in the presence of an excess of  $\text{Me}_3\text{NO}$ , whereas with 2–4 equiv., mono- and dioxotungsten derivatives, which are likely intermediates in the formation of the ketone, are instead obtained.**

We have recently established a novel synthetic route to  $\mu$ -alkylidene complexes of palladium and tungsten of molybdenum, in which the carbon atom bridging the two metals has been synthesized through the formal insertion of tungsta- or molybda-alkylidyne units into the Pd–C bonds of cyclopalladated compounds.<sup>1</sup> The structural and spectral data of the complexes we have reported, make it difficult to rationalise the exact nature of the Pd( $\mu$ -C)W or Pd( $\mu$ -C)Mo bonds, or to assess the importance of the metal–metal interaction. We thus hoped that reactivity studies will allow us to gain a better understanding of the structure of these species. So far, despite the large number of related bimetallic compounds reported in the literature,<sup>2</sup> very few reactivity studies have been performed with them.<sup>3</sup> It is thus of real interest to evaluate their potential in synthetic chemistry.

We have shown recently that whereas the terminal carbonyl ligand can be readily displaced by *tert*-butyl isocyanide,<sup>4</sup> the other carbonyl group of these compounds, which is semibridging to the palladium atom, seemed to be much more strongly bonded to the tungsten or molybdenum atom. In order to stabilize this CO ligand with the hope to obtain more reactive species, we treated the palladium–tungsten derivative with an excess of trimethylamine oxide (TAO). Thus, addition of TAO to a solution of complex **1** in dichloromethane induces  $\text{CO}_2$  evolution and a change from orange to black–yellow. A mixture of several products can be obtained, depending on the quantity of TAO employed.

When  $\geq 5$  equiv. of TAO was used, the reaction is most selective, and from the black residue obtained, the ketone  $\text{O}=\text{C}(4\text{-MeC}_6\text{H}_4)(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)$  **2** can be extracted as an orange–yellow oil in 77% yield (Scheme 1).<sup>†</sup>

Thus, the reaction between **1** and an excess of TAO leads to a breakdown of the  $\mu$ -alkylidene geometry and the bridging carbene fragment is oxidized and liberated as a ketone. The remaining metal complexes have not yet been characterized. However further information on the reaction pathway that is followed by the reaction has been obtained by analysis of the reaction products of incomplete reactions. As noted above, the reaction between **1** and TAO usually leads to a mixture of products, in which the ketone **2** may be found. When  $< 5$  equiv.

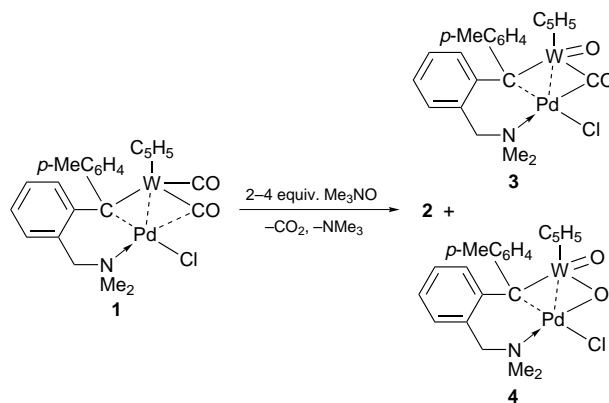


Scheme 1

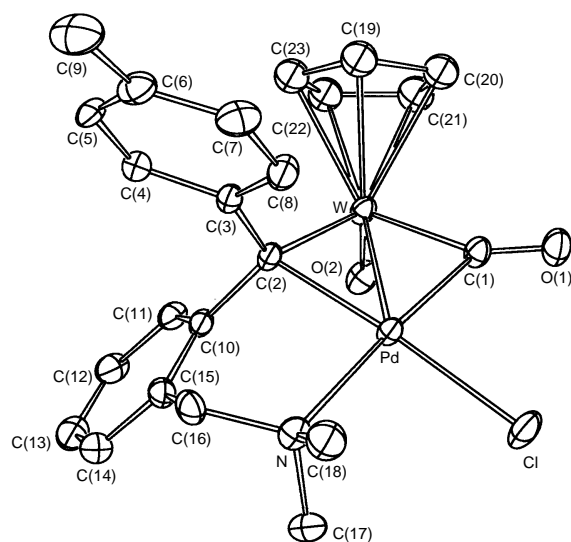
of TAO is used in the reaction with **1** in dichloromethane, a similar gas evolution and colour change are observed, but novel metal complexes whose structures are related to that of **1** can be isolated.

2–4 Equiv. of TAO react with **1** in dichloromethane to afford one major product, which has been identified as the novel oxo complex  $\{(\eta\text{-C}_5\text{H}_5)(\text{O})(\mu\text{-CO})\text{W}\}\{\mu\text{-C}(4\text{-MeC}_6\text{H}_4)(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{PdCl}\}$  **3** in low yield (21%, Scheme 2).<sup>†</sup>

The structure of **3** has been established by an X-ray diffraction study,<sup>‡</sup> and an ORTEP diagram is shown in Fig. 1. A complex similar to **3** which, however, was only obtained in trace amounts



Scheme 2

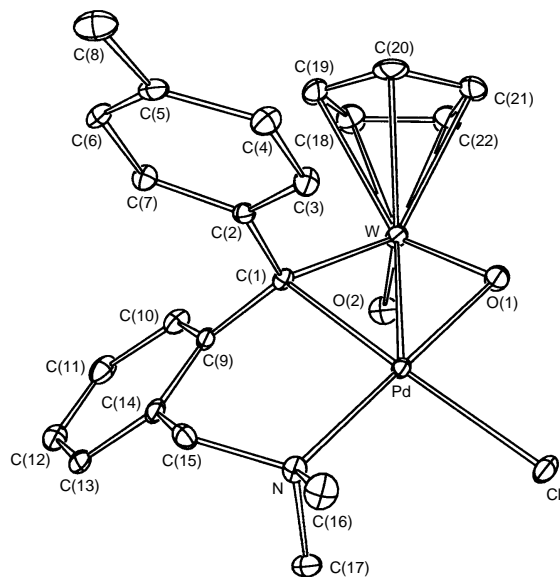


**Fig. 1** ORTEP diagram of **3** with atom labelling scheme (50% ellipsoids). Hydrogen atoms have been omitted for clarity. Bond distances (Å) and angles (°): Pd–Cl 2.409(2), Pd–C(2) 2.142(6), Pd–C(1) 2.009(7), Pd–N 2.268(6), Pd...W 2.6939(6), W–C(1) 2.075(7), W–O(2) 1.694(5), W–C(2) 2.074(6), Cl–Pd–C(2) 175.9(2), C(1)–Pd–C(2) 96.6(3), N–Pd–C(1) 174.2(2), C(2)–W–O(2) 107.2(2), C(1)–W–O(2) 101.2(3), W–C(1)–O(1) 146.6(6), Pd–C(1)–O(1) 130.8(5).

could be separated from **3** by column chromatography, and has also been characterized by an X-ray structure analysis, as the dioxo complex  $[(\eta\text{-C}_5\text{H}_5)(\text{O})(\mu\text{-O})\text{W}\{\mu\text{-C}(\text{4-MeC}_6\text{H}_4)(2\text{-C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\}\text{PdCl}]$  **4** (Scheme 2). Attempts to obtain complex **4** in better yields have not been successful so far, and as a result, complex **4** has only been partially characterized.† An X-ray diffraction study‡ could however be carried out on a crystal of complex **4**, and the ORTEP diagram is shown in Fig. 2, together with selected interatomic distances and angles.

The most remarkable feature of the structures of compounds **3** and **4** is their similarity, as far as the interactions within the palladium–tungsten–alkylidene units are concerned, with those of compounds analogous to the starting material **1**, or of the related compound obtained with *tert*-butyl isocyanide<sup>4</sup> even though in these derivatives many fragments of the molecules are different. Thus, in both compounds **3** and **4**, the palladium atom is in close interaction with three atoms of the tungstaalkylidene unit, *i.e.* the tungsten atom, the alkylidene carbon and the C atom of the carbonyl C(1)O(1) or the O(1) atom in **3** and **4**, respectively. The W–C(2) and W–C(1) bond lengths in **3** and **4**, respectively, are close to that expected for tungsten–alkylidene units; in fact they are notably shorter than the corresponding distance in a compound analogous to **1** [2.158(4) Å],<sup>1</sup> in  $[(\text{OC})_5\text{W}=\text{CPh}_2]$  [2.14(2) Å]<sup>5</sup> or in a dimetallacyclopropene compound  $[(\text{CO})_5\text{W}\{\mu\text{-C}(\text{OMe})\text{Ph}\}\text{Pt}(\text{PMe}_3)_2]$  [2.48(1) Å].<sup>6</sup> The tungsten–oxygen distances are in accord for W=O bonds.<sup>7</sup>

The behaviour of compound **1** towards a moderate oxidant such as Me<sub>3</sub>NO leading to a ketone is akin to that of ‘classical’ monometallic Fischer-type metallocarbenes.<sup>8</sup> It appears thus that compounds related to **1** are most likely to be the result of the interaction of an anionic tungsten–carbene unit with a cationic Pd centre. This would lead to a bonding mode involving a covalent bond between Pd and C(1) in **3** and between Pd and O(1) in **4** together with a  $\eta^2$ -interaction between the W=C unit and Pd in both compounds which accounts *inter alia* for the



**Fig. 2** ORTEP diagram of **4** with atom labelling scheme (50% ellipsoids). Hydrogen atoms have been omitted for clarity. Bond distances (Å) and angles (°): Pd–Cl 2.395(1), Pd–N 2.121(4), Pd–C(1) 2.125(4), Pd...W 2.6753(4), Pd–O(1) 2.037(3), W–C(1) 2.100(4), W–O(1) 1.817(4), W–O(2) 1.712(4), N–Pd–O(1) 179.6(1), C(1)–Pd–O(1) 90.2(2), C(1)–W–O(1) 97.4(2), C(1)–W–O(2), O(1)–W–O(2) 107.9(2), W–O(1)–Pd 87.7(1).

short distances found between Pd and W in both compounds. The formation of **3** and **4** establish that the tungsten atom has been oxidised in a stepwise manner by TAO concomitantly with the oxidation of the CO groups to CO<sub>2</sub>, prior to the oxidation of the alkylidene unit. Somewhat related oxoalkylidene–tungsten complexes have been synthesised recently following completely different routes.<sup>9</sup> The major information that can be drawn from this study is that it demonstrates that not only Fischer-type metallaalkylidene complexes interact with Pd<sup>II</sup> as in compounds of type **1**, but this can also be encountered with molybda- or tungsta-alkylidenes in which the metal has a +VI oxidation state as in Schrock-type carbene complexes. Further work which makes use of this result is under way.<sup>10</sup>

## Footnotes

\* E-mail: pfeffer@chimie.u-strasbg.fr

† *Selected analytical data:* **2**: C<sub>17</sub>H<sub>19</sub>NO. Mass spectrum: *m/z* 253 ([M]<sup>+</sup>, 43%); <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 7.39–7.29 (m, 4 H, dmba), 7.64, 7.22 (AB pattern, 4 H, <sup>3</sup>J<sub>HH</sub> 8.1 Hz, 4-tol), 3.39 (s, 2 H, NCH<sub>2</sub>), 2.41 (s, 3 H, 4-Me), 1.94 (s, 6 H, NMe<sub>2</sub>); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>), δ 196.9 (C=O), 142.8, 139.7, 139.1, 135.6 (C<sub>quat</sub> arom.), 129.4, 129.2, 128.9, 128.8, 128.4, 126.9 (CH arom.), 61.1 (CH<sub>2</sub>), 44.4 (NMe<sub>2</sub>), 21.7 (Me); IR ν<sub>CO</sub>, 1652 cm<sup>-1</sup>.

**3**: <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 8.27 (d, 1 H, <sup>2</sup>J<sub>HH</sub> 7.5 Hz, dmba), 7.50–7.42 (m, 1 H, dmba), 7.34–7.19 (m, 2 H, dmba), 6.90 (br, 2 H, 4-tol), 6.57 (br, 2 H, 4-tol), 5.70 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.07, 2.79 (AB pattern, 2 H, <sup>2</sup>J<sub>HH</sub> 12.4 Hz, NCH<sub>2</sub>), 2.70, 2.36, 2.26 (3s, 9 H, NMe<sub>2</sub> and 4-Me); <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ 204.8 (CO), 152.6, 152.3, 138.5, 137.1, 134.6, 130.6, 128.4, 127.9 (C arom.), 104.4 (C<sub>5</sub>H<sub>5</sub>), 64.5 (C arom. CH<sub>2</sub>), 49.9, 47.0 (NMe<sub>2</sub>), 20.7 (4-Me); IR (KBr), ν<sub>CO</sub> 1830, ν<sub>W=O</sub> 958 cm<sup>-1</sup>.

**4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 7.63 (d, 1 H arom., <sup>3</sup>J<sub>HH</sub> 7.7 Hz), 7.55 (d, 1 H arom., <sup>3</sup>J<sub>HH</sub> 8.0 Hz), 7.42–7.34 (m, 1 H arom.), 7.29–7.13 (m, 3 H arom.), 6.99, 6.54 (AB pattern, 2 H, <sup>3</sup>J<sub>HH</sub> 8.0 Hz, 4-tol), 6.16 (s, 5 H, C<sub>5</sub>H<sub>5</sub>), 3.15, 2.68 (AB pattern, 2 H, <sup>2</sup>J<sub>HH</sub> 12.2 Hz, NCH<sub>2</sub>), 2.98, 2.56 (2 s, 6 H, NMe<sub>2</sub>), 2.33 (s, 3 H, 4-Me).

‡ *Crystal data:* **3**: C<sub>23</sub>H<sub>24</sub>ClNO<sub>2</sub>PdW, *M* = 672.16, monoclinic, space group P2<sub>1</sub>/c, *a* = 12.579(4), *b* = 10.994(4), *c* = 16.165(5) Å, β = 97.47(2)°, *U* = 2216 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.01 g cm<sup>-3</sup>; *R*(*F*) = 0.025, [*R*<sub>w</sub>(*F*) = 0.031] using 2561 reflections with *I* > 3σ(*I*).

**4**: C<sub>23</sub>H<sub>24</sub>ClNO<sub>2</sub>PdW, *M* = 660.15, monoclinic, space group P2<sub>1</sub>/c, *a* = 11.663(4), *b* = 10.958(4), *c* = 16.661(3) Å, β = 94.37(2)°, *U* = 2123 Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 2.07 g cm<sup>-3</sup>; *R*(*F*) = 0.023, [*R*<sub>w</sub>(*F*) = 0.047] using 3359 reflections with *I* > 3σ(*I*).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/419.

## References

- P. F. Engel, M. Pfeffer and J. Fischer, *Organometallics*, 1994, **13**, 4751.
- W. A. Herrmann, *Adv. Organomet. Chem.*, 1982, **20**, 159; *Pure Appl. Chem.*, 1982, **54**, 65.
- J. E. Hahn, *Prog. Inorg. Chem.*, 1984, **31**, 205; J. C. Jeffery and M. J. Went, *Polyhedron*, 1988, **7**, 775.
- A. Macchioni, P. Pregosin, P. E. Engel, S. Mecking, M. Pfeffer, J. C. Daran and J. Wassermann, *Organometallics*, 1995, **14**, 1637.
- C. P. Casey, T. J. Burkhardt, C. A. Bunnell and J. C. Calabrese, *J. Am. Chem. Soc.*, 1977, **99**, 2127.
- T. V. Ashworth, J. A. K. Howard, M. Laguna and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1980, 1593.
- P. Legzdins, S. T. Rettig and L. Sanchez, *Organometallics*, 1985, **4**, 1470.
- K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587.
- P. Legzdins, E. C. Phillips and L. Sanchez, *Organometallics*, 1989, **8**, 940.
- P. Lohner and M. Pfeffer, to be published.

Received in Cambridge, UK, 31st January 1997; Com. 7/00741H