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Reversible Intramolecular C–H Oxidative Addition of Cyclopentadienyl Ligands at Ditungsten(I) Centers. A General Intermediate Step in the Way to Unsaturated Dimetal Cyclopentadienyl Carbonyl Complexes?

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Transition-metal cyclopentadienyl complexes constitute a vast area of study in current organometallic chemistry.[1] The metal–metal bonded carbonyl dimers $[M_2(CO)_xCp_2]$ (x = 2–6) and the monomers $[M(CO)_xCp]$ (x = 2–4), (Cp = η^5-C_5H_5, M = transition metal) form an important class within this great family of compounds, and much effort has been made to establish their chemical behavior. Loss of CO from these species can generate reactive unsaturated dimers with metal–metal bonds of orders up to 3.[2] However, although the primary processes in these reactions have been extensively studied,[3] they are still the object of current research.[4] Unsaturated dimetal carbonyl complexes are attractive synthetic reagents, as they are very reactive toward a great variety of molecules under mild conditions.[5] We are interested in the chemistry of these species, stabilized with bridging phosphorus–donor ligands such as dppm ($Ph_2PCH_2PPh_2$).[6] Our previous work on $[Mo_2(CO)_4(\mu\text{-dppm})Cp_2]$ revealed that intramolecular oxidative addition of a P–C(sp^3) bond of dppm occurs along with the loss of two CO molecules.[7] Here we report that a reversible and intramolecular C–H oxidative addition of a cyclopentadienyl ligand occurs as an intermediate step upon decarbonylation in the ditungsten analogue $[W_2(CO)_4(\mu\text{-dppm})Cp_2]$ (**1**) under thermal or photochemical conditions, a reaction leading finally to the triply bonded $[W_2(\mu\text{-CO})_2(\mu\text{-dppm})Cp_2]$ (**3**). To our knowledge, this is the first time that an intramolecular cyclopentadienyl C–H oxidative addition has been observed in transition-metal complexes. Moreover, further experiments indicate that such an addition does not require special thermal or photochemical activation in the above tungsten dimers. Finally, the reversibility of the oxidative additions here reported led us to consider the possibility that related processes could be involved more generally than suspected as intermediate steps in reactions leading to unsaturated cyclopentadienyl transition-metal dimers. To check this hypothesis, we decided to reinvestigate the extensively studied[3,4c,d] photochemical decarbonylation of the dimers $[M_2(CO)_2Cp_2]$ (M = Cr, Mo, W). Remarkably, a new finding emerged: cyclopentadienyl C–H activation steps are involved in the decarbonylation of $[W_2(CO)_6Cp_2]$.

Compound **1**[8] was prepared by a procedure similar to that used for its molybdenum analogue.[9] UV irradiation of **1** at 0 °C gives the hydrido cyclopentadienylidene complex $[W_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(CO)_3(\mu\text{-dppm})Cp]$ (**2**) in 95% yield.[10] The oxidative addition of a cyclopentadienyl C–H bond involved in the formation of **2** can be reversed through either carbonylation or decarbonylation processes. Thus, **2** reacts instantaneously with CO at room temperature to regenerate **1**. On the other hand, further irradiation of **2** at 15 °C gives $[W_2(\mu\text{-CO})_2(\mu\text{-dppm})Cp_2]$ (**3**).[11] The molecular structure of **3** has been determined through an X-ray study.[12] The short W–W distance (2.515(1) Å) is similar to those found for the triply metal–metal bonded dimers $[Mo_2(CO)_4(\eta^5\text{-L})_2]$ (L = Cp,[13a] C_5Me_5,[13b] C_9H_7[13c]) and $[W_2(\mu\text{-CO})_2(CO)(\eta^2\text{-}C_2Ph_2)(\eta^5\text{-}C_5Ph_4R)Cp]$.[14]

Compound **3** is more conveniently prepared by refluxing an octane solution of **1**. IR and NMR monitoring of this thermal reaction revealed again the presence of **2** as an intermediate in the formation of **3**. Because of this, it was thought that the C–H oxidative addition leading to **2** does not require special thermal or photochemical activation. Instead, it could be a spontaneous way of relieving the electronic unsaturation in the primary intermediate $[W_2(CO)_3(\mu\text{-dppm})Cp_2]$, generated from **1** after (thermally or photochemically induced) ejection of a CO molecule.

The above hypothesis was indirectly confirmed by the reaction of **3** with ^{t}BuNC at room temperature, which gave the hydrido cyclopentadienylidene complex $[W_2(\mu\text{-H})(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(CO)_2(CN^tBu)(\mu\text{-dppm})Cp]$ (**5**) in quantitative yield. Spectroscopic data for **5**[15] indicate a close structural analogy with **2**. During the formation of **5**, an intermediate species can be detected. The corresponding spectroscopic data[16] support its

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[1] (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; p 164–175. (b) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 8, Chapter 59.

[2] Winter, M. J. *Adv. Orgamomet. Chem.* **1989**, *29*, 101–162.

[3] (a) Meyer, T. J.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187–218. (b) Stufkens, D. J. In *Chemical Bonds. Better Ways to Make them and Break them*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Chapter 3. (c) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

[4] (a) Zhang, S.; Brown, T. L. *J. Am. Chem. Soc.* **1992**, *114*, 2723–2725. (b) Pope, K. R.; Wrighton, M. S. *Ibid.* **1987**, *109*, 4545–4552. (c) Hooker, R. H.; Rest, A. J. *J. Chem. Soc., Dalton Trans.* **1990**, 1221–1229. (d) Baker, M. L.; Bloyce, P. E.; Campen, A. K.; Rest, A. J.; Bitterwolf, T. E. *Ibid.* 2825–2832. (e) Bloyce, P. E.; Campen, A. K.; Hooker, R. H.; Rest, A. J.; Thomas, N. R.; Bitterwolf, T. E.; Shade, J. E. *Ibid.* 2833–2841.

[5] The chemistry developed around $[Mo_2(CO)_4Cp_2]$ is a relevant example. For a recent review, see: Curtis, M. D. *Polyhedron* **1987**, *6*, 759–782.

[6] (a) Puddephatt, R. J. *Chem. Soc. Rev.* **1983**, *12*, 99–127. (b) Chaudret, B.; Delavaux, B.; Poilblanc, R. *Coord. Chem. Rev.* **1988**, *86*, 191–243.

[7] Riera, V.; Ruiz, M. A.; Villafañe, F.; Bois, C.; Jeannin, Y. *J. Organomet. Chem.* **1989**, *375*, C23–C26.

[8] ν(CO) (cm^{-1}, toluene) 1911 m, 1875 vs, 1837 m, 1815 m. NMR spectra similar to those of the analogous molybdenum compound.

[9] Riera, V.; Ruiz, M. A.; Villafañe, F. *Organometallics* **1992**, *11*, 2854–2863.

[10] General conditions for NMR data: spectra recorded at 23 °C in CD_2Cl_2 solution, unless otherwise stated; chemical shifts (δ) in ppm relative to internal TMS [^{1}H at 300.13 MHz and ^{13}C (proton decoupled) at 75.47 MHz]; coupling constants in hertz. Selected spectroscopic data for **2**: ν(CO) (cm^{-1}, THF) 1930 vs, 1851 s, 1780 m; ^{1}H NMR δ 5.74, 5.30, 5.14, 4.58 (4 m, 4 H, C_5H_4), 5.19 (d, J_{HP} = 1, 5 H, Cp), −13.35 (ddd, J_{HP} = 37, 26, J_{HH} = 2, J_{HW} = 51, 41, 1 H, μ-H); ^{13}C NMR (−50 °C) δ 246.8 (d, J_{CP} = 9, CO), 239.4 (d, J_{CP} = 17, CO), 231.1 (s, J_{CW} = 166, CO), 172.5 (s, J_{CW} = 81, μ-C (C_5H_4)), 115.6, 84.0, 79.4 (3 s, 3 CH (C_5H_4)), 105.2 (d, J_{CP} = 5, CH (C_5H_4)), 88.5 (s, Cp).

[11] Selected spectroscopic data for **3**: ν(CO) (THF) 1730 vs; ^{1}H NMR (−50 °C) δ 6.13 (t, J_{HP} = 11, 2 H, CH_2), 4.61 (s, 10 H, Cp); ^{13}C NMR (−50 °C) δ 240.7 (s, J_{CW} = 131 (ca. 25% by area), CO), 88.2 (s, Cp), 69.7 (t, J_{CP} = 28, CH_2).

[12] Alvarez, M. A.; García, M. E.; Riera, V.; Ruiz, M. A.; Bois, C.; Jeannin, Y., results to be published. A possible disorder involving the bridging carbonyl ligands in compound **3** is currently under study.

[13] (a) Klingler, R. J.; Butler, W. M.; Curtis, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5034–5039. (b) Huang, J.-S.; Dahl, L. F. *J. Organomet. Chem.* **1983**, *243*, 57–68. (c) Greaney, M. A.; Merola, J. S.; Halbert, T. R. *Organometallics* **1985**, *4*, 2057–2058.

[14] Carriedo, G. A.; Howard, J. A. K.; Lewis, D. B.; Lewis, G. E.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1985**, 905–912.

[15] Selected spectroscopic data for **5**: IR (Nujol mull) ν(CO) 1819 vs, 1732 vs; ν(CN) 2078 m, 2040 m; ^{1}H NMR (CH_2Cl_2) δ 5.85, 5.04, 4.94, 4.47 (4 m, 4 H, C_5H_4), 5.06 (d, J_{HP} = 1.5, 5 H, Cp), −13.28 (ddd, J_{HP} = 37, 22, J_{HH} = 1, J_{HW} = 50, 40, 1 H, μ-H); ^{13}C NMR δ 246.8 (d, J_{CP} = 17, CO), 236.8 (s, CO), 181.4 (d, J_{CP} = 21, *C*NR), 159.7 (s, μ-C (C_5H_4)), 115.2, 77.4 (2 d, J_{CP} = 2, 2 CH (C_5H_4)), 103.1 (d, J_{CP} = 6, CH (C_5H_4)), 88.6 (s, CH (C_5H_4)), 87.8 (s, Cp).

[16] Compound **4** could not be isolated in a pure state, being always contaminated with substantial amounts of **5**. Selected spectroscopic data for **4**: IR (toluene) ν(CO) 1822 s, 1773 vs; ν(CN) 1623 m; ^{1}H NMR (C_6D_6) δ 6.0 (t, J_{HP} = 9, 2 H, CH_2), 4.75 (s, 5 H, Cp), 4.33 (s, 5 H, Cp), 2.11 (s, 9 H, Me).

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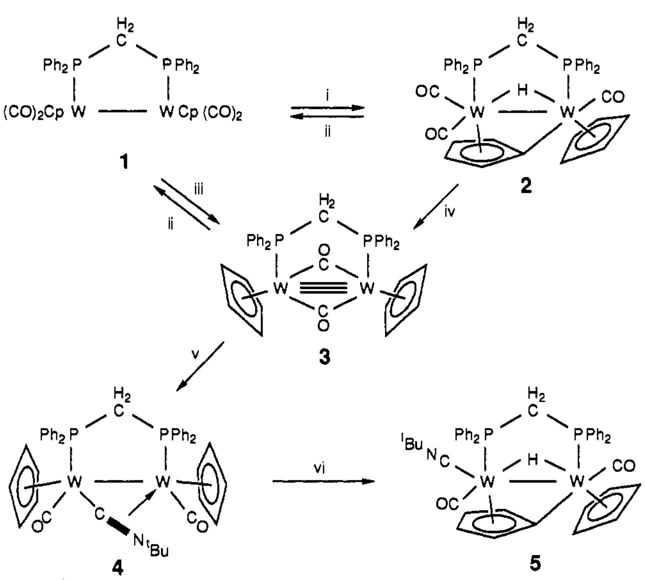
formulation as $[W_2(\mu\text{-}\eta^1,\eta^2\text{-CN}^t\text{Bu})(CO)_2(\mu\text{-dppm})Cp_2]$ (**4**), which can be related to the known complexes $[W_2(\mu\text{-}\eta^1,\eta^2\text{-CNR})(CO)_4Cp_2]$ (R = ^{t}Bu, Me).[17] Compound **4** transforms completely into **5** within 2 h at room temperature. Interestingly, although the $\mu\text{-}\eta^1,\eta^2$ coordination of the isocyanide makes the ditungsten center electron precise, just as cyclopentadienyl C-H oxidative addition does, thermodynamics seems to favor the latter. The structure of **5** has been confirmed through an X-ray study[12] except for the presence of the bridging hydrido ligand, which could not be located. The W-W length (3.179(2) Å) is consistent with the presence of a single metal-metal bond (for example, W-W = 3.222(1) Å in $[W_2(CO)_6Cp_2]$[18]). On the other hand, C-C and C-W lengths in the bridging cyclopentadienylidene ligand support its η^1,η^5 formulation and are similar to those found for related Mo_2 complexes.[19]

Although cyclopentadienylidene complexes are not unusual species,[20] the formation of **3** or **5** by intramolecular cyclopentadienyl C-H oxidative addition differs from previous methods. The closest ones involve intermolecular hydrogen[21] or methane[22] elimination, intramolecular hydridocomplex elimination,[23] or more complicated processes.[19b,20,24] With one exception,[22a] all these C-H cleavage reactions cannot be reversed. It is interesting to note that cyclopentadienyl C-H oxidative addition has been postulated on some occasions as a transient step in these reactions.

The above results prompted us to reinvestigate decarbonylation reactions on $[W_2(CO)_6Cp_2]$. UV irradiation of this compound in toluene at -50 °C yielded a mixture containing, as major products, the dihydride $[W_2(\mu\text{-H})_2(CO)_4Cp_2]$[25] and a new brown compound, tentatively formulated as $[W_3(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(CO)_7Cp_2]$ (**6**). Spectroscopic data for **6**[26] do not allow a complete characterization but clearly establish the presence of a cyclopentadienylidene ligand in the molecule. This result is quite remarkable, as the photochemical reactions of the dimers $[M_2(CO)_6Cp_2]$ (M = Cr, Mo, W) have been extensively studied.[3,4c,d] Surprisingly, it seems that C-H oxidative addition processes have never been detected nor even postulated in these reactions. However, our findings about the easy reversibility of these processes (ii and iv in Scheme I) suggest that they could have passed undetected in a number of occasions, and this is the origin of the question mark contained in the title of this paper. Further studies are now in progress to test the generality of the above cyclopentadienyl activation reactions.

Scheme I[a]



[a] (i) $h\nu$, N_2 purge, THF, 0 °C, 2 h. (ii) CO, CH_2Cl_2, 20 °C, 5 min. (iii) Octane, N_2 purge, 120 °C, 1 h. (iv) $h\nu$, N_2 purge, THF, 15 °C, 1 h. (v) CN^{t}Bu (1 equiv), THF, 0 °C, 30 min. (vi) THF, 20 °C, 2 h.

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Supplementary Material Available: ^{31}P NMR data for compounds **2**–**5** and ORTEP diagrams and interatomic bond distances and angles for compounds **3** and **5** (3 pages). Ordering information is given on any current masthead page.

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(17) Adams, H.; Bailey, N. A.; Bannister, C.; Faers, M. A.; Fedorko, P.; Osborn, V. A.; Winter, M. J. *J. Chem. Soc., Dalton Trans* **1987**, 341–348.

(18) Adams, R. D.; Collins, D. M.; Cotton, F. A. *Inorg. Chem.* **1974**, *13*, 1086–1090.

(19) (a) Bashkin, J.; Green, M. L. H.; Poveda, M. L.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1982**, 2485–2494. (b) Herrmann, W. A.; Krietchbaum, G.; Bauer, C.; Guggolz, E.; Zielgler, M. L. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 815–817.

(20) Coville, N. J.; du Plooy, K. E.; Pickl, W. *Coord. Chem. Rev.* **1992**, *116*, 1–267.

(21) (a) Pregosin, P. S.; Togni, A.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 668–669. (b) Gell, K. I.; Harris, T. V.; Schwartz, J. *Inorg. Chem.* **1981**, *20*, 481–488. (c) Berry, M.; Cooper, N. J.; Green, M. L. H.; Simpson, S. J. *J. Chem. Soc., Dalton Trans.* **1980**, 29–40. (d) Berry, M.; Elmitt, K. Green, M. L. H. *Ibid.* **1979**, 1950–1958.

(22) (a) Hoxmeier, R. J.; Blickensderfer, J. R.; Kaesz, H. D. *Inorg. Chem.* **1979**, *18*, 3453–3461. (b) Hoxmeier, R. J.; Knobler, C. B.; Kaesz, H. D. *Ibid.* 3462–3466. (c) Pasynskii, A. A.; Skripkin, Y. V.; Kalinnikov, V. T.; Porai-Koshits, M. A.; Antsyshkina, A. S.; Sadikov, G. G.; Ostrikova, V. N. *J. Organomet. Chem.* **1980**, *201*, 269–281.

(23) (a) Casey, C. P.; Palermo, R. E.; Jordan, R. F. *J. Am. Chem. Soc.* **1985**, *107*, 4597–4599. (b) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205–221.

(24) Ho, J.; Stephan, D. W. *Organometallics* **1992**, *11*, 1014–1016.

(25) Alt, H. G.; Mahmoud, K. A.; Rest, A. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 544–545.

(26) This compound can be fairly separated from the other products by chromatography on alumina at -30 °C. However, slow decomposition of its solutions occurs at -20 °C. Attempts (so far unsuccessful) are being made to grow crystals of **6**. Selected spectroscopic data: ν(CO) (toluene) 1977 s, 1925 vs, 1909 m, 1875 s, 1833 m; ^{1}H NMR (C_7D_8, -40 °C) δ 5.55, 4.61, 4.51, 3.88 (4 m, 4 H, C_5H_4), 4.75 (s, 5 H, Cp), 4.69 (s, 5 H, Cp).