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Preliminary communication

Synthesis and reactivity of the phosphido-bridged complex $[Cp_2Ta(\mu\text{-}CO)(\mu\text{-}PMe_2)Cr(CO)_4]$

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Abstract

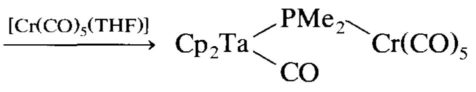
The heterobimetallic complex $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_5]$ **1** was prepared by reaction of $[Cp_2Ta(CO)(PMe_2)]$ with $[Cr(CO)_5THF]$. Irradiation of **1** afforded the dibridged compound $[Cp_2Ta(\mu\text{-}CO)(\mu\text{-}PMe_2)Cr(CO)_4]$ **2**. Addition reactions between **2** and Lewis bases L (L = phosphines, or isonitriles) produced $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_4(L)]$ **3**(**a**, **b**) with L regiospecifically coordinating to Cr. Depending on L, the reaction may be stereospecific, since the coordination of L can lead to *cis* or *trans* arrangements on the Cr site.

Keywords: Tantalum; Chromium; Dibridged complex; Phosphido bridges; Metal–metal bond; Isonitrile complexes

In the course of our work on heterobimetallic systems, we have recently developed a new synthetic approach involving Group 5 terminal phosphido complexes. These metallaphosphines are synthesized from d^2 monohydrido complexes and chlorophosphines and are able to bind unsaturated organometallic fragments to give μ-phosphido-bridged complexes [1]. Interest in such heteronuclear systems is obvious from both fundamental and reactivity considerations [2]. We now wish to report preliminary results concerning a tantalum–chromium heterobimetallic μ-phosphido complex.

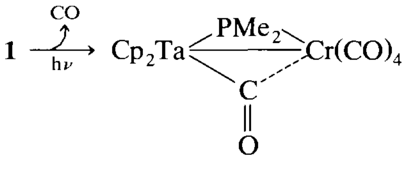
Complex **1** is obtained by the reaction sequence outlined below. Treatment of $[Cp_2TaH(CO)]$ with PMe_2Cl in toluene leads to the phosphine salt $[Cp_2Ta(CO)(PMe_2H)]Cl$ which is deprotonated in aqueous KOH. The resulting $[Cp_2Ta(PMe_2)(CO)]$ reacts in THF with $[Cr(CO)_5THF]$ affording complex **1** (overall yield 45%). Irradiation converts **1** to the μ-CO, μ-P dibridged complex **2** (yield 72%).

$$[Cp_2TaH(CO)] \xrightarrow[2)\ KOH]{1)\ PMe_2Cl} [Cp_2Ta(PMe_2)(CO)]$$



$$\xrightarrow{[Cr(CO)_5(THF)]} Cp_2Ta(\mu\text{-}PMe_2)(CO)Cr(CO)_5$$

1



$$1 \xrightarrow[h\nu]{-CO} Cp_2Ta(\mu\text{-}PMe_2)(\mu\text{-}CO)Cr(CO)_4$$

2

Structures of **1** and **2** were established from their spectra [3]. In particular, very characteristic of the dibridged structure **2** is the weak IR absorption at 1725 cm^{-1} for μ-CO and the dramatic downfield shift of the ^{31}P resonance ($\delta = 94.2$ ppm/H_3PO_4) indicating a large decrease in angle with respect to the parent complex **1**. These data are consistent with a Ta–Cr bond, which results from a donor–acceptor interaction

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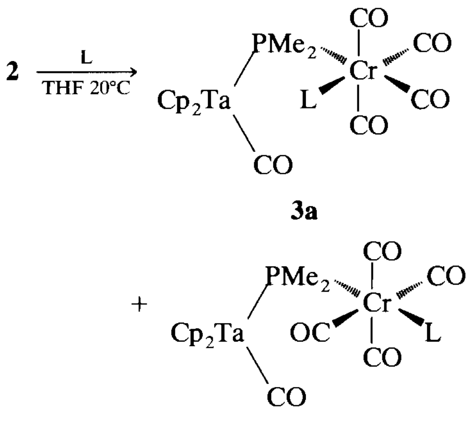
between the filled $1a^1$ orbital of the tantalum atom and a vacant orbital on Cr, allowing this metal to reach an 18-electron configuration. The semibridging carbonyl allows electron-transfer from chromium to the tantalocene fragment and helps to remove some of its excess of electron density. We have recently characterized such structural features by X-ray analysis in a related dibridged Nb–Fe complex [4].

In order to determine whether the Ta–Cr bond can be readily broken by two-electron donors L, we have allowed complex **2** to react with phosphines and isonitriles. The reactions proceed quickly, and the products are easily isolated and characterized. However, coordination of L concomitantly with the removal of the direct Ta–Cr bond can lead to *cis* or *trans* arrangements at the Cr site.



3a

3b

With PMe_2Ph, complex **2** leads to a mixture of "open" structures **3a** and **3b** with a slight excess of the *cis* isomer 3a (60%) [5]. Stereospecific addition in the *trans* position is observed with the bulky PPh_3 [6]. These results illustrate the dependence of the coordination site on the bulk of incoming ligands (cone angles 122° and 145° for PMe_2Ph and PPh_3, respectively [7]). The isonitriles ${}^tBuNC$ and PhC^*HMeNC give exclusively *cis* isomers **3a** [8] in accordance with the relatively small steric requirements of this type of ligand. Attempts to introduce a chiral group (by using racemic PhC^*HMeNC) at the chromium fragment does not lead to the expected ^1H NMR anisochrony differentiation of the Cp resonances. This surprising effect could be due to conformational effects which move the metallocene moiety away from the asymmetric ligand and place the two cyclopentadienyl rings in almost identical environments.

IR data establish unambiguously the geometry around chromium atom a *cis* arrangement giving rise to four absorptions whereas only one band would be for a *trans* isomer. The ^1H NMR data are informative on the stereospecificity of the addition to Cr but cannot show whether a *cis* or *trans* configuration arrangement is formed. More information is available from ^{31}P NMR spectra, since a *trans* configuration involves a systematic deshielding of phosphido phosphorus resonances [9]. However, in disubstituted chromium fragments, *cis* and *trans* $^2J_{PP}$ values are very similar and do not afford conclusive structural informations [10].

Work involving diphosphines and further chiral donors are underway.

References and notes

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[2] (a) A.J. Carty, S.A. MacLaughlin and D. Nucciarone, *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*, VCH, 1987, p. 559. (b) P. Braunstein, E. de Jesus, A. Dedieu, M. Lanfranchi and A. Tiripicchio, *Inorg. Chem., 31* (1992) 399.

[3] $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_5]$ **1**: Anal. Calc. for $C_{18}H_{16}CrO_6PTa$: C, 36.51; H, 2.72; Found: C, 36.56; H, 2.71%. IR (THF, ν_{CO}) 2038m, 1938s, 1917vs, 1910vs cm^{-1}. ^1H NMR (200 MHz, TDF) δ 5.21 (d, $J = 1.9$ Hz, Cp), 1.58 (d, $J = 5.8$ Hz, Me). ^{31}P NMR (81 MHz, TDF) δ −77.8 (s). ^{13}C NMR (50 MHz, TDF) δ 26.1 (d, $J = 10.1$ Hz, Me), 91.3 (s, Cp), 221.8 (d, $J = 10.4$ Hz, CO), 224.8 (d, $J = 8.4$ Hz, CO), 249.9 (d, $J = 5.2$ Hz, CO). $[Cp_2Ta(\mu\text{-}CO)(\mu\text{-}PMe_2)Cr(CO)_4]$ **2**: Anal. Calc. for $C_{17}H_{16}CrO_5PTa$: C, 36.19; H, 2.86; Found: C, 35.91; H, 2.99%. IR (THF, ν_{CO}) 1987s, 1907w, 1892s, 1875s, 1725w cm^{-1}. ^1H NMR (200 MHz, TDF) δ 5.08 (d, $J = 1.7$ Hz, Cp), 1.86 (d, $J = 9.1$ Hz, Me). ^{31}P NMR (81 MHz, TDF) δ 94.2 (s). ^{13}C NMR (50 MHz, TDF) δ 16.2 (d, $J = 20.9$ Hz, Me), 94.2 (s, Cp), 218.6 (d, $J = 8.4$ Hz, CO), 227.3 (s*, CO), 229.1 (s*, CO), 312.5 (s, CO) (* broad signal).

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[5] $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_4(PMe_2Ph)]$ (inseparable mixture): MS (EI, 70 eV), m/z (%): 702 (7.9) $[M^+]$, 620 (27.7), 452 (25.9), 424 (87.1), 372 (78.1), 312 (100). IR (THF, ν_{CO}) 1980w, 1907vs, 1877vs, 1867vs, 1848s cm^{-1}. ^1H NMR (200 MHz, C_6D_6) assigned to *cis* isomer) δ 4.58 (d, $J = 1.8$ Hz, Cp), 1.52 (d, $J = 6.5$ Hz, Me), 1.27 (d, $J = 5.3$ Hz, Me), 6.95–7.57 (m, Ph). ^{31}P NMR (81 MHz, C_6D_6) δ −75.7 (d, $J = 34$ Hz, $\mu\text{-}PMe_2$), 17.8 (d, $J = 34$ Hz, $Cr\text{-}PMe_2Ph$). ^1H NMR (200 MHz, C_6D_6) (assigned to *trans* isomer) δ 4.62 (d, $J = 1.9$ Hz, Cp), 1.84 (d, $J = 5.5$ Hz, Me), 1.61 (d, $J = 7.0$ Hz, Me), 6.95–7.57 (m, Ph). ^{31}P NMR (81 MHz, C_6D_6) δ −61.9 (d, $J = 29$ Hz, $\mu\text{-}PMe_2$), 38.2 (d, $J = 29$ Hz, $Cr\text{-}PMe_2Ph$).

[6] $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_4(PPh_3)]$: MS (EI, 70 eV), m/z (%): 826 (1.9) $[M^+]$, 686 (4.7), 592 (83.4), 536 (28.4), 452 (55,0), 424 (93.5), 372 (66.2), 312 (69.8), 262 (100). IR (THF, ν_{CO}) 1909s, 1855vs cm^{-1}. ^1H NMR (200 MHz, C_6D_6) δ 4.63 (d, $J = 1.9$ Hz, Cp), 1.92 (d, $J = 5.6$ Hz, Me), 6.99–7.15 and 7.79–7.87 (m, Ph). ^{31}P NMR (81 MHz, C_6D_6) δ −61.4 (d, $J = 25$ Hz, $\mu\text{-}PMe_2$), 78.6 (d, $J = 25$ Hz, $Cr\text{-}PPh_3$).

[7] (a) T.L. Brown, *Inorg. Chem., 31* (1992) 1286. (b) C.A. Tolman, *Chem. Rev., 77* (1977) 313.

[8] (a) $[Cp_2Ta(CO)(\mu\text{-}PMe_2)Cr(CO)_4({}^tBuNC)]$: IR (THF) ν_{CN}: 2115m, ν_{CO}: 1984s, 1907s, 1894s, 1878vs, 1861s cm^{-1}. MS (EI, 70 eV), m/z (%): 647 (68.9) $[M^+]$, 563 (18.5), 535 (52.9), 507 (100), 372 (25.5). ^1H NMR (200 MHz, C_6D_6) δ 4.65 (d, $J = 1.9$

Hz, Cp), 1.69 (d, $J = 5.4$ Hz, Me), 0.93 (s, ^{t}Bu). ^{31}P NMR (81 MHz, C_6D_6) δ -74.7 (s, μ-PMe_2). (b) [$Cp_2Ta(CO)(\mu$-$PMe_2)Cr(CO)_4(PhC^*HMeNC)$]: IR (THF) ν_{CN}: 2115m, ν_{CO}: 1984s, 1907s, 1896s, 1880vs, 1863s cm^{-1}. MS (EI, 70 eV), *m/z* (%): 695 (25.2) [M^+], 592 (30.9), 555 (36.7), 536 (10.8), 480 (23.0), 452 (31.2), 424 (100). ^{1}H NMR (200 MHz, C_6D_6) δ 4.59 (d, $J = 1.9$ Hz, Cp), 1.64 (d, $J = 5.3$ Hz, Me), 1.13 (d, $J = 6.8$ Hz, Me), 4.11 (dq, $J = 4.5$ Hz, $J = 1.8$ Hz, Me), 6.92–7.13 (m, Ph). ^{31}P NMR (81 MHz, C_6D_6) δ -72.2 (s, μ-PMe_2).

[9] (a) C.J. Jameson and H.S. Gutowsky, *J. Chem. Phys.*, *40* (1964) 1914; (b) M.M. Kubicki, J.F. Le Gall, R. Kergoat and L.C. Gomes De Lima, *Can. J. Chem.*, *40* (1987) 1292.

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