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Preliminary communication

Studies pertaining to the mechanism of "$Pt(PCy_3)$" addition. The reaction of $MPt(\mu\text{-}H)(\mu\text{-}P^nPr_2)Pt(CO)(PCy_3)$ with $Pt(C_2H_4)_2(PCy_3)$

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Abstract

The reaction of $Pt(C_2H_4)_2(PCy_3)$ with $(OC)_4M(\mu\text{-}H)(\mu\text{-}P^nPr_2)Pt(CO)(PCy_3)$, (**1**: M = Cr, Mo, W) occurs in a highly specific, kinetically controlled manner to give $MPt_2(\mu^2_{M-Pt}\text{-}CO)(\mu^2_{Pt-Pt}\text{-}H)(\mu^2_{M-Pt}\text{-}P^nPr_2)(CO)_4(PCy_3)_2$ (**5**), as the first formed trimer. The trimer **5** (M = Mo, W) isomerizes to give $MPt_2(\mu^2_{Pt-Pt}\text{-}CO)((\mu^2_{M-Pt}\text{-}H)(\mu^2_{M-Pt}\text{-}P^nPr_2)(CO)_4(PCy_3)_2$ (**6**) which in turn isomerizes to $MPt_2(\mu^2_{M-Pt}\text{-}CO)(\mu^2_{M-Pt}\text{-}H)(\mu^2_{Pt-Pt}\text{-}P^nPr_2)(CO)_4(PCy_3)_2$ (**7**), as the final isolable product. These results provide a detailed insight into the mechanism of "$Pt(PCy_3)$ addition", a cluster assembly process.

The homo- and hetero-metallic cluster compounds of platinum exhibit an interesting and varied chemistry [1–5]. Whilst much has been achieved in rationalising their structural and chemical properties, studies pertaining to the mechanism(s) whereby such clusters are assembled remain sparse. Herein we report preliminary observations concerning the formation of "MPt_2" trimeric complexes from the reaction of $(OC)_4M(\mu\text{-}H)(\mu\text{-}PPr_2)Pt(CO)(PCy_3)$ (**1**: M = Cr, Mo, W) [6] with $Pt(C_2H_4)_2(PCy_3)$, systems in which the relative rates of sequential events, together with ready spectroscopic characterization of solution intermediates (^1H and $^{31}P\{^1H\}$ NMR) provide considerable insight into the mechanism of the $Pt(PCy_3)$ addition process.

Complexes **1** are readily obtained in high yield from the oxidative addition of the P–H bond of $(OC)_5M(P^nPr_2H)$ to a molar equivalent of $Pt(C_2H_4)_2(PCy_3)$ [6]. It is likely that **1** is formed via the sequences **3** → **2** → **1** (Scheme 1). Whilst **2** and **3** cannot be observed, directly structural analogs that have been characterized include $(OC)_3(PEt_3)Mo(\mu\text{-}CO)(\mu\text{-}PPh_2)PtH(PCy_3) \rightleftharpoons (OC)_3(PEt_3)Mo(\mu\text{-}H)(\mu\text{-}PPh_2)Pt(CO)(PCy_3)$ [6] (similar to the postulated **2** ⇌ **1** equilibrium) and $(OC)_4(PMe_3)Cr(\mu\text{-}P^tBu_2)NiCl(PMe_3)$ [7] (a structural analog of **3**). When $(OC)_4Mo(\mu\text{-}H)(\mu\text{-}P^nPr_2)Pt(CO)(PCy_3)$ (**1b**) is allowed to react with a molar equivalent of

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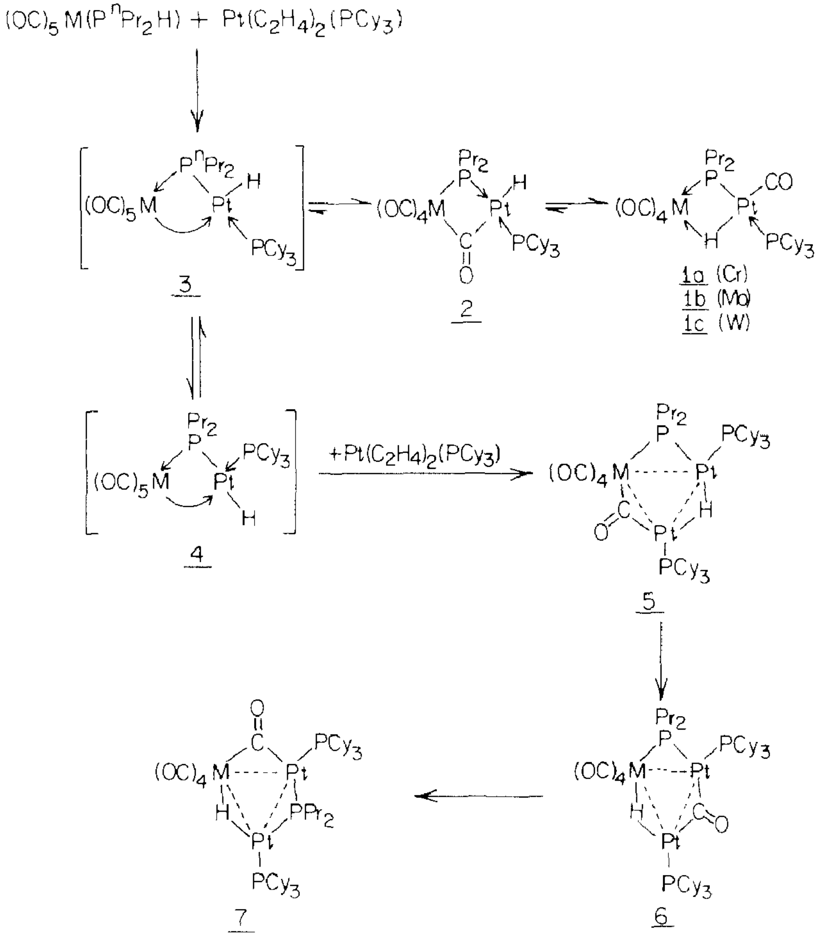

Scheme 1.

$Pt(C_2H_4)_2(PCy_3)$ in CD_2Cl_2, 20 °C (NMR monitoring), there is a rapid reaction to form **5b** (M = Mo) as to the first formed trimer (structurally characterized by NMR, see Table 1). The two large ${}^1J({}^{195}Pt-{}^1H)$ values of 440 and 400 Hz confirm a $Pt(\mu\text{-}H)Pt$ structure, whilst the $\delta(P\mu)$ value [8] and the observation of one large ${}^1J({}^{195}Pt-{}^{31}P\mu)$ and one smaller ${}^2J({}^{195}Pt-{}^{31}P\mu)$ are consistent with a $Mo(\mu\text{-}P^nPr_2)Pt$ unit in **5b** as shown. The complex **5b** (M = Mo) rapidly rearranges (within 5–10 min) to give the isomeric trimer **7b** as the final product. During this process a very small steady state concentration of the trimeric complex **6b** (Scheme 1) is observed. The tungsten system $(OC)_4W(\mu\text{-}H)(\mu\text{-}P^nPr_2)Pt(CO)(PCy_3)$ (**1c**) reacts similarly but considerably more slowly with $Pt(C_2H_4)_2(PCy_3)$. Whilst only very weak resonances

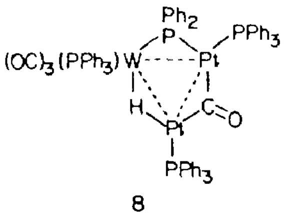

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Table 1

^1H and $^{31}P\{^1H\}$ NMR data (CD_2Cl_2 solution, 20 °C) δ(H) (TMS) δ(P)(85% H_3PO_4) ppm, *J*-values in Hz.

	5a(Cr)	**5b**(Mo)	**6b**(Mo)	**6c**(W)	**7b**(Mo)	**7c**(W)
δ(H)	−10.5	−8.4	−7.8	−6.3	−3.7	−2.8
$J(^{195}Pt-^1H)$	423, 420	440, 400	n.r.	800, 28	840, n.r.	800, 10 [a]
$J(^{31}P-^1H)$	70, 51, 19	68, 51, 14	24, 8	24, 7	87, 18, 0	85, 16.2
$\delta(P\mu)$	225	206	[b]	274	307	332
$J(^{195}Pt-^{31}P\mu)$	1700, 89	1555, 82		1877, 123	2636, 2379	2657, 2343
$J(^{31}P-^{31}P\mu)$	18, 12	16, 11		12, 0	28, 0	26, 6
$\delta(PCy_3)$	53	54		72	71	74.5
$J(^{195}Pt-^{31}P)$	5340, 225	5778, 304		4840, 506	3486, 100	3550, 90
$\delta(PCy_3)$	45	43		60	52	58
$J(^{195}Pt-^{31}P)$	4420, 191	4725, 257		3817, 396	3384, 170	3400, 160
$J(^{31}P-^{31}P)$ [c]	22	14		37	89	88

[a] $J(^{183}W-^1H)$ 40 Hz. [b] **6b** too short lived to obtain $^{31}P\{^1H\}$ data. [c] Coupling of ^{31}P nuclei of PCy_3 ligands; n.r. - not resolved.

(^1H), tentatively assignable to **5c** are observed, the concentration and lifetime of the isomeric trimer **6c** (considerably longer than that of **6b**) is sufficient to obtain both ^1H and $^{31}P\{^1H\}$ NMR data (Table 1). The data are consistent with the structure shown containing W(μ-H)Pt and W(μ-P^nPr_2)Pt units. The spectral data for **6** are very similar to those of the complex **8** (obtained from the reaction of *cis*-$(OC)_4W(PPh_3)(PPh_2H)$ with $Pt(C_2H_4)(PPh_3)_2$ in CH_2Cl_2 after 14 days [9]). The molecular structure of **8** has been determined by single crystal X-ray diffraction [9]. Upon completion the trimeric complexes **7b** and **7c** (Scheme 1) are the sole products of the reaction. The spectroscopic data of **7** (Table 1) readily confirm the presence of Pt(μ-PPr_2)Pt, M(μ-H)Pt and M(μ-CO)Pt (ν(μ-CO) 1765 (Mo) and 1778 (W) cm^{-1}).

The formation of **5** as the kinetic product followed by the **5** to **6** to **7** isomerization allows one to make reasonably specific inferences with regard to the mechanism of $Pt(PCy_3)$ addition and strongly suggests the reaction sequences shown in Scheme 1. Reorganization of **1** to **3** (via **2**) followed by an H $\rightleftarrows$ PCy_3 site isomerization results in the formation of the postulated species **4**. Although **4** is not observed, a structurally similar species $(OC)_4(PEt_3)W(\mu\text{-}PPh_2)Pt(PEt_3)Cl$ with PEt_3's *cis* to μ-PPh_2 has been prepared in our laboratory [10]. The postulated intermediate **4** has a sterically accessible (OC)M–PtH unit which, upon reaction with $Pt(C_2H_4)_2(PCy_3)$ (may be perceived as nucleophilic substitution of C_2H_4) leads to **5** as the kinetically formed trimer. The reorganization of **5** to **6** involves a μ-H $\rightleftarrows$ μ-CO site interchange and is reasonably fast for both Mo and W systems. The **6** → **7** rearrangement, which involves an intra molecular migration of a μ-PPr_2, is much slower for W (> 90% complete in 24 h), than for Mo (essentially complete in minutes, CD_2Cl_2, 20 °C). This suggests that M–Pμ bond breaking (i.e. dissociative step) contributes significantly to the rate-determining step of the **6** to **7** isomerization [11]. The reaction of **1a** (M = Cr) with $Pt(C_2H_4)_2(PCy_3)$ leads initially to **5a** (Table 1) which then undergoes decomposition to give $Pt_3(CO)_3(PCy_3)_3$ as the major Pt-containing product.

The above observations of highly specific kinetic control on the addition of a $Pt(PCy_3)$ unit to **1** point to initial reorganization of **1** to the intermediate **4** with a sterically accessible M(CO)-PtH unit as a prerequisite for Pt(PCy_3) addition. Whilst $Pt(C_2H_4)_n(PR_3)_{3-n}$ ($n = 1$–3) complexes are frequently used as precursors for the synthesis of a wide range of chemically interesting Pt_x and M_yPt_x cluster compounds, the above observations are the first definitive mechanistic results that clearly delineate a Pt(PR_3) assembly process.

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