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Preparation of μ-$Ph_2PCH_2PPh_2$ Platinum(II)–Tungsten(0), –Molybdenum(0) or –Chromium(0) Complexes by Transmetallation: Crystal Structure of $[(p\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-}Ph_2PCH_2PPh_2)_2W(CO)_3]$

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We have described previously the synthesis of platinum–tungsten complexes of type $[(RC{\equiv}C)_2Pt(\mu\text{-}dppm)_2W(CO)_3]$ (R = Me, Ph or *p*-tolyl) formed by the action of *trans*-$[(RC{\equiv}C)_2Pt(\eta^1\text{-}dppm)_2]$ on *fac*-$[W(CO)_3(NCMe)_3]$ [1]. These preparations were accompanied by other products which were difficult to remove, including the diplatinum complex $[Pt_2(C{\equiv}CR)_4(\mu\text{-}dppm)_2]$, and the yields were only *ca.* 40%. We now find that $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2W(CO)_3]$ is much better prepared by transmetallation [2] of $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$, using *fac*-$[W(CO)_3(NCMe)_3]$ in boiling benzene (2 h): the isolated yield was 61% and purification was much easier than with the previous method of synthesis [1].

Encouraged by the success in preparing the platinum–tungsten complex by transmetallation we have similarly attempted to prepare corresponding complexes of molybdenum or chromium. Treatment of $[Mo(CO)_3(\text{cycloheptatriene})]$ with an equivalent amount of $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ in boiling benzene gave $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Mo(CO)_3]$ in 72% isolated yield, as orange-red crystals; no other phosphorus-containing product was formed. This formulation is based on microanalytical and IR data and particularly on NMR data, *e.g.* $^{31}P\text{-}\{^1H\}$: δP_A = 2.3 ppm., $^1J(PtP_A)$ = 2598 Hz; δP_B = 36.4 ppm, $^3J(PtP) = 24$ Hz; $^2J(P_AP_B) + {}^4J(P_AP_{B'}) = 61$ Hz. $^1H\text{-}\{^{31}P\}$: $\delta(CH_2)$ = 3.71 ppm, $^3J(PtCH_2)$ = 36.4 Hz (fluxional at +20 °C whereas at –60 °C the CH_2 hydrogens are non-equivalent and the complex is non-fluxional). The same complex was formed in high yield when $[Mo(CO)_4(\text{cycloocta-1,5-diene})]$ was treated with $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ but treatment of $[Mo(CO)_4(\text{cyclo-octa-1,5-diene})]$ with $[(PhC{\equiv}C)_2Pt(\eta^1\text{-}dppm)_2]$ gave a mixture of products, including $[Pt_2(C{\equiv}CPh)_4(\mu\text{-}dppm)_2]$, and the desired complex $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Mo(CO)_3]$ was isolated with difficulty and in only 23% yield.

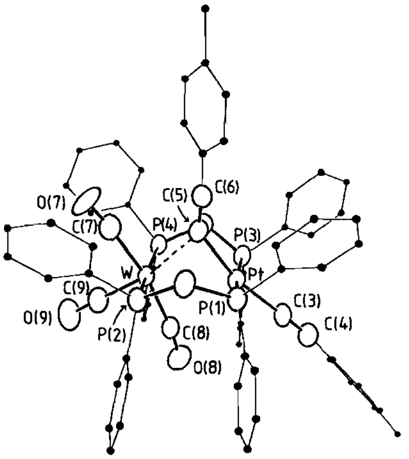
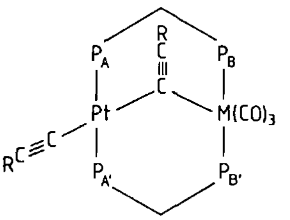


Fig. 1. Molecular structure of $[(p\text{-}MeC_6H_4C{\equiv}C)_2Pt(\mu\text{-}Ph_2PCH_2PPh_2)_2W(CO)_3]$. Selected bond lengths: Pt–P(1) 2.307(3), Pt–P(3) 2.302(2), W–P(2) 2.454(3), W–P(4) 2.442(2), Pt–C(3) 2.000(8), C(3)–C(4) 1.19(1), C(5)–C(6) 1.19(1), W–C(7) 2.05(1), W–C(8) 2.04(1), W–C(9) 1.92(1), C(7)–O(7) 1.14(1), C(8)–O(8) 1.14(1), and C(9)–O(9) 1.18(1) Å. Selected angles: Pt–C(5)–C(6) 136.8(8), W–C(5)–C(6) 138.4(8), C(5)–C(6)–C(tolyl) 175(1), C(3)–Pt–C(5) 166.7(4), and C(9)–W–C(5) 166.6(4)°.



We have also treated $[Cr(CO)_4(\text{norbornadiene})]$ with $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ in refluxing benzene. This gave, after a few minutes, a deep purple solution which, by $^{31}P\text{-}\{^1H\}$ NMR spectroscopy, contained only $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2AgCl]$ and another species which, from its $^{31}P\text{-}\{^1H\}$ NMR parameters, was most likely $[(PhC{\equiv}C)_2Pt(\mu\text{-}dppm)_2Cr(CO)_3]$ (*1*) (R = Ph, M = Cr): δP_A = 5.5 ppm, $^1J(PtP_A)$ = 2567 Hz, δP_B = 60.8 ppm, $^3J(PtP_B)$ = 34 Hz, $^2J(P_AP_B) + {}^4J(P_AP_{B'})$ = 71 Hz. However, on further boiling this species gradually decomposed, and considerable amounts of $[Pt_2(C{\equiv}CPh)_4(\mu\text{-}dppm)_2]$ and other phosphorus-containing species formed as the platinum-silver complex disappeared. We have thus far been unable to isolate this purple complex in a pure state. When $[Cr(CO)_4(\text{norbornadiene})]$ or $[Cr(CO)_3(NCMe)_3]$ was treated with $[(PhC{\equiv}C)_2Pt(\eta^1\text{-}dppm)_2]$ none of the purple complex was produced, the products being mainly

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$[Pt_2(C{\equiv}CPh)_4(\mu\text{-dppm})_2]$ and (probably) dppm-chromium carbonyl complexes.

Thus transmetallation has distinct advantages for the synthesis of Pt(μ-dppm)–W, –Mo, or –Cr complexes over direct methods involving η^1-dppm moieties [1]. Similar attempts to effect transmetallation of silver by tungsten with the monoacetylide complexes of type $[(RC{\equiv}C)ClPt(\mu\text{-dppm})_2AgCl]$ [2] led to rapid decomposition and no platinum–tungsten complex was isolated.

The structure of (*1*) (R = *p*-tolyl, M = W) has been determined by X-ray crystallography (Fig. 1)*. The 8-membered PtP_4C_2W ring is in the 'boat' conformation and the Pt···W distance 3.037(1) Å is substantially longer that generally accepted for a Pt–W bond (*ca.* 2.8 Å) [3]. The two metal centres are asymmetrically bridged by one of the tolylidyne groups such that Pt–C(5) is 2.094(9) Å and W–C(5) is 2.398(9) Å. The latter separation is somewhat longer than that (2.1–2.3 Å) found for W–C(alkyl) σ-bonds [4], but does constitute a strong interaction which completes the octahedral coordination about the tungsten atom. Uncharacteristically for a semi-bridging acetylide there is no π-interaction of the C≡C acetylenic linkage with either metal atom (see parameters in caption to Fig. 1). We similarly formulate the molybdenum or chromium complexes as (*1*) (R = Ph, M = Mo or Cr).

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**Crystal data*: $C_{71}H_{58}O_3P_4PtW$, monoclinic, space group $P2_1$, a = 11.847(3), b = 16.023(4), c = 18.351(4) Å, β = 116.23(1)°, Z = 2. The current R is 0.026 for 4043 independent absorption-corrected F_o having $I > 2\sigma(I)$. The alternative enantiomorphic specification gave significantly larger R-factors. Pt, W, P and O atoms were assigned anisotropic thermal parameters and hydrogen atoms were included in calculated positions. The aromatic rings were refined as rigid bodies with idealised geometry.