Structural Differences in η^5-C_5H_5 and η^5-$P_3C_2Bu^t_2$ Tetrametallic Complexes. Synthesis of $[PtM_2Cl(P_3C_2Bu^t_2)(CO)_8(PEt_3)_2]$ and $[Pt_2M_2(P_3C_2Bu^t_2)_2(CO)_6(PEt_3)_2]$, (M = Cr, Mo, W). Crystal and Molecular Structure of $[Pt_2W_2(P_3C_2Bu^t_2)_2(CO)_6(PEt_3)_2]$

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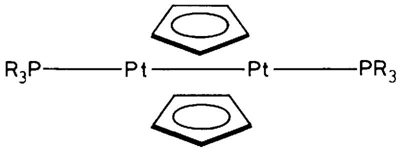
The two tetrametallic complexes $[Pt_2Cr_2(\eta^5\text{-}C_5H_5)_2(CO)_6(PEt_3)_2]$ and $[Pt_2W_2(\eta^5\text{-}P_3C_2Bu^t_2)_2(CO)_6(PEt_3)_2]$ have completely different molecular structures.

The isolobal concept[1] provides an important description of complex organometallic compounds and is a powerful aid to the planning of synthetic strategies.[2] Recently Hofmann and Schmidt[3] described the interesting isolobal analogy between the cyclopentadienyl anion $(C_5H_5)^-$ and the tricarbonyl metalate anions $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$, (M = Cr, Mo, W), in which the transition metals have a d^6 configuration.

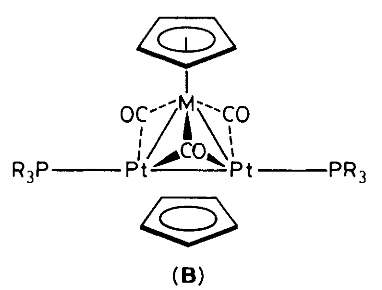
Structures in which the $C_5H_5^-$ and $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ fragments can replace each other are shown in (**A**)—(**C**).[4—6] The mononuclear systems $[M(PR_3)_2]^+$ (M = Ni, Cu, Rh), $[Ni(\eta^5\text{-}C_5H_5)(CO)]^+$, and $[Co(\eta^4\text{-}C_4Me_4)]^+$ can function as binding partners towards the $[M(\eta^5\text{-}C_5H_5)(CO)_3]^-$ fragment, where it has been recognised that the latter can function as a two-, four- or six-electron donor.[1,3,7—11]

In recent papers we have shown that the triphosphacyclopentadienyl ring $(P_3C_2Bu^t_2)$ (X) can act as an η^5-ligand in a variety of transition metal complexes typified by $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$,[12] $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$,[12] $[Cr(\eta^5\text{-}P_3C_2Bu^t_2)_2]$,[13] $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)]$,[14] $[Co(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^4\text{-}P_3C_2Bu^t_2H)]$,[15] $[Ni(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^3\text{-}P_2C_3Bu^t_3)]$,[16] and as an η^1-ligand in complexes of the type $[PtI(P_3C_2Bu^t_2)(PPh_3)_2]$, $[PtCl(P_3C_2Bu^t_2)(PEt_3)_2]$, and $[Pt(P_3C_2Bu^t_2)_2(PEt_3)_2]$.[17,18]

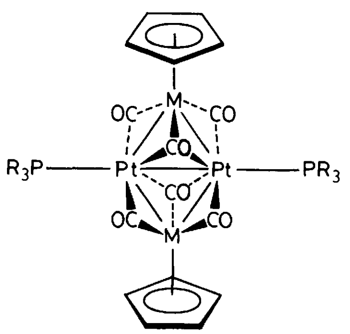
A further ligating feature, not available to the η^5-C_5H_5 analogues, is the use of the lone pair of electrons on one of the



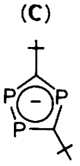
(**A**)



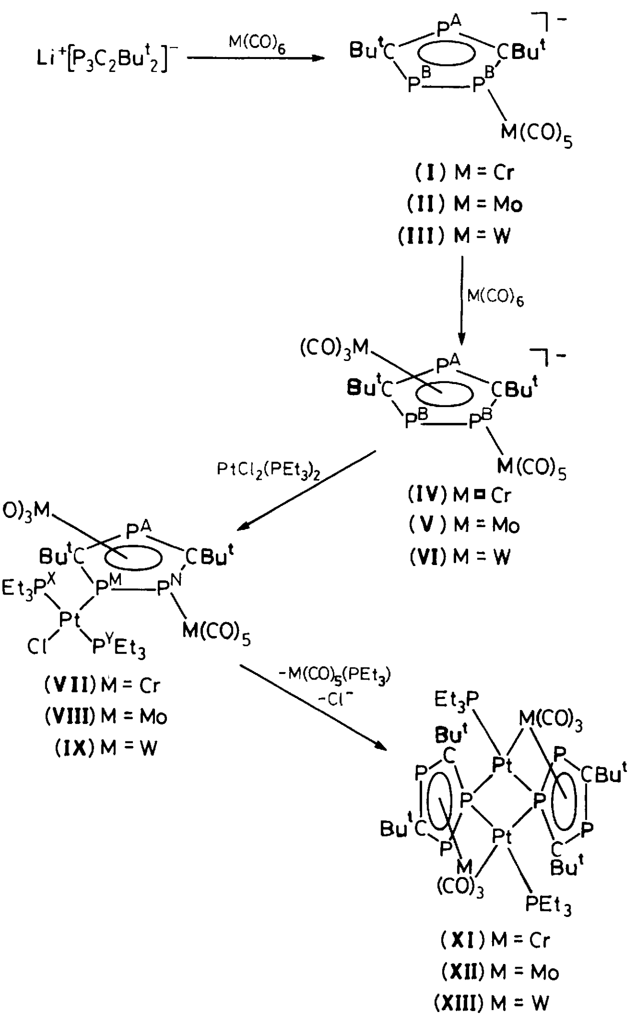
(**B**)



(**C**)



(X)



Scheme 1

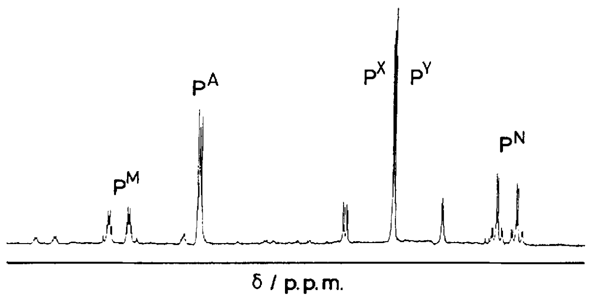


Figure 1. The $^{31}P\{^1H\}$ NMR spectrum of *trans*-$[PtCr_2Cl(\eta^1\text{-}\eta^5\text{-}P_3C_2Bu^t_2)(CO)_3(CO)_5(PEt_3)_2]$ (**VII**).

phosphorus atoms in the ring to interact with a second metal centre as in $[Fe(\eta^5\text{-}C_5H_5)(\eta^5\text{-}P_3C_2Bu^t_2)W(CO)_5]$.[14] We now describe further novel features of the ($\eta^5\text{-}P_3C_2Bu^t_2$) ring system that are distinct from its η^5-cyclopentadienyl analogue in its ligating behaviour towards transition metals.

Treatment of the lithium salt of $(P_3C_2Bu^t_2)^-$ in dimethoxyethane with an equivalent quantity of $[M(CO)_6]$ (M = Cr, Mo, W) gives the η^1-complexes $Li[M(CO)_5(\eta^1\text{-}P_3C_2Bu^t_2)]$, (**I**) M = Cr, (**II**) M = Mo, (**III**) M = W, which have not been isolated but their structures have been assigned on the basis of their ^{31}P NMR spectra.† At higher temperatures complexes (**I**)—(**III**) react further with $[M(CO)_6]$ to give the deep red coloured η^1-η^5-ligated complexes $Li[M(CO)_5M(CO)_3(\eta^1\text{-}\eta^5\text{-}P_3C_2Bu^t_2)]$, (**IV**) M = Cr, (**V**) M = Mo, and (**VI**) M = W (see Scheme 1),† which on treatment with $[PtCl_2(PEt_3)_2]$ for several days gave deep red complexes *trans*-$[PtM_2Cl(\eta^1\text{-}\eta^5\text{-}P_3C_2Bu^t_2)(CO)_3(CO)_5(PEt_3)_2]$, (**VII**) M = Cr, (**VIII**) M = Mo, and (**IX**) M = W. The $^{31}P\{^1H\}$ NMR spectrum of (**VII**) is presented in Figure 1. Treatment of the complex *trans*-$[PtCl(\eta^1\text{-}P_3C_2Bu^t_2)(PEt_3)_2]$,[18] (**X**), with $[M(CO)_6]$ at elevated temperatures also leads to the formation of (**VII**)—(**IX**).[19] Toluene solutions of complexes (**VII**)—(**IX**) undergo a further reaction and elimination of $[M(CO)_5(PEt_3)]$ to yield orange crystals of the dimeric clusters $[Pt_2M_2(P_3C_2Bu^t_2)_2(CO)_6(PEt_3)_2]$ as toluene solvates, (**XI**) M = Cr, (**XII**) M = Mo, (**XIII**) M = W [ν(CO), nujol mull, (**XI**) 1950s, 1890w, 1870w; (**XII**) 1950s, 1920w, br., 1890w, 1875m; (**XIII**) 1950s, 1890w, 1870m cm^{-1}].

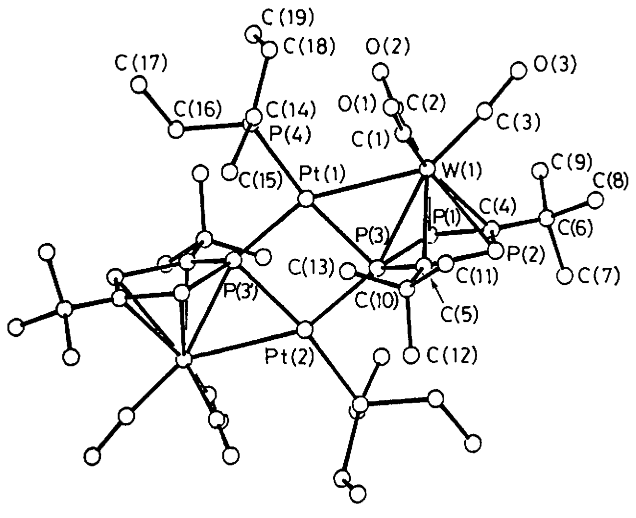


Figure 2. The molecular structure of $[Pt_2W_2(P_3C_2Bu^t_2)_2(CO)_6(PEt_3)_2]$ (**XIII**).

A single crystal *X*-ray structure determination on (**XIII**)‡ revealed the molecular structure shown in Figure 2. Interestingly the reaction of (**I**)—(**III**) with $[PtCl_2(PEt_3)_2]$ led to the loss of the $[M(CO)_5]$ fragment and formation of the known complex *trans*-$[PtCl(\eta^1\text{-}P_3C_2Bu^t_2)(PEt_3)_2]$ (**X**).[18]

The most interesting features of the structure of (**XIII**) are: (i) the bridging nature of the ($P_3C_2Bu^t_2$) rings with respect to the platinum atoms, (ii) the absence of any Pt–Pt bond, and (iii) unexpected differences compared to the known structure of $[Pt_2Cr_2(C_5H_5)_2(CO)_6(PEt_3)_2]$, (**XIV**), reported previously by Braunstein *et al.*[20] [see structure (**C**)].

An important factor responsible for the electronic relationship between $C_5H_5^-$ and the $[M(C_5H_5)(CO)_3]^-$ (M = Cr, Mo, W) systems relates to the HOMO 1a, and 1e orbitals of the latter which have d_{z^2}, $d_{x^2-y^2}$, and d_{xy} metal character and also contain bonding contributions from the π* of the 3 CO ligands mixed into these MOs. The areas of the wave functions of $[M(C_5H_5)(CO)_3]^-$ which are available for bonding to other fragments involve both the C atoms of the carbonyls *and* the metal centre of the second ML_n fragment[3] as found in (**C**) typified by the complex $[Pt_2Cr_2(C_5H_5)_2(CO)_6(PEt_3)_2]$, (**XIV**).

In (**XIII**), however, although it is potentially isolobal with (**XIV**), a different structure results because of the ready availability of the lone pair of electrons on each of the two directly bonded P atoms of the $P_3C_2Bu^t_2$ rings which are η^5-ligated to the $[W(CO)_3]$ units. In this case each Pt in (**XIII**) is directly bonded to tungsten and one phosphorus of the $P_3C_2Bu^t_2$ ring and the 3 COs attached to W play no bonding role towards the $[Pt(PEt_3)]$ moiety.

Similar structural differences are also to be expected in related complexes when the $P_3C_2Bu^t_2$ ring replaces its C_5H_5 analogue, and this is being studied further.

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† *$^{31}P\{^1H\}$ NMR data* (referenced to H_3PO_4), for (**I**): δP^A 162.3, δP^B 192.6 p.p.m., J_{pApB} 46 Hz; (**II**), δP^A 153.2, δP^B 186.5 p.p.m., J_{pApB} 45 Hz; (**III**), δP^A 245.1, δP^B 207.9 p.p.m., J_{pApB} 38 Hz. For (**IV**): δP^A 86.2, δP^B 80.5 p.p.m., J_{pApB} 45 Hz; (**V**), δP^A 86.8, δP^B 68.8 p.p.m., J_{pApB} 44 Hz; (**VI**), δP^A 65.4, δP^B 27.5 p.p.m., J_{pApB} 46 Hz. For (**VII**): δP^A 43.1 p.p.m., J_{pApM} 51, J_{pApN} 50 Hz; δP^M 55.5 p.p.m., $J_{\mathrm{PtP^M}}$ 3436, J_{pMpN} 456, J_{pMpA} 51 Hz; δP^N −5.7 p.p.m., $J_{\mathrm{PtP^N}}$ 176, J_{pNpM} 456, J_{pNpA} 35 Hz; δP^X 12.3 p.p.m., $J_{\mathrm{PtP^X}}$ 2270, J_{pXpM} 28 Hz; δP^Y 12.1 p.p.m., $J_{\mathrm{PtP^Y}}$ 2205, J_{pYpM} 28 Hz. For (**VIII**): δP^A 51.6 p.p.m., J_{PApM} 46, J_{pApN} 36 Hz; δP^M 49.0 p.p.m., $J_{\mathrm{PtP^M}}$ 3320, J_{pMpN} 461 Hz; δP^N 4.0 p.p.m., $J_{\mathrm{PtP^N}}$ 212, J_{pNpM} 458, J_{pNpA} 36 Hz; δP^X 11.1 p.p.m., $J_{\mathrm{PtP^X}}$ 2254, J_{pXpM} 23 Hz; δP^Y 16.8 p.p.m., $J_{\mathrm{PtP^Y}}$ 2300, J_{pYpM} 39 Hz. For (**IX**): δP^A 30.6 p.p.m., J_{pApM} 20, J_{pApN} 17 Hz; δP^M 26.7 p.p.m., $J_{\mathrm{PtP^M}}$ 3360, J_{pMpN} 445 Hz; δP^N 24.4 p.p.m., $J_{\mathrm{PtP^N}}$ 173, J_{pNpM} 451, J_{pNpA} 34 Hz; δP^X 10.9 p.p.m., $J_{\mathrm{PtP^X}}$ 2200, J_{pXpM} 23 Hz; δP^Y 8.2 p.p.m., $J_{\mathrm{PtP^Y}}$ 2304, J_{pYpM} 39 Hz. *$^{195}Pt\{^1H\}$ NMR data* (referenced to K_2PtCl_4) for (**VII**): δPt −2923.0 p.p.m., $J_{\mathrm{PtP^M}}$ 3450, $J_{\mathrm{PtP^N}}$ 234, $J_{\mathrm{PtP^X\ or\ p^Y}}$ 2261 Hz; for (**VIII**): δPt −2906.0 p.p.m., $J_{\mathrm{PtP^M}}$ 3283, $J_{\mathrm{PtP^N}}$ 210, $J_{\mathrm{PtP^X\ or\ p^Y}}$ 2206 Hz; for (**IX**): δPt −2941.0 p.p.m. $J_{\mathrm{PtP^M}}$ 3380, $J_{\mathrm{PtP^N}}$ 207, $J_{\mathrm{PtP^X\ or\ p^y}}$ 2306 Hz.

‡ *Crystal data* for $C_{38}H_{66}O_6P_8Pt_2W_2 \cdot C_7H_8$: M = 1716.8, monoclinic, space group $P2_1/n$, a = 16.011(4), b = 11.161(3), c = 17.225(5) Å, β = 113.05(2)°, U = 2832.5 Å^3, Z = 2, D_c = 2.01 g cm^{-3}. Data were collected using monochromated Mo-K_α radiation, λ = 0.71069 Å, μ = 93.8 cm^{-1} on an Enraf-Nonius CAD4 diffractometer. A total of 4169 unique reflections were measured and 2521 with $|F^2| > 3\sigma(F^2)$ used in the refinement. The structure was solved by routine heavy atom methods and non H-atoms refined by a full matrix least squares with only Pt and W atoms anisotropic. The final residuals were R = 0.042, R_w = 0.054. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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