

Structural Differences in $\eta^5\text{-C}_5\text{H}_5$ and $\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2$ Tetrametallic Complexes. Synthesis of $[\text{PtM}_2\text{Cl}(\text{P}_3\text{C}_2\text{Bu}^t_2)(\text{CO})_8(\text{PET}_3)_2]$ and $[\text{Pt}_2\text{M}_2(\text{P}_3\text{C}_2\text{Bu}^t_2)_2(\text{CO})_6(\text{PET}_3)_2]$, ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). Crystal and Molecular Structure of $[\text{Pt}_2\text{W}_2(\text{P}_3\text{C}_2\text{Bu}^t_2)_2(\text{CO})_6(\text{PET}_3)_2]$

Peter B. Hitchcock, Mohamed F. Meidine, John F. Nixon,* and Gary J. D. Sillett

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex, U.K.

The two tetrametallic complexes $[\text{Pt}_2\text{Cr}_2(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})_6(\text{PET}_3)_2]$ and $[\text{Pt}_2\text{W}_2(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2(\text{CO})_6(\text{PET}_3)_2]$ have completely different molecular structures.

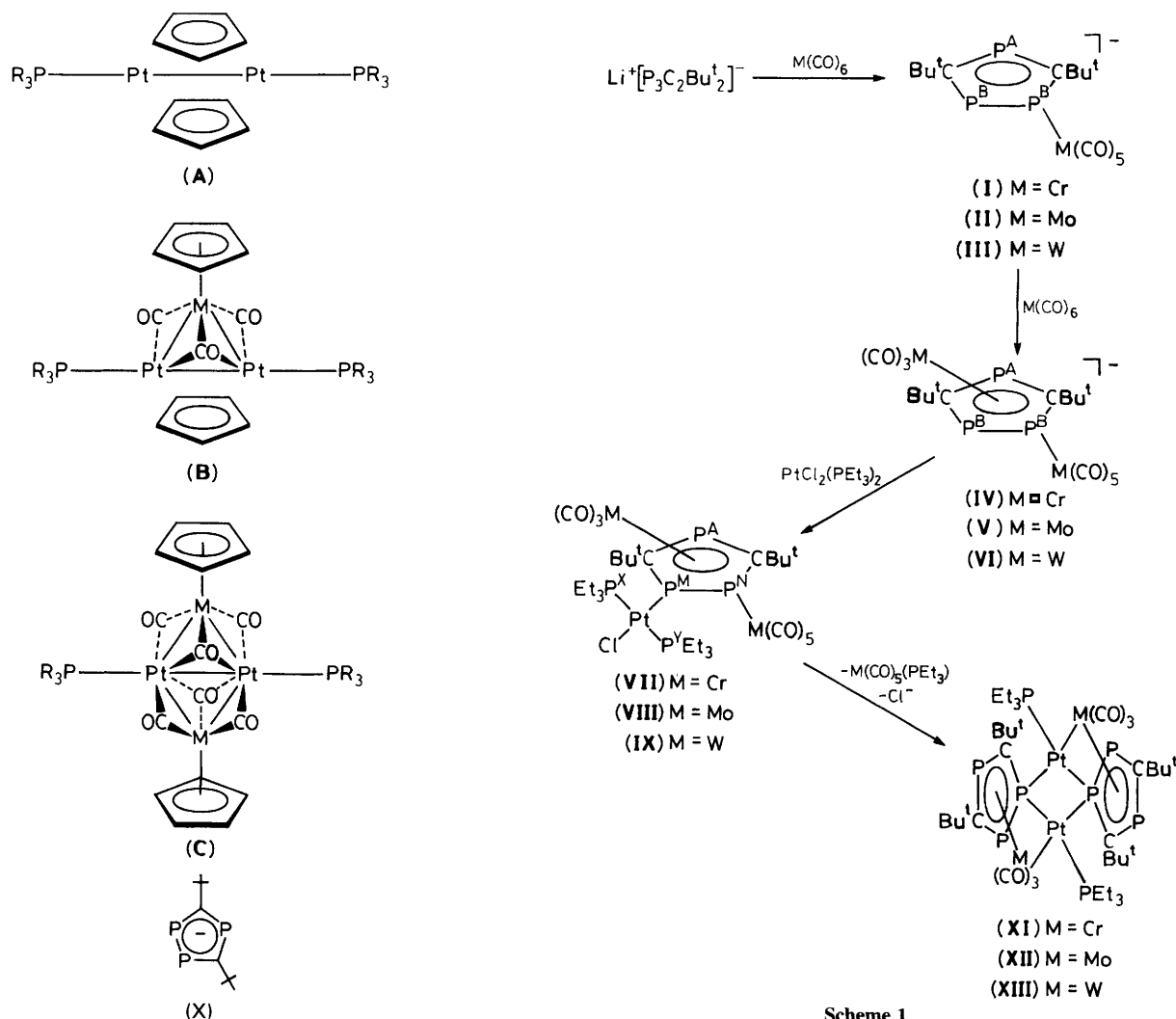
The isolobal concept¹ provides an important description of complex organometallic compounds and is a powerful aid to the planning of synthetic strategies.² Recently Hofmann and Schmidt³ described the interesting isolobal analogy between the cyclopentadienyl anion (C_5H_5^-) and the tricarbonyl metalate anions $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$, ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$), in which the transition metals have a d^6 configuration.

Structures in which the C_5H_5^- and $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ fragments can replace each other are shown in (A)–(C).^{4–6} The mononuclear systems $[\text{M}(\text{PR}_3)_2]^+$ ($\text{M} = \text{Ni}, \text{Cu}, \text{Rh}$), $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})]^+$, and $[\text{Co}(\eta^4\text{-C}_4\text{Me}_4)]^+$ can function as binding partners towards the $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ 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 ($\text{P}_3\text{C}_2\text{Bu}^t_2$) (X) can act as an η^5 -ligand in a variety of transition metal complexes typified by $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$,¹² $[\text{Fe}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\eta^5\text{-P}_2\text{C}_3\text{Bu}^t_3)]$,¹² $[\text{Cr}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)_2]$,¹³ $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)]$,¹⁴ $[\text{Co}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\eta^4\text{-P}_3\text{C}_2\text{Bu}^t_2\text{H})]$,¹⁵ $[\text{Ni}(\eta^5\text{-P}_3\text{C}_2\text{Bu}^t_2)(\eta^3\text{-P}_2\text{C}_3\text{Bu}^t_3)]$,¹⁶ and as an η^1 -ligand in complexes of the type $[\text{Pt}(\text{P}_3\text{C}_2\text{Bu}^t_2)(\text{PPh}_3)_2]$, $[\text{PtCl}(\text{P}_3\text{C}_2\text{Bu}^t_2)(\text{PET}_3)_2]$, and $[\text{Pt}(\text{P}_3\text{C}_2\text{Bu}^t_2)_2(\text{PET}_3)_2]$.^{17,18}

A further ligating feature, not available to the $\eta^5\text{-C}_5\text{H}_5$ analogues, is the use of the lone pair of electrons on one of the



Scheme 1

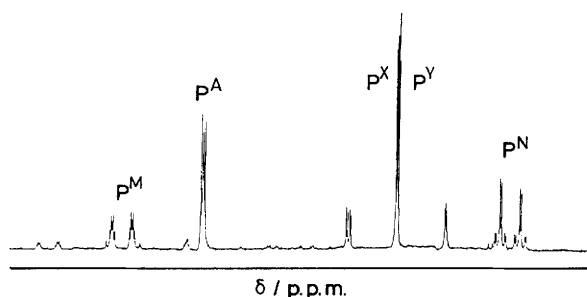


Figure 1. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of *trans*-[PtCr₂Cl(η¹-η⁵-P₃C₂Bu₂)(CO)₃(CO)₅(PEt₃)₂] (**VII**).

phosphorus atoms in the ring to interact with a second metal centre as in [Fe(η⁵-C₅H₅)(η⁵-P₃C₂Bu₂)W(CO)₅].¹⁴ We now describe further novel features of the (η⁵-P₃C₂Bu₂) ring system that are distinct from its η⁵-cyclopentadienyl analogue in its ligating behaviour towards transition metals.

Treatment of the lithium salt of (P₃C₂Bu₂)⁻ in dimethoxyethane with an equivalent quantity of [M(CO)₆] (M = Cr, Mo, W) gives the η¹-complexes Li[M(CO)₅(η¹-P₃C₂Bu₂)], (**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 η¹-η⁵-ligated complexes Li[M(CO)₅M(CO)₃(η¹-η⁵-P₃C₂Bu₂)], (**IV**) M = Cr, (**V**) M = Mo, and (**VI**) M = W (see Scheme 1),[†] which on treatment with [PtCl₂(PEt₃)₂] for several days gave deep red complexes *trans*-[PtM₂Cl(η¹-η⁵-P₃C₂Bu₂)(CO)₃(CO)₅(PEt₃)₂], (**VII**) M = Cr, (**VIII**) M = Mo, and (**IX**) M = W. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of (**VII**) is presented in Figure 1. Treatment of the complex *trans*-[PtCl(η¹-P₃C₂Bu₂)(PEt₃)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(PEt₃)] to yield orange crystals of the dimeric clusters [Pt₂M₂(P₃C₂Bu₂)₂(CO)₆(PEt₃)₂] as toluene solvates, (**XI**) M = Cr, (**XII**) M = Mo, (**XIII**) M = W [v(CO), nujol mull, (**XI**) 1950s, 1890w, 1870w; (**XII**) 1950s, 1920w, br., 1890w, 1875m; (**XIII**) 1950s, 1890w, 1870m cm⁻¹].

[†] $^{31}\text{P}\{^1\text{H}\}$ NMR data (referenced to H₃PO₄), 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*_{PtPM} 3436, *J*_{PtPN} 456, *J*_{PMPA} 51 Hz; δP^N -5.7 p.p.m., *J*_{PtPN} 176, *J*_{PtPM} 456, *J*_{PtPA} 35 Hz; δP^X 12.3 p.p.m., *J*_{PtPX} 2270, *J*_{PtPM} 28 Hz; δP^Y 12.1 p.p.m., *J*_{PtPY} 2205, *J*_{PtPM} 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*_{PtPM} 3320, *J*_{PtPN} 461 Hz; δP^N 4.0 p.p.m., *J*_{PtPN} 212, *J*_{PtPM} 458, *J*_{PtPA} 36 Hz; δP^X 11.1 p.p.m., *J*_{PtPX} 2254, *J*_{PtPM} 23 Hz; δP^Y 16.8 p.p.m., *J*_{PtPY} 2300, *J*_{PtPM} 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*_{PtPM} 3360, *J*_{PtPN} 445 Hz; δP^N 24.4 p.p.m., *J*_{PtPN} 173, *J*_{PtPM} 451, *J*_{PtPA} 34 Hz; δP^X 10.9 p.p.m., *J*_{PtPX} 2200, *J*_{PtPM} 23 Hz; δP^Y 8.2 p.p.m., *J*_{PtPY} 2304, *J*_{PtPM} 39 Hz. ¹⁹⁵Pt{¹H} NMR data (referenced to K₂PtCl₄) for (**VII**): δPt -2923.0 p.p.m., *J*_{PtPM} 3450, *J*_{PtPN} 234, *J*_{PtPX} or *PtPY 2261 Hz; for (**VIII**): δPt -2906.0 p.p.m., *J*_{PtPM} 3283, *J*_{PtPN} 210, *J*_{PtPX} or *PtPY 2206 Hz; for (**IX**): δPt -2941.0 p.p.m., *J*_{PtPM} 3380, *J*_{PtPN} 207, *J*_{PtPX} or *PtPY 2306 Hz.***

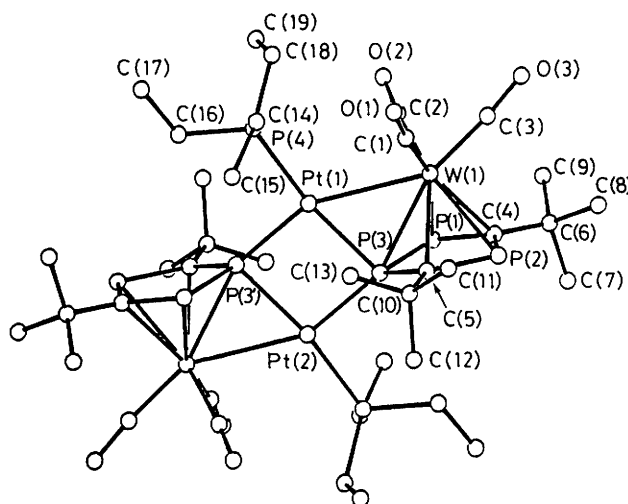


Figure 2. The molecular structure of [Pt₂W₂(P₃C₂Bu₂)₂(CO)₆(PEt₃)₂] (**XIII**).

A single crystal X-ray structure determination on (**XIII**)[‡] revealed the molecular structure shown in Figure 2. Interestingly the reaction of (**I**)–(**III**) with [PtCl₂(PEt₃)₂] led to the loss of the [M(CO)₅] fragment and formation of the known complex *trans*-[PtCl(η¹-P₃C₂Bu₂)(PEt₃)₂] (**X**).¹⁸

The most interesting features of the structure of (**XIII**) are: (i) the bridging nature of the (P₃C₂Bu₂) 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 [Pt₂Cr₂(C₅H₅)₂(CO)₆(PEt₃)₂], (**XIV**), reported previously by Braunstein *et al.*²⁰ [see structure (C)].

An important factor responsible for the electronic relationship between C₅H₅⁻ and the [M(C₅H₅)(CO)₃]⁻ (M = Cr, Mo, W) systems relates to the HOMO 1a, and 1e orbitals of the latter which have d_{z²}, d_{x²-y²}, 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(C₅H₅)(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 fragment³ as found in (C) typified by the complex [Pt₂Cr₂(C₅H₅)₂(CO)₆(PEt₃)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 P₃C₂Bu₂ rings which are η⁵-ligated to the [W(CO)₃] units. In this case each Pt in (**XIII**) is directly bonded to tungsten and one phosphorus of the P₃C₂Bu₂ ring and the 3 COs attached to W play no bonding role towards the [Pt(PEt₃)] moiety.

Similar structural differences are also to be expected in related complexes when the P₃C₂Bu₂ ring replaces its C₅H₅ analogue, and this is being studied further.

[‡] Crystal data for C₃₈H₆₆O₆P₈Pt₂W₂·C₂H₈: M = 1716.8, monoclinic, space group P2₁/n, a = 16.011(4), b = 11.161(3), c = 17.225(5) Å, β = 113.05(2)°, U = 2832.5 Å³, Z = 2, D_c = 2.01 g cm⁻³. Data were collected using monochromated Mo-Kα 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 |F²| > 3σ(F²) 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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References

- 1 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.
- 2 F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 85 and references therein.
- 3 P. Hofmann and H. R. Schmidt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 837.
- 4 H. Werner, *Adv. Organomet. Chem.*, 1981, **19**, 155.
- 5 H. Werner, H.-J. Kraus, and P. Thometzek, *Chem. Ber.*, 1982, **115**, 2914.
- 6 R. Bender, P. Braunstein, J.-M. Jud, and Y. Dusauroy, *Inorg. Chem.*, 1983, **22**, 3394.
- 7 T. Madach and H. Vahrenkamp, *Chem. Ber.*, 1980, **113**, 2675.
- 8 L. Carlton, W. E. Lindsell, K. J. McCullough, and P. N. Preston, *Organometallics*, 1985, **4**, 1138.
- 9 L. Carlton, W. E. Lindsell, K. J. McCullough, and P. N. Preston, *J. Chem. Soc. Dalton Trans.*, 1984, 1693.
- 10 P. Braunstein, J. Fischer, D. Matt, and M. Pfeffer, *J. Am. Chem. Soc.*, 1984, **106**, 410.
- 11 P. Härter, H. Pfisterer, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 839.
- 12 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1987, 1146.
- 13 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **356**, C1.
- 14 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1988, **344**, C37.
- 15 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Chem. Soc., Chem. Commun.*, 1988, 819.
- 16 R. Bartsch, P. B. Hitchcock, and J. F. Nixon, *J. Organomet. Chem.*, 1989, **373**, C17.
- 17 R. Bartsch, D. Carmichael, P. B. Hitchcock, M. F. Meidine, J. F. Nixon, and G. J. D. Sillett, *J. Chem. Soc., Chem. Commun.*, 1988, 1615.
- 18 P. B. Hitchcock, J. F. Nixon, and G. J. D. Sillett, *New J. Chem.*, 1989, **13**, 353.
- 19 P. B. Hitchcock, J. F. Nixon, and G. J. D. Sillett, unpublished results.
- 20 R. Bender, P. Braunstein, J.-M. Jud, and Y. Dusauroy, *Inorg. Chem.*, 1984, **23**, 4489.