First syntheses, structural and theoretical studies of η^5-1,2,4-triphosphole metal tricarbonyl complexes of Cr, Mo and W

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Evidence for an η^5-ligated 1,2,4-triphosphole ring system which exhibits some aromatic character is presented *via* the first syntheses, structural and theoretical studies of η^5-1,2,4-triphosphole metal tricarbonyl complexes of zero-valent Cr, Mo and W.

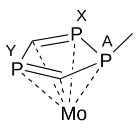
Although phospholes, RPC_4H_4, are known to be non-aromatic ring systems,[1] it has recently been shown by theoretical calculations[2] that stepwise replacement of the C=C double bonds by conjugatively similar P=C units[3] increases the planarity and aromatic character of the five-membered ring system owing to a combination of ring strain effects and a lower inversion barrier at the $\sigma^3\lambda^3$-phosphorus. Thus, the recently synthesized[4] di-*tert*-butyl-1,2,4-triphosphole $P_3C_2Bu^t_2CH(SiMe_3)_2$ **1** (which to date is the only known triphosphole), is expected to exhibit greater aromatic character than the parent phosphole. Here we present the first results which support this proposal exemplified by (*i*) the synthesis and structural characterisation of the compounds $[M(CO)_3\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ (M = Cr **2**, Mo **3**, W **4**) in which the ring acts as a 6e donor to the metal and (*ii*) theoretical calculations on the parent 1,2,4-triphosphole $HP_3C_2H_2$ **5** and its hypothetical complex $[M(CO)_3(\eta^5\text{-}HP_3C_2H_2)]$ (M = Mo) **6**. These triphosphole metal tricarbonyl complexes can therefore be considered as being closely related to the long-known $[M(CO)_3(\eta^6\text{-arene})]$ compounds.

Treatment of $P_3C_2Bu^t_2CH(SiMe_3)_2$ **1** with $[M(CO)_4(\eta^4\text{-nbd})]$ (M = Cr, Mo; nbd = norbornadiene) in tetrahydrofuran affords the red complexes $[M(CO)_3\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ (M = Cr **2**, Mo **3**).† Likewise reacting **1** with $[W(CO)_5(thf)]$ gives $[W(CO)_3\{\eta^5\text{-}P_3C_2Bu^t_2CH(SiMe_3)_2\}]$ **4**. Complexes **2** and **3** were also prepared directly from **1** and the appropriate $[M(CO)_3(\eta^6\text{-chp})]$ complex, (M = Cr, Mo; chp = cycloheptatriene).

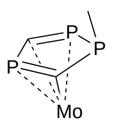
The $^{31}P\{^1H\}$ NMR spectra of **2–4**† each showed the characteristic pattern of lines expected for [AXY] spin systems, significantly chemically shifted from **1** but with $^1J_{P^AP^X}$, $^2J_{P^AP^Y}$ and $^2J_{P^XP^Y}$ coupling constants similar in magnitude to values found for the free di-*tert*-butyl-1,2,4-triphosphole **1**.[4]

Compounds **2** and **3** were also fully structurally characterised by single-crystal X-ray diffraction studies‡ and the molecular structure of **3** is shown in Fig. 1. Specially noteworthy is the observation that in both **2** and **3** the metal tricarbonyl fragment is coordinated to all five atoms of the 1,2,4-triphosphole ring system which is planar. The distances between the metal and the plane of the ring defined by P(1)P(2)P(3)C(1)C(2) are 1.799 and 1.962 Å for **2** and **3** respectively, and the sums of the bond angles around the formally sp^3-hybridised phosphorus atom are 356.6° for **2** and 352.2° for **3**. The metal to $\sigma^3\lambda^3$-phosphorus [P(2)] distance in both structures **2** and **3** is significantly shorter than to the $\sigma^2\lambda^3$ phosphorus ring atoms P(1) and P(3). The 1,2,4-triphosphole rings in complexes **2–4** can therefore be considered as donating six electrons to the metal centre. As expected the P–C and P···P bond lengths within the coordinated 1,2,4-triphosphole lie between the values expected for single and double bonds, and are quite close to those found in both the penta- and hexa-phosphaferrocenes $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ and $[Fe(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ which contain the η^5-ligated aromatic di- and tri-phospholyl anions.[5] Prior to this work transition-metal complexes of phospholes had only involved ligation of the ring *via* the phosphorus lone pair electrons and/or through the diene system.[1]

We have also carried out theoretical studies in order to better understand the interaction between the 1,2,4-triphosphole ring system and the group 6 metal tricarbonyl moieties. Geometry optimization§ of the tricarbonyl Mo complex **6** of the hypothetical H-substituted triphosphole $HP_3C_2H_2$ **5** resulted in two different structures at the Hartree–Fock level (HF) of the theory. One of them involved η^5-ligation of the ring to the metal (A) while the other utilised η^4-coordination (B). The η^4-coordinated compound was more stable only by 0.02 kcal mol^{-1} (1 cal = 4.184 J) however on reoptimization using the density functional method, only the η^5-structure was obtained, even when starting from the η^4-HF optimized geometry. Although only the η^5-complex was also obtained experimentally (*vide infra*), in agreement with the density functional calculations, this computational behaviour indicates that the η^4-complex should not be much less stable than its η^5-counterpart, and furthermore the 1,2,4-triphosphole ring



A



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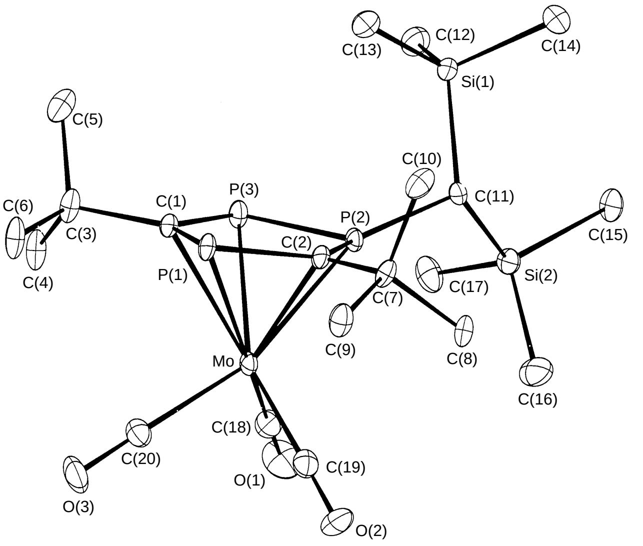

Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): P(2)–P(3) 2.105(3), P(2)–C(2) 1.745(7), P(3)–C(1) 1.767(7), P(1)–C(2) 1.761(7), P(1)–C(1) 1.777(8), P(2)–C(3) 1.799(7); P(2)–P(3)–C(1) 94.2(3), P(1)–C(1)–P(3) 124.1(4), C(1)–P(1)–C(2) 99.6(3), P(1)–C(2)–P(2) 116.6(4), P(3)–P(2)–C(2) 105.5(3), P(3)–P(2)–C(3) 120.7(3), C(2)–P(2)–C(3) 126.0(4).

Table 1 Experimental (X-ray), HF and B3LYP optimized structural parameters (in Å) and Wiberg bond indices for 1,2,4-triphosphole **5** and its $Mo(CO)_3$ complex **6**

	1,2,4-Triphosphole **5**				$Mo(CO)_3$ complex **6**			
	Exptl.[a]	HF	B3LYP	I_{Wib}	Exptl.[b]	HF	B3LYP	I_{Wib}
P^1P^2	2.098	2.173	2.187	1.065	2.105	2.168	2.204	1.017
P^2C^3	1.734	1.791	1.780	1.031	1.745	1.782	1.794	1.006
C^3P^4	1.720	1.672	1.710	1.667	1.761	1.726	1.736	1.278
P^4C^5	1.763	1.803	1.797	1.020	1.777	1.767	1.798	1.051
C^5P^1	1.718	1.675	1.713	1.707	1.767	1.734	1.739	1.315
MoP_1		—	—	—	2.585	2.652	2.525	0.388
MoP_2		—	—	—	2.424	2.545	2.654	0.328
MoC_3		—	—	—	2.472	2.374	2.691	0.321
MoP_4		—	—	—	2.609	2.599	2.514	0.403
MoC_5		—	—	—	2.426	2.407	2.784	0.288

[a] X-Ray structural data for **1** from ref. 4. [b] X-Ray structural data refers to complex **3**.

systems are borderline cases between aromatic and non-aromatic molecules. Interestingly attempts to synthesise complexes involving different ligating modes of the di-*tert*-butyl-1,2,4-triphosphole ring, for example $[M(CO)_5(\eta^1\text{-}RP_3C_2Bu^t{}_2)]$ or $[M(CO)_4(\eta^4\text{-}RP_3C_2Bu^t{}_2)]$ [R = $CH(SiMe_3)_2$; M = Cr, Mo, W] using either $[M(CO)_5(thf)]$, $[M(CO)_4(\eta^4\text{-nbd})]$, or $[M(CO)_3(\eta^6\text{-chp})]$ as precursors, only led to the tricarbonyl complexes **2**–**4** and no other intermediates could be detected when the reactions were carefully monitored by ^{31}P NMR spectroscopy.

Calculations on the hypothetical complex $[Mo(CO)_3(\eta^5\text{-}HP_3C_2H_2)]$ **6** show that it exhibits remarkable stability towards dissociation to 1,2,4-triphosphole **5** and $Mo(CO)_3$ (39.91 and 27.22 kcal mol^{-1} at the HF and DFT levels respectively); and for comparison the stabilization of the corresponding benzene complex $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$ was calculated to be 33.82 and 24.21 kcal mol^{-1} respectively at the above two levels.

The calculated structural characteristics§ (Table 1) of the η^5-complex (A) are comparable to the values obtained experimentally from the X-ray structural analyses on **2** and **3**, however, the P···P separation and some of the Mo–P and Mo–C bond lengths are not reproduced particularly well by the calculations. Similarly, the structures of the parent triphosphole calculated at the HF and B3LYP levels had considerably longer single bond lengths than in the X-ray structure of the alkylated derivative (Table 1). This behaviour is in accordance with an increased aromaticity, due to the alkylation. Indeed, the bis(trimethylsilyl)methyl group has a partial flattening effect on the $\sigma^3.\lambda^3$-phosphorus.[6] The increased planarity then enhances the aromaticity of the system. Changes in bond lengths upon complexation of the 1,2,4-triphosphole ring to the metal centre are well accounted for by the calculations, *i.e.* the formal double bonds become slightly longer, while the other bond lengths only undergo small changes. The η^5-nature of complex **6** is also clearly shown by the Wiberg covalent bond indices[7] listed in Table 1, from which it is evident that all Mo–C and Mo–P indices are of similar magnitude. Comparing the parent and the complexed triphosphole, the largest change is again in the Wiberg indices of the formal double bond, in accordance with its increasing length noted above.

The present results clearly provide the first evidence for an η^5-ligated 1,2,4-triphosphole ring system which exhibits some aromatic character, and complements the recently reported[8] ready displacement of naphthalene by the di-*tert*-butyl-1,2,4-triphosphole **1** from the zerovalent ruthenium complex $[Ru(\eta^6\text{-}C_{10}H_8)(\eta^4\text{-}C_8H_{12})]$ to afford $[Ru\{\eta^5\text{-}P_3C_2Bu^t{}_2[CH(SiMe_3)_2]\}(\eta^4\text{-}C_8H_{12})]$, in which the triphosphole also behaves as a 6e donor.

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Footnotes

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† *NMR data*. **2**: $\delta_P{}^A$ −59.2, $\delta_P{}^X$ 106.6, $\delta_P{}^Y$ 35.6; $^1J_{P_AP_X}$ 502.9, $^2J_{P_AP_Y}$ 32.6, $^2J_{P_XP_Y}$ 54.9. **3**: $\delta_P{}^A$ −44.4, $\delta_P{}^X$ 99.8, $\delta_P{}^Y$ 46.9; $^1J_{P_AP_X}$ 507.7, $^2J_{P_AP_Y}$ 30.5, $^2J_{P_XP_Y}$ 50.5. **4** $\delta_P{}^A$ −72.8, $\delta_P{}^X$ 76.3, $\delta_P{}^Y$ 24.2; $^1J_{P_AP_X}$ 496.8, $^2J_{P_AP_Y}$ 31.4, $^2J_{P_XP_Y}$ 53.4. (*J* in Hz.)

‡ *Crystal data*: **2**: T = 173 K; $C_{20}H_{37}CrO_3P_3Si_2$, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.858(4), b = 16.288(5), c = 16.972(3) Å, Z = 4, D_c = 1.28 g cm^{-3}, U = 2725(2) Å^3, Mo-Kα (λ = 0.710 73 Å), $F(000)$ = 1112, crystal dimensions 0.40 × 0.40 × 0.25 mm, the structure was solved by direct methods and refined to R_1 = 0.078, $wR2$ = 0.215 for 2425 observed reflections with $I > 2\sigma(I)$ (total unique reflections 2708), no of parameters = 262, on an Enraf-Nonius CAD4 diffractometer. Max., min. residual electron density = 0.78, −1.69 e Å^{-3} (near Cr), programs used SHELXS-86, SHELXL-93, MolEN.

3: $C_{20}H_{37}MoO_3P_3Si_2$, monoclinic, space group $P2_1/n$ (no. 14), a = 9.704(3), b = 16.558(8), c = 17.040(4) Å, β = 95.58(2)°, Z = 4, D_c = 1.39 g cm^{-3}, U = 2725(2) Å^3, $F(000)$ = 1184, crystal dimensions 0.40 × 0.40 × 0.20 mm, other details as above; R_1 = 0.065, $wR2$ = 0.160 for 3772 observed reflections (total unique reflections 4777), no of parameters = 262. Max., min residual electron density = 1.31, −1.04 e Å^{-3}.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/454.

§ Please consult the authors for full details of the calculations.

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