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A comparison of $C_3R_3P_3$ and $C_6R_3H_3$ as ligands using photoelectron spectroscopy and density functional theory

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Photoelectron spectra have been recorded for $[M(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$ (M = Cr, Mo or W) and $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t_3H_3)]$. They are assigned by comparison with analogous spectra and density functional calculations. The phospha-arene complexes show a higher first IE than carbocyclic analogues. Electronic structure analysis indicates stronger bonding in the former as a result of greater metal–ligand back donation to the lower lying LUMOs of the P substituted ring.

Introduction

The past decade has seen the rapid development of a rich new area of organometallic chemistry in which phosphorus atoms replace CH fragments in the more familiar unsaturated organic ligands. There is now an extensive range of phospha-organometallic compounds containing phospha-alkynes, -alkenes, -dienes, -allyls, -cyclobutadienes, -cyclopentadienyls and -arenes as well as tetraphospha-cubanes and -barrelenes. The area has recently been comprehensively reviewed.[1,2]

It is of interest to compare the relative bonding properties of unsaturated organic and phospha-organic ring systems towards main group and transition metals. To date, results of theoretical and photoelectron spectroscopic studies[3] on cyclobutadiene metal complexes of the type $[Fe(\eta^4\text{-}C_4H_4)(CO)_3]$ and $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_4H_4)]$ have been compared with their 1,3-diphosphacyclobutadiene analogues, $[Fe(\eta^4\text{-}C_2Bu^t_2P_2)(CO)_3]$ and $[Co(\eta^5\text{-}C_5H_5)(\eta^4\text{-}C_2Bu^t_2P_2)]$ and have established a significantly stronger π interaction between the metal and the phosphorus-containing ring system.

The very recently synthesized 1,3,5-triphosphabenzene ring system $C_3Bu^t_3P_3$,[4] whose structure and He I photoelectron spectra have been determined,[5] together with the availablility of η^6 complexes of the type $[M(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$ (M = Mo or W),[6] has enabled us to carry out similar comparative studies with complexes of the corresponding η^6-ligated 1,3,5-tri-*tert*-butylbenzene, $C_3H_3Bu^t_3$, which is the subject of this paper. Comparative studies on complexes of the type $[In(\eta^5\text{-}C_5H_5)]$ with $[In(\eta^5\text{-}C_3Bu^t_3P_2)]$ and $[In(\eta^5\text{-}C_2Bu^t_2P_3)]$, as well as $[M(\eta^5\text{-}C_5H_5)_2]$ (M = Fe or Ni), with $[M'(\eta^5\text{-}C_3Bu^t_3P_2)_2]$ (M′ = Ni, Pd or Pt), will be the subject of future publications.[7,8]

Experimental

Synthesis

All experiments were carried out under an inert atmosphere of Ar or N_2 using standard Schlenk and glove-box techniques. Solvents were pre-dried and distilled from appropriate drying agents under an inert atmosphere. NMR spectra were acquired at room temperature on a Bruker Avance 300DPX spectrometer and referenced to the residual proton/carbon shifts in the internal deuteriated solvent (^1H and ^{13}C) or external H_3PO_4 (^{31}P). Mass spectra were acquired on a VG AutoSpec mass spectrometer operating in EI mode, solution infrared spectra in cyclohexane on a Perkin-Elmer 1710 Infrared Fourier Transform spectrometer using a Graseby-Specac solution IR cell with CaF_2 windows. Elemental analysis was performed by MEDAC LTD., UK. 1,3,5-Tri-*tert*-butylbenzene (Aldrich, 97%) was sublimed prior to use. 2,4,6-Tri-*tert*-butyl-1,3,5-triphosphabenzene[4] and $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$[4] were prepared in accordance with the literature, $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t_3H_3)]$ prepared through a modification of the literature procedure[9] as described below.

$[Mo(CO)_3(\eta^6\text{-}C_6Bu^t_3H_3)]$. The compound $[Mo(CO)_3(CH_3CN)_3]$ (0.493 g, 1.63 mmol) and $C_6Bu^t_3H_3$ (0.813 g, 3.30 mmol) were refluxed in hexane (40 mL) for 14 h. The reaction mixture was filtered to afford a yellow solution. Removal of the solvent *in vacuo* yielded a yellow solid. Excess of $C_6Bu^t_3H_3$ was sublimed out at 40 °C, 3×10^{-6} mbar to leave $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t_3H_3)]$ as a yellow powder (0.140 g, 20%).

The compound $[W(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$ was prepared on a similar scale to that of the previously reported synthesis,[6] however, it was necessary to heat the THF solution of $[W(CO)_3(\eta^6\text{-}C_6H_5Me)]$ and $C_3Bu^t_3P_3$ at 40 °C for 2.5 d in order to drive the reaction to completion.

$[Cr(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$. The compound $[Cr(CO)_6]$ (1.10 g, 5.00 mmol) and 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (0.500 g, 1.67 mmol) were combined and di-*n*-butyl ether (50 mL) was added. The reaction mixture was refluxed for a total of 25 h during which time the sublimed $[Cr(CO)_6]$ was washed down periodically. The reaction mixture was initially orange but became deep red after 8 h. Following filtration, the solvent was removed *in vacuo* at 40 °C to yield a dark orange gum which was dried *in vacuo* for 8 h. A large amount of unchanged $[Cr(CO)_6]$ sublimed out and that remaining was sublimed onto a liquid nitrogen cooled cold finger by heating at 50 °C. The product was extracted with pentane (25 mL), filtered and the solvent removed *in vacuo*. The resulting orange solid was again extracted with pentane (25 mL), filtered and concentrated. The compound $[Cr(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$ precipitated as an orange crystalline solid at −44 °C. The supernatant was decanted and the product washed with pentane (2 mL) at −60 °C. The combined supernatant and washings were concentrated to obtain a second crop of crystals at −44 °C. The product was dried

Table 1 Calculated bond distances (Å) and angles (°) for $C_3H_3P_3$, $C_3Bu^t{}_3P_3$, $[M(CO)_3(\eta^6\text{-}C_3H_3P_3)]$ (M = Cr, Mo or W), $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$, $C_6Bu^t{}_3H_3$ and $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ and crystallographic data for $C_3Bu^t{}_3P_3$[5] and $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$.[9]

	Cr $C_3H_3P_3$ Calc.	Mo $C_3H_3P_3$ Calc.	W $C_3H_3P_3$ Calc.	$C_3H_3P_3$ Calc.	Mo $C_3Bu^t{}_3P_3$ Calc.	$C_3Bu^t{}_3P_3$ Calc.	$C_3Bu^t{}_3P_3$ Exp.
M–P	2.453	2.570	2.611		2.574		
M–C	2.259	2.390	2.456		2.425		
C–P	1.754	1.760	1.763	1.737	1.773	1.745	1.719(4)–1.729(5)
M–CO	1.821	1.978	2.015		1.970		
C–O	1.145	1.154	1.154		1.157		
C–P–C	103.2	103.8	104.3	105.4	107.2	108.6	109.0(2)–109.6(2)
P–C–P	136.7	136.1	135.5	134.6	132.8	131.4	130.3(3)–130.9(3)

	Mo $C_6Bu^t{}_3H_3$ Calc.	Mo $C_6Bu^t{}_3H_3$ Exp.	$C_6Bu^t{}_3H_3$ Calc.
Mo–C(Bu^t)	2.376	2.394(3)	
Mo–C(H)	2.323	2.394(3)	
C–C	1.413	1.411(4)	1.39
Mo–CO	1.947	1.949(3)	
C–O	1.163	1.153(4)	
C–C(H)–C	122.9		121.8
C–C(Bu^t)–C	116.9		118.2

in vacuo (0.215 g, 30%). It was possible slowly to sublime the product without decomposition at 75 °C, 5×10^{-7} mbar. ^1H NMR (300.130 MHz, C_6D_6): δ 1.38 (s, $C(CH_3)_3$). $^{13}C\text{-}\{^1H\}$ NMR (75.468 MHz, C_6D_6): δ 227.4 (s, CO), 134.0 (td, $^1J_{PC}$ 84.3, $^3J_{PC}$ 3.7, ring C), 41.5 (t, $^2J_{PC}$ 21.9, *C*(CH_3)) and 35.5 (t, $^3J_{PC}$ 13.0 Hz, C(*C*H_3)). $^{31}P\text{-}\{^1H\}$ NMR (121.5 MHz, C_6D_6): δ 66.5 (s, ring P). IR (cyclohexane): $\tilde{\nu}_{CO} = 1979$s and 1926s cm^{-1}. MS (EI+): *m*/*z* 436 [M^+], 408 [$M - CO^+$], 380 [$M - 2CO^+$] and 352 [$M - 3CO^+$]. Calc. for $C_{18}H_{27}CrO_3P_3$: C, 49.55; H, 6.24. Found: C, 49.28; H, 6.39%.

Photoelectron spectroscopy

Photoelectron spectra were measured using a PES laboratories 0078 spectrometer interfaced with an Atari microprocessor. Spectra were calibrated with He, Xe and N_2. Spectra for all three $[M(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$ were difficult to acquire. As the temperature was raised, counts became evident around 90 °C. However, as the temperature was raised further in an attempt to attain counting rates of over 100 counts per second on the main band the signal (including the helium self ionisation band) disappeared. Plenty of sample remained and there was no decomposition. The spectra were therefore acquired at a low counting rate holding the temperature between 90 and 95 °C. The tendency of these complexes to capture electrons prevented acquisition of a He II spectrum. In contrast, measurement of the PE spectrum of $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ was routine.

Theoretical methods

All calculations were performed using density functional methods of the Amsterdam Density Functional package (Version 2.3).[10] The basis set used triple-ζ accuracy sets of Slater type orbitals, with relativistic corrections, with a single polarisation functional added to the main group atoms. The cores of the atoms were frozen [C (1s), P (2p), Cr (2p), Mo(3d), W (5p)]. The GGA (non-local) method was used, using Vosko, Wilk and Nusair's local exchange correlation[11] with non-local-exchange corrections by Becke[12] and non-local correlation corrections by Perdew.[13] The non-local correction terms were not utilised in calculating gradients during geometry optimisations. Vertical ionisation energies were estimated, using the optimised structure, from the difference between the total energy for the molecule and that for the molecular ion in the appropriate state. Convergence was most readily achieved for the ion states when the input basis function for the SCF calculation was the MOs of the molecular calculation. This also enabled a ready check on how precisely the "hole" in the ion could be described as a single MO in the molecule.

Fragment analyses were carried out on $[M(CO)_3(\eta^6\text{-}C_3H_3P_3)]$ (M = Cr, Mo or W), $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$ and $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$. This involved single point calculations using the MOs of the $M(CO)_3$ and ring fragments as the basis set for the molecular calculations. The fragments retain the geometries found for the optimised molecular structures.

Results and discussion

Synthetic strategy for forming triphosphabenzenes and their complexes requires the presence of bulky groups such as a *tert*-butyl attached to the ring carbons. Computational simplicity and efficiency favours study of model systems where hydrogens replace these bulky groups. However, a direct comparison between say $C_3Bu^t{}_3P_3$ and C_6H_6 would leave unresolved the question as to whether differences were due to ring P atoms or the Bu^t substituents. In this study we adopt the methodology of effecting a full experimental and theoretical comparison for $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$ and $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$, and of studying the experimental trends within Group 6 metals on the compounds $[M(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$ (M = Cr, Mo or W) and the theoretical trends on the model systems $[M(CO)_3(\eta^6\text{-}C_3H_3P_3)]$.

The ligands

Structural studies. Geometry optimisation of $C_3H_3P_3$, $C_3Bu^t{}_3P_3$, C_6H_6 and $C_6Bu^t{}_3H_3$ gave the distances and angles reported in Table 1 together with the published experimental data for $C_3Bu^t{}_3P_3$. The agreement between calculated and experimental results is good, in particular the non-hexagonal nature of the C_3P_3 ring is well reproduced, and the C–P bond length is predicted within 3σ of the experimental value. A comparison of calculated values for $C_3H_3P_3$ and $C_3Bu^t{}_3P_3$ shows that introduction of the Bu^t groups slightly lengthens the P–C distances and also reduces the P–C–P angles and increases the C–P–C angles. A similar distortion from 120° was found for $C_6Bu^t{}_3H_3$. Calculations on (HCP) trimers have been published recently by Schleyer and co-workers.[14]

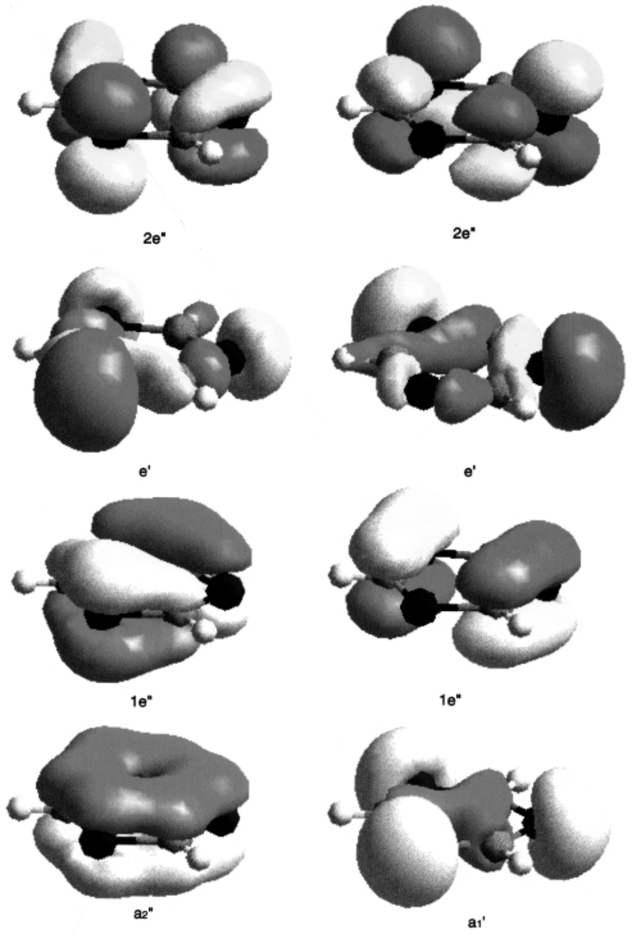

Fig. 1 Frontier orbitals of $C_3H_3P_3$.

Electronic structure. The frontier orbitals calculated for $C_3P_3H_3$ are represented in Fig. 1. The orbital structure of $C_3Bu^t_3P_3$ has been established in a PE and theoretical study by Gleiter *et al.*[5] The e(π) ring orbitals and e(σ) combination of phosphorus "lone pairs" lie close in energy and give rise to a single complex band in the PE spectrum with vertical ionisation energy (IE) of 8.2 and 8.3 eV. The next ionisation at 10.0 eV, a shoulder on the main spectral band, is assigned to the ring $a_1(\pi)$ ionisation. Ionisation from the $a_1(\sigma)$ combination of phosphorus lone pairs cannot be distinguished in the spectrum, and Gleiter *et al.* give no orbital energy for this MO.

Fig. 2 compares the orbital energies of $C_3H_3P_3$ with those of C_6H_6 and shows in each case the effect of the introduction of three Bu^t groups. Benzene shows a greater spread of energies of its π orbitals (a_{2u}–e_{2u}) than $C_3H_3P_3$ (a_2''–2e″). This is presumably due to the smaller pπ overlap of the phosphorus atoms. The occupied 1e″ (π) orbitals of $C_3H_3P_3$ are of comparable energy to those of benzene lying 0.4 eV below the e_{1g} orbitals. There is a much greater contrast in the LUMOs. The unoccupied 2e″ (π) orbitals of $C_3H_3P_3$ are just over 2 eV more stable than the e_{2u} orbitals of benzene. The other major difference is the presence in the frontier region of $C_3H_3P_3$ of the phosphorus lone pair orbitals. The e′ (σ) set are the HOMOs for $C_3H_3P_3$ and lie close to the 1e″ (π) orbitals; the $a_1'(\sigma)$ P based orbital shows bonding characteristics and lies close to the a_2'' (π) orbital.

On *tert*-butyl substitution all orbitals are raised in energy, the energy shift being greatest for the lower lying occupied orbitals, so the relationship between the energies of the π orbitals in the substituted pair is similar to that of the unsubstituted analogues. The phosphorus lone pair orbitals are shifted by comparable amounts to the π levels.

From these energy considerations one can expect $C_3Bu^t_3P_3$ and $C_6Bu^t_3H_3$ to be similar in their π donor ability but $C_3Bu^t_3P_3$ to be a better π acceptor than $C_6Bu^t_3H_3$. However, overlap considerations may also be important in determining the relative bonding of the two ligands.

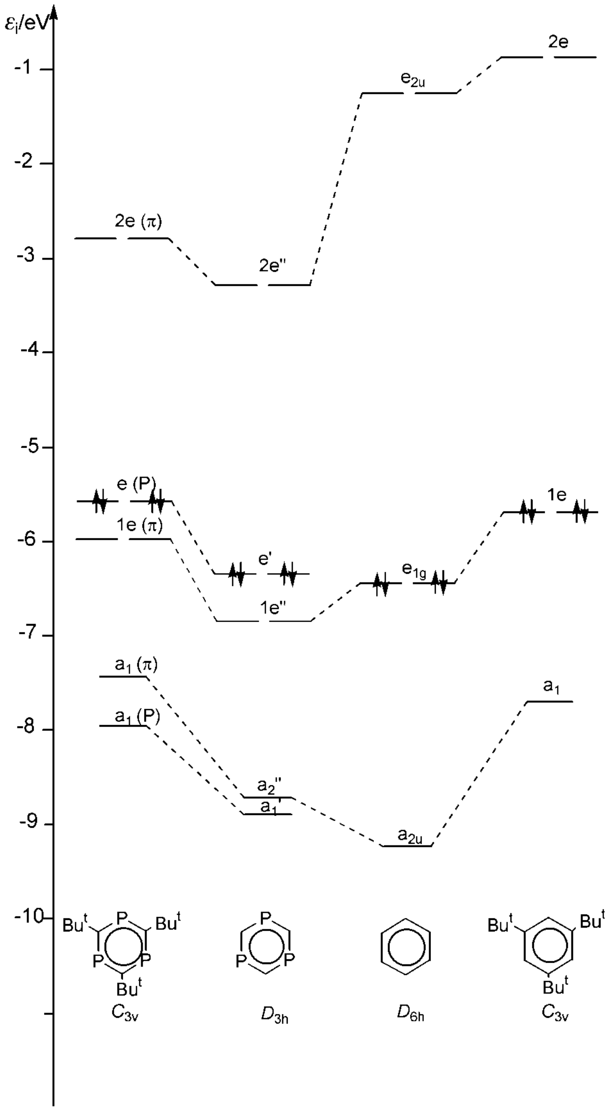

Fig. 2 Frontier orbital energies for $C_3Bu^t_3P_3$, $C_3H_3P_3$, C_6H_6 and $C_6Bu^t_3H_3$.

Calculated values for the IE of $C_3Bu^t_3P_3$ and $C_6Bu^t_3H_3$ are compared with experimental values[5] in Table 2. The agreement is good, lending weight to the validity of the orbital picture developed above.

The complexes

Bonding in d^6 molecules of the class $[M(CO)_3(\eta^n\text{-}C_nH_n)]$ has been studied extensively and is well understood.[15–17] Coordination of the carbocyclic ring is normally described in terms of donation from the top filled π orbitals and back donation into the lowest unfilled π orbitals. As the ring increases in size, and the π orbitals with the same nodal characteristics become more stable, donation tends to decrease and back donation increases. The relative amounts of these two interactions are also a function of other groups bound to a metal. Carbonyl groups being excellent acceptor groups enhance the donor properties of other ligands and decrease the potential of the metal for back donation. Back donation from a d^6 $M(CO)_3$ unit involves three d orbitals of a_1 and e symmetry in a C_{3v} point group, and the three resulting MOs lie close in energy.

Structural studies. Geometry optimisation of $[M(CO)_3(\eta^6\text{-}C_3H_3P_3)]$ (M = Cr, Mo or W), $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t_3P_3)]$, and

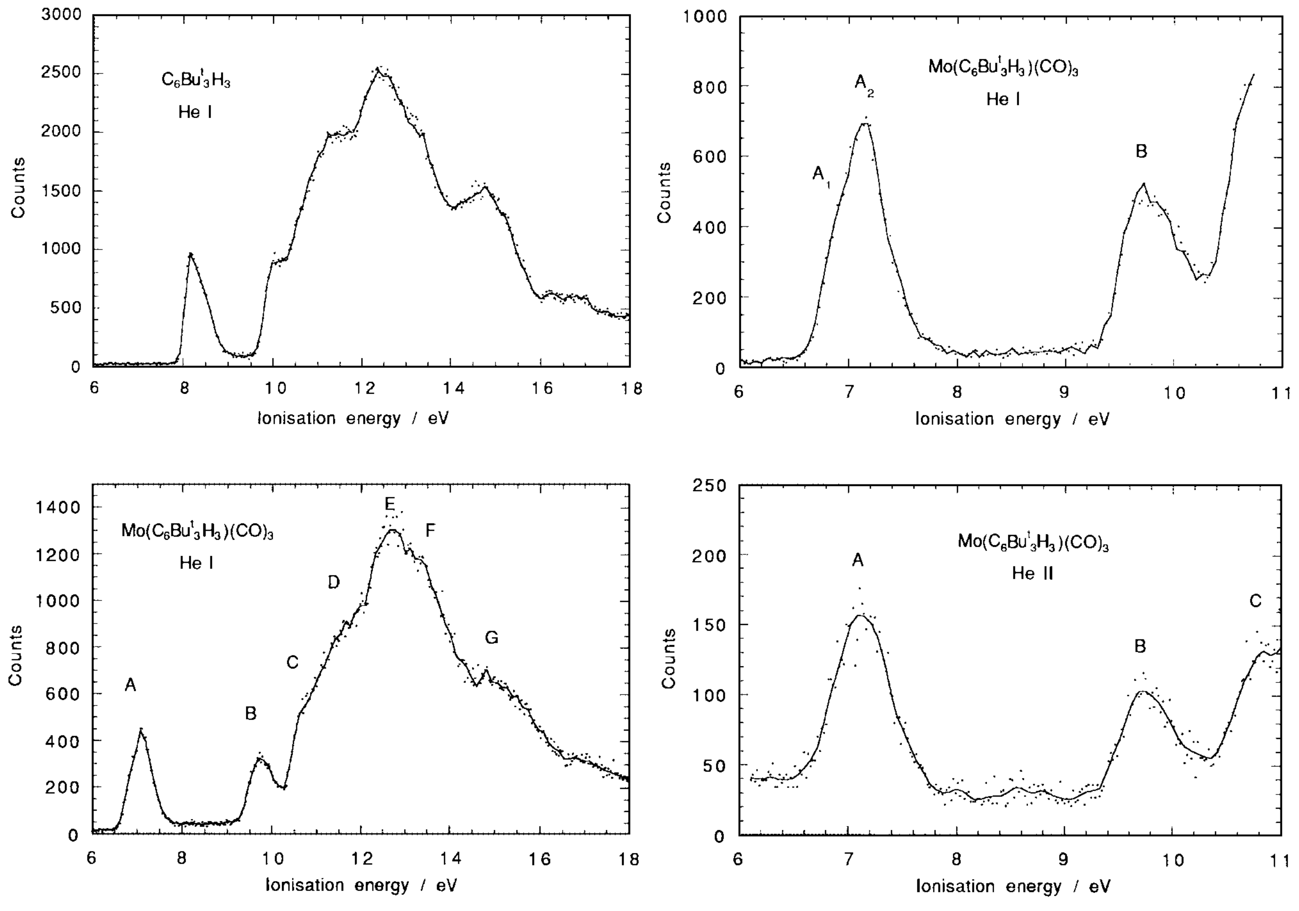

Fig. 3 He I and He II PE spectra of $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$.

Table 2 Calculated and experimental IE (eV) for C_6H_6,[21] $C_6Bu^t{}_3H_3$, $C_3Bu^t{}_3P_3$,[5] $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ and $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$

Compound	IE		Orbital type
	exp.	calc.	
C_6H_6	9.25	9.42	e_{1g} π
	12.38	12.25	a_{2u} π
$C_6Bu^t{}_3H_3$	8.16	8.09	1e π
$[Mo(CO)_3(C_6Bu^t{}_3H_3)]$	6.89	7.19	e d
	7.14	7.46	a_1 d
	9.7	9.49	e π
$C_3Bu^t{}_3P_3$	8.2	7.71	e P σ
	8.3	8.09	1e π
	10	9.36	a_1 π
			a_1 P σ
$[Cr(CO)_3(C_3Bu^t{}_3P_3)]$	7.1		$11a_1$ d
	7.36		12e d
	8.6		11e P σ
	9.37		10e π
	10.3		$10a_1$ π
$[Mo(CO)_3(C_3Bu^t{}_3P_3)]$	7.33	7.4	$11a_1$ d
	7.56	7.68	12e d
	8.55	8.21	11e P σ
	9.35	9.22	10e π
	10.2	9.58	$10a_1$ π
			$9a_1$ P σ
$[W(CO)_3(C_3Bu^t{}_3P_3)]$	7.1		$11a_1$ d
	7.47		12e d
	8.7		11e P σ
	9.39		10e π
	10.2		$10a_1$ π

$[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ gave the structural data summarised in Table 1. Experimental values for $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ are also given.[9] Comparison of the geometries of the free and bound rings show a ring P–C and a ring C–C bond lengthening on co-ordination. This may be due to either donation from the HOMOs or back donation into the LUMOs or both. Little change is found in the ring angles on binding and the rings stay almost planar.

The M–CO and C–O distances may be used as indicators of M–CO back donation. In $[Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)]$ the Mo–CO distance is calculated to be longer and the C–O distance to be shorter than in $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$. This is an indication that either the triphosphabenzene ligand is a better acceptor than the arene, as it is competing more successfully with the CO ligands for the metal d electrons, or that it is a worse donor. By the same criteria, not surprisingly, $C_3H_3P_3$ is predicted to be a better π acceptor or a worse π donor than $C_3Bu^t{}_3P_3$.

The biggest change down the series of $[M(CO)_3(\eta^6\text{-}C_3H_3P_3)]$ (M = Cr, Mo or W) is the increase in M–C, M–P and M–CO distances associated with the increase in the size of the metal on descending the group. Other changes in structural parameters are very small.

Photoelectron spectroscopy. The PE spectra of $C_6Bu^t{}_3H_3$ and $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ are shown in Fig. 3. That of the complex closely resembles that of other Group 6 arene tricarbonyl complexes.[17,18] The d band, A, of $[Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)]$ has a vertical IE of 7.14 eV and a shoulder on the low IE edge can be seen at 6.9 eV. The increase in relative intensity in the He II spectrum of this band confirms its essential d origin. The analogous band in the PE spectrum of $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$[19] has a higher first IE of 7.65 eV whereas that of $[Mo(CO)_3(\eta^6\text{-}C_6Me_3H_3)]$ lies in between at 7.35 eV.[20] The second band, B, at 9.7 eV can be correlated with that of the free arene, $C_6Bu^t{}_3H_3$, at 8.1 eV. The latter arises from the 1e (π) orbitals of the ring which are significantly stabilised on co-ordination to the metal. The shift of IE on binding of 1.6 eV can be compared with 1.4 eV for $[Mo(CO)_3(\eta^6\text{-}C_6H_6)]$ and 1.63 eV for $[Mo(CO)_3(\eta^6\text{-}C_6Me_3H_3)]$. The resemblance of the main band in the complex to that of the ligand is evident.

Table 3 Population analysis of the MO of [$M(CO)_3(C_3H_3P_3)$] in terms of the orbitals of the $C_3H_3P_3$ and $M(CO)_3$ fragments

M	Orbital	Energy/ eV	$C_3H_3P_3$	$M(CO)_3$
Cr	13e LUMO	−3.25	77% $2e''$	16% 7e
	$11a_1$ HOMO	−5.65	6% a_1' 4% a_2''	85% $7a_1$
	12e	−6.13	16% $2e''$ 7% e'	70% 7e
	11e	−7.09	90% e'	
	10e	−8.08	71% $1e''$	11% 8e
	$10a_1$	−8.86	65% a_2'' 4% a_1'	9% $7a_1$ 18% $6a_1$
	$9a_1$	−9.75	87% a_1'	
Mo	13e LUMO	−3.37	71% $2e''$	19% 7e
	$11a_1$ HOMO	−5.78	6% a_1' 4% a_2''	87% $7a_1$
	12e	−6.21	19% $2e''$ 7% e'	64% 7e
	11e	−7.08	90% e'	
	10e	−8.16	74% $1e''$	8% 8e 6% 7e
	$10a_1$	−8.97	76% a_2''	5% $7a_1$ 17% $6a_1$
	$9a_1$	−9.75	88% a_1'	
W	13e LUMO	−3.52	68% $2e''$	20% 7e
	$11a_1$ HOMO	−5.83	6% a_2''	87% $7a_1$
	12e	−6.25	20% $2e''$ 6% e'	65% 7e
	11e	−7.13	88% e' 8% $1e''$	
	10e	−8.27	71% $1e''$ 5% e'	9% 8e 6% 7e
	$10a_1$	−9.24	72% a_2'' 7% a_1'	5% $7a_1$ 10% $6a_1$
	$9a_1$	−9.84	84% a_1' 7% a_2''	

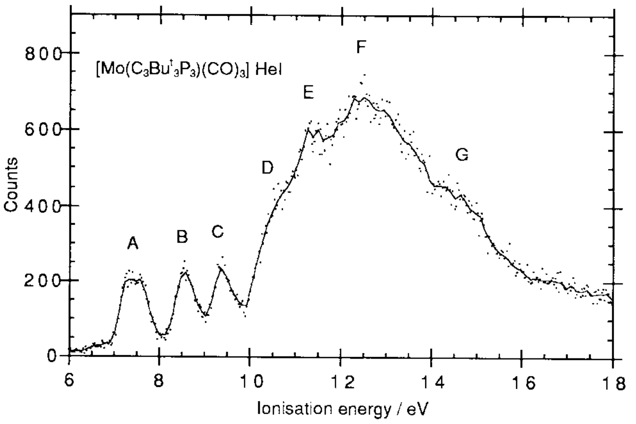

Fig. 4 He I PE spectrum of [$Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)$].

The full range He I PE spectrum of [$Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)$] is given in Fig. 4. In contrast to [$Mo(CO)_3(\eta^6\text{-}C_6Bu^t{}_3H_3)$], there are three bands at lower IE than the main band. The first band A may be assigned to the d band, the second band, B, lies in the same IE region as the first band of $C_3Bu^t{}_3P_3$, whereas the third band, C, has a significantly higher IE. The obvious interpretation is that the ring e(π) electrons give rise to band C and are considerably stabilised on co-ordination whereas the P e(σ) electrons, which give rise to band B, are only slightly shifted. The shift in the e(π) IE between $C_3Bu^t{}_3P_3$ and [$Mo(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)$] is 1.05 eV, significantly less than found for $C_6Bu^t{}_3H_3$ and its analogous complex. The IE of the d band is *circa* 0.4 eV greater.

Fig. 5 presents the low energy region of the PE spectra of the three complexes [$M(CO_3)(\eta^6\text{-}C_3Bu^t{}_3P_3)$] (M = Cr, Mo or W). The three complexes have three related bands in the low IE region. The d band, A, grows in intensity on descending the group. This is a common trend in the He I ionisation cross sections of d bands.[20] In all three d bands structure is evident consistent with the presence of two overlapping bands. The changes in IE for related bands are small.

Calculated IE, given in Table 2, are in excellent agreement with the experimental values. We may thus have confidence in inferring the relative amounts of donation and back donation from the calculated electronic structures.

Electronic structure. A MO scheme for [$Mo(CO)_3(\eta^6\text{-}C_3H_3P_3)$] is given in Fig. 6. Mulliken population analysis (Table 3) gives the contribution by the orbitals of the $Mo(CO)_3$ and $C_3H_3P_3$ fragments to orbitals of the molecule. The $11a_1$ HOMO is largely unchanged from the $Mo(CO)_3$ fragment and has very little mixing with the ring orbitals. The 12e orbital is a source of covalent bonding and has a 64% contribution from the highest occupied e orbitals of the $Mo(CO)_3$ fragment and a 19% contribution from the $2e''$ LUMO of the ring; it thus represents the back donation. The 10e orbital represents donation from the $1e''$ orbital of the ring (74%) into the 8e LUMO of the $Mo(CO)_3$ fragment. The phosphorus lone pair orbitals 11e and $9a_1$ are largely ring in character. The $10a_1$ orbital which is predominantly ring a_2'' undergoes mixing with occupied a_1 orbitals of the metal fragment but does not appear to donate into the empty $8a_1$ orbital of $Mo(CO)_3$. Throughout there is a small amount of mixing between phosphorus lone pairs and ring π orbitals of equivalent symmetry but not enough to represent any significant rehybridisation at the P atoms. A similar pattern for the orbitals is apparent for the chromium and tungsten analogues.

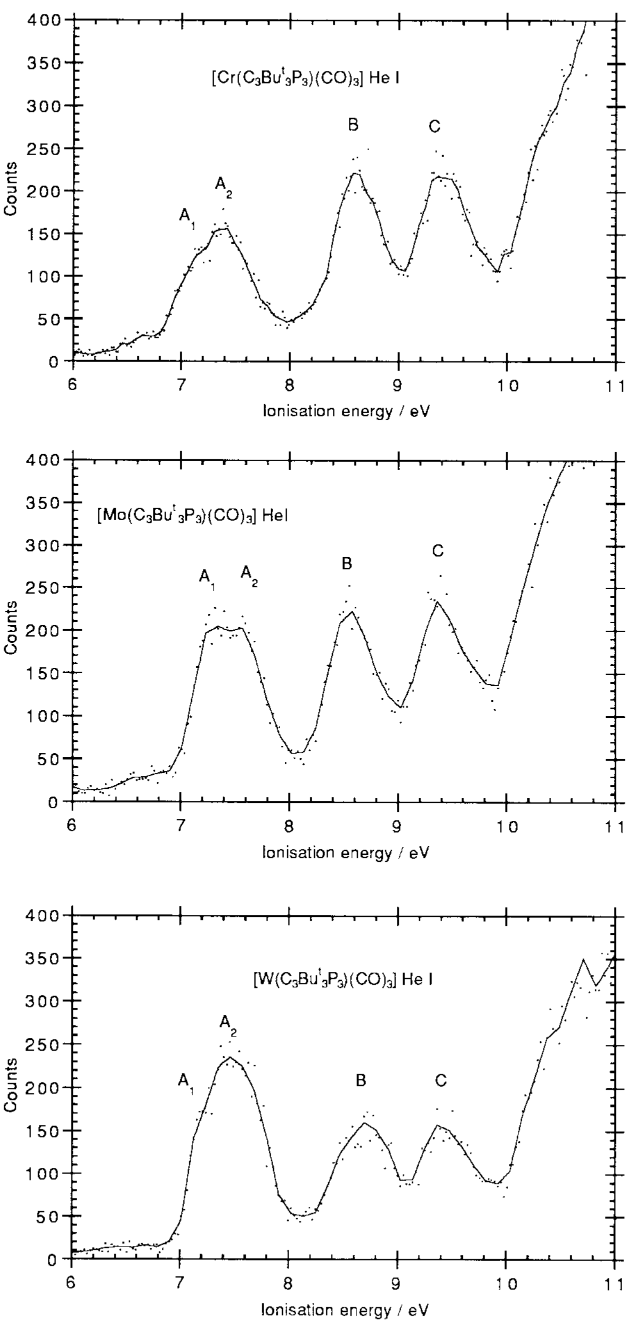

Fig. 5 Low energy region of the He I PE spectra of [$M(CO)_3(\eta^6\text{-}C_3Bu^t{}_3P_3)$] (M = Cr, Mo or W).

Table 4 Gross occupation (electrons) of fragment e symmetry orbitals in the [Mo(CO)$_3$(η^6-C$_3$H$_3$P$_3$)], [Mo(CO)$_3$(η^6-C$_6$Bu$^t_3$P$_3$)] and [Mo(CO)$_3$-(η^6-C$_3$Bu$^t_3$H$_3$)]

Compound	Binding energy/eV	Ring→metal donation		Metal→ring back donation	
		Ring 1e″	M(CO)$_3$ 8e	M(CO)$_3$ 7e	Ring 2e″
[Mo(CO)$_3$(η^6-C$_3$H$_3$P$_3$)]	−3.36	3.46	0.54	3.02	0.83
[Mo(CO)$_3$(η^6-C$_6$Bu$^t_3$P$_3$)]	−3.23	3.52	0.48	3.10	0.78
[Mo(CO)$_3$(η^6-C$_3$Bu$^t_3$H$_3$)]	−2.03	3.40	0.54	3.60	0.50

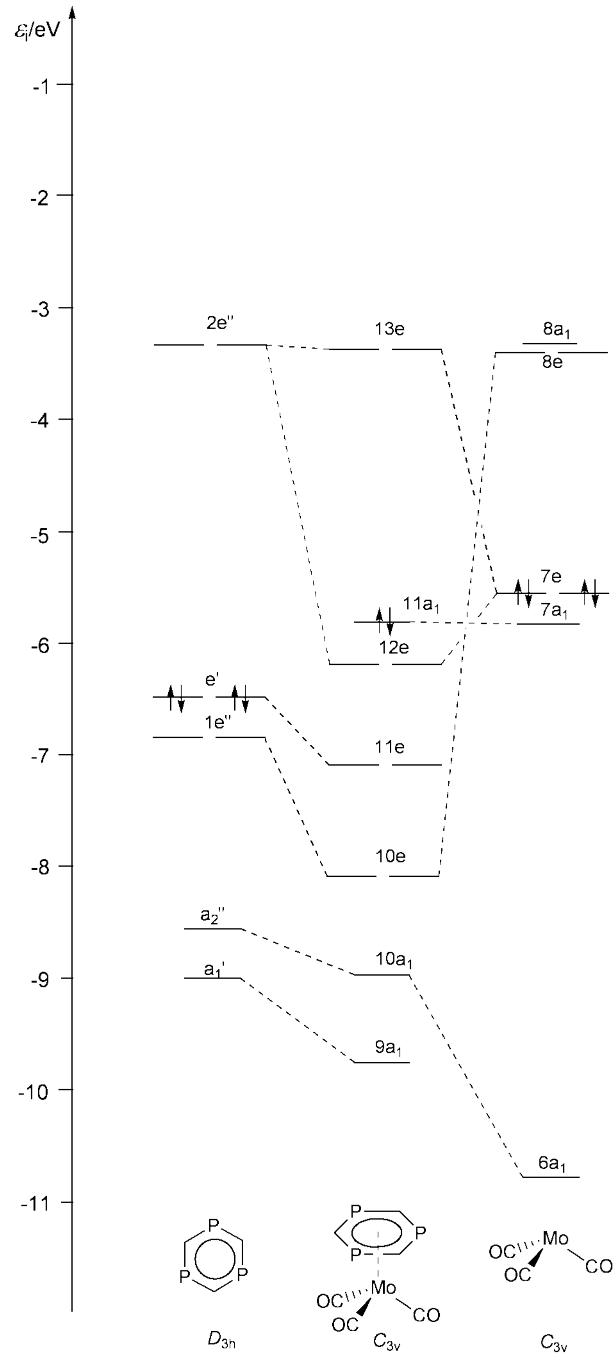

Fig. 6 MO scheme for [M(CO)$_3$(η^6-C$_3$H$_3$P$_3$)].

A quantitative estimate of the amount of donation and back donation involved for the molybdenum series of complexes is best made from the occupation of the relevant e symmetry fragment orbitals in the three complexes. These are given in Table 4. The occupation numbers in the table are in units of electrons. Though donation appears to be similar among the three compounds, back donation decreases from [Mo(CO)$_3$(η^6-C$_3$H$_3$P$_3$)] to [Mo(CO)$_3$(η^6-C$_3$Bu$^t_3$P$_3$)] as might be expected from the introduction of the butyl substituents. It is considerably less in [Mo(CO)$_3$(η^6-C$_6$Bu$^t_3$H$_3$)]. This change in back donation is reflected in the ring to M(CO)$_3$ binding energies which become less negative along the series.

Conclusion

1,3,5-Triphosphabenzenes are seen to bind more strongly to transition metal tricarbonyls than their carbocyclic analogues. The principal reason for this is the lower energy of the ring acceptor orbitals when P atoms are present in the ring and the consequent greater back donation.

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