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Electronic structure of [M(η-$P_3C_2Bu^t_2$)(CO)$_3$] (M = Mn or Re): a study by photoelectron spectroscopy and density functional calculations

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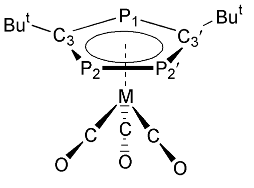
Received 30th January 2001, Accepted 2nd April 2001
First published as an Advance Article on the web 3rd May 2001

The compounds [M(η^5-$P_3C_2Bu^t_2$)(CO)$_3$] (M = Mn **1** or Re **2**) are reported and their He I and He II photoelectron spectra assigned. Their electronic structure has been investigated by means of density functional calculations and reasonable agreement between experimental and calculated ionisation energies is achieved. The bonding between the metal and the ring is predominantly donation from the ring to the metal. Back donation into the highest π orbitals of the ring is minimal. The calculations suggest substantial mixing between the ring σ and π orbitals on coordination to the metal. Calculations on [Mn(η^5-$P_3C_2Bu^t_2$)$_2$] reproduce the unusual ^2A ground state and show that this results from stabilisation of the metal e_2 type orbitals by formation of a δ bond with the unoccupied π orbitals of the rings.

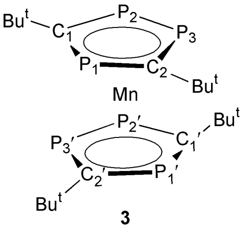
Introduction

The combination of photoelectron (PE) spectroscopy and density functional (DF) calculations has proved effective in studying the binding of phosphorus substituted carbocyclic rings to metals. The systems studied include analogues of classic systems such as ferrocene[1] and metal arene tricarbonyls,[2] and more unusual molecules such as a low spin titanocene analogue [Ti(η^5-$P_3C_2Bu^t_2$)$_2$][3] and the indium phospholyls [In(η^5-$P_3C_2Bu^t_2$)] and [In(η^5-$P_2C_3Bu^t_3$)].[4] A general pattern has emerged from these studies which points to the P substituted rings being potentially better acceptors than the carbocyclic analogues and forming significant δ bonds with transition metals. With respect to their donor properties the phospholyls and the carbocyclic rings appear to be very similar.

In a continuation of this study we report below the preparation, PE spectra and DF calculations of the triphospholyl complexes [M(η^5-$P_3C_2Bu^t_2$)(CO)$_3$] (M = Mn **1** or Re **2**). The parent carbocyclic analogues [M(η^5-C_5H_5)(CO)$_3$] have extensively been studied by PE spectroscopy[5–10] and are the subject of many theoretical investigations.[6,7,11–18] A molecular orbital description is readily achieved by considering the interaction between the ring and the metal tricarbonyl fragment. The frontier orbitals of a C_{3v} [M(CO)$_3$] unit consist of one of a_1 symmetry, mainly d_{z^2}, and two pairs of e symmetry, the lower in energy, 1e, being mainly d_{xy} and $d_{x^2-y^2}$ and the higher, 2e, being mainly d_{xz} and d_{yz}. The a_1 and 1e orbitals are metal carbonyl back bonding and the 2e orbitals are metal carbonyl σ antibonding. The principal interaction with the cyclopentadienyl ring is donation from the e_1' π levels of the ring into the 2e orbitals. There also exists the possibilty of back donation from the 1e orbitals to the ring e_2'' π orbitals.



1 M = Mn
2 M = Re



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We seek to assess the relative importance of these interactions for **1** and **2**, since in both there will also be extra valence levels of similar energy to the ring π and orbitals consisting of σ orbitals of the ring largely localised on the P atoms.[1,3,4]

In the course of this work the preparation of **1** was reported together with that of [Mn(η^5-$P_3C_2Bu^t_2$)$_2$], **3**.[19] The latter compound is unusual for a d^5 metallocene in possessing a $^2A_1$ ground state. [Mn(η^5-C_5H_5)$_2$] is known to have a $^6A_1$ ground state, whereas [Mn(η^5-C_5Me_5)$_2$] has a $^2E_2$ ground state. Density functional calculations showed little ligand character mixed into the occupied d levels. These results contrast with our recent findings[3] for [Ti(η^5-$P_3C_2Bu^t_2$)$_2$] where the strong δ bond between the metal and the rings is responsible for the diamagnetic ground state. We therefore have also examined the electronic structure of **3**.

Results and discussion

The yellow crystalline compound [Mn(η^5-$P_3C_2Bu^t_2$)(CO)$_3$)] **1** was prepared previously by Zenneck and co-workers[19] by treatment of the stannyltriphosphole $Ph_3SnP_3C_2Bu^t_2$ with [Mn(CO)$_5$Br] and was also converted into its [Cr(CO)$_5$] adduct. Our synthetic route utilises the reaction between the recently available [K($P_3C_2Bu^t_2$)][20] as the ring transfer reagent and the reactive complex [Mn(MeCN)$_3$(CO)$_3$][PF_6].

Spectroscopic data for **1** were in good agreement with those recently published in reference 19 and single crystals of **1** were grown and subjected to an X-ray diffraction study. Although the expected overall molecular structure of **1** was established, unfortunately it could not satisfactorily be refined owing to disorder within the tertiary butyl groups.

The new complex [Re(η^5-$P_3C_2Bu^t_2$)(CO)$_3$)] **2** was prepared in a similar fashion by refluxing equimolar mounts of [Re(CO)$_5$Br] and [K($P_3C_2Bu^t_2$)] in THF. The resulting colourless crystalline compound (mp 83 °C), is very soluble in organic solvents such as hexane, toluene and diethyl ether and is readily sublimable *in vacuo*. It was fully characterised by ^{31}P-{^1H} NMR spectroscopy, exhibiting the expected AB_2 spectrum. The

DOI: 10.1039/b101014j

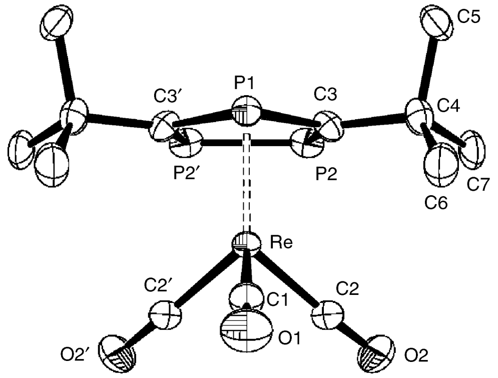

Fig. 1 Molecular structure of [Re (η^5-$P_3C_2Bu^t_2$)(CO)$_3$] **2**. Selected bond distances (Å) and angles (°): Re–C(1) 1.948(11), Re–C(2) 1.935(7), Re–M(1) 1.932(7), Re–P(1) 2.534(3), Re–P(2) 2.557(2), Re–C(3) 2.395(7), P(2)–P(2)′ 2.129(4), P(1)–C(3) 1.774(7), P(2)–C(3) 1.780(7), C(1)–O(1) 1.132(12), C(2)–O(2) 1.146(8); M(1)–Re–C(2) 125.6(4), M(1)–Re–C(1) 121.9(4), C(2)–Re–C(2)′ 91.2(4), C(2)–Re–C(1) 91.2(4), O(1)–C(1)–Re 176.4(11), O(2)–C(2)–Re 177.8(6), C(3)–P(1)–C(3)′ 99.7(5), C(3)–P(2)–P(2)′ 99.4(2), P(1)–C(3)–P(2) 120.7(4). M(1) is the centroid of the $P_3C_2Bu^t_2$ ring.

chemical shifts of P_A (δ 96.7) and P_B (δ 99.1) were both lower than those found for the corresponding manganese complex [Mn(η^5-$P_3C_2Bu^t_2$)(CO)$_3$)] **1** (P_A δ 111.8; P_B, 114), in agreement with previous trends established on a wide series of tertiary phosphine complexes of transition metals in the same group.[21] The ^1H NMR spectrum of **2** showed the expected singlet for the two equivalent Bu^t groups. The ^{13}C-{^1H} NMR spectrum showed a slightly broad signal at δ 191.2, readily assigned to the carbonyl groups, and the remaining three sets of resonances centred at δ 158.9, 39.2 and 37.8 could be attributed to the C (ring), C(Bu^t) and C(Me) carbons, respectively. The detailed fine structure of each resonance could be successfully simulated as (i) C (ring), the A part of an AMXY spin system, (ii) C(Bu^t), the A part of an AMXX′ spin system and (iii) C(Me), the A part of an AMXX′ spin system. Chemical shift and coupling constant data are summarised in the Experimental section.

The IR spectrum of **2** in the carbonyl stretching region showed the expected bands, the frequencies being slightly higher (ν_{CO} 2031(s), 1952(b) cm^{-1}), compared to those of the analogous [Re(η^5-C_5H_5)(CO)$_3$] complex (ν_{CO} 2023(s), 1937(s), 1902(s) cm^{-1}),[22] suggesting that the η^5-$P_3C_2Bu^t_2$ ligand has a greater electron withdrawing effect than η^5-C_5H_5. Previous electrochemical studies on phospha-metallocenes also support this observation.[23–25]

Molecular structure of 2

The molecular structure of **2**, which was determined by a single crystal X-ray diffraction study, is shown in Fig. 1. As expected the η^5-ligated $P_3C_2Bu^t_2$ ring in **2** is essentially planar and the metal to ring centroid distance (Re–M(1)) is 1.932(7) Å, which is slightly shorter than that found in the corresponding [Re(η^5-C_5H_5)(CO)$_3$] compound (1.957 Å).[26] The average Re–C–O angle (177.1°), deviates only slightly from linearity perhaps because of a packing effect in the solid state, since a similar small deviation was observed for the cyclopentadienyl analogue [Re(η^5-C_5H_5)(CO)$_3$].

Photoelectron spectroscopy

He I and He II PE spectra of **1** and **2** are shown in Figs. 2 and 3. Vertical ionisation energies (IEs) of key features are given in Table 1. The bands of principal interest are A–E which have IE less than 10.5 eV. These are associated with ionisation from the metal orbitals and the ring upper π and Pσ orbitals. Bands F–I are assigned to lower lying ligand levels. Preliminary assignment of the spectra may be made by comparison with those of related compounds.

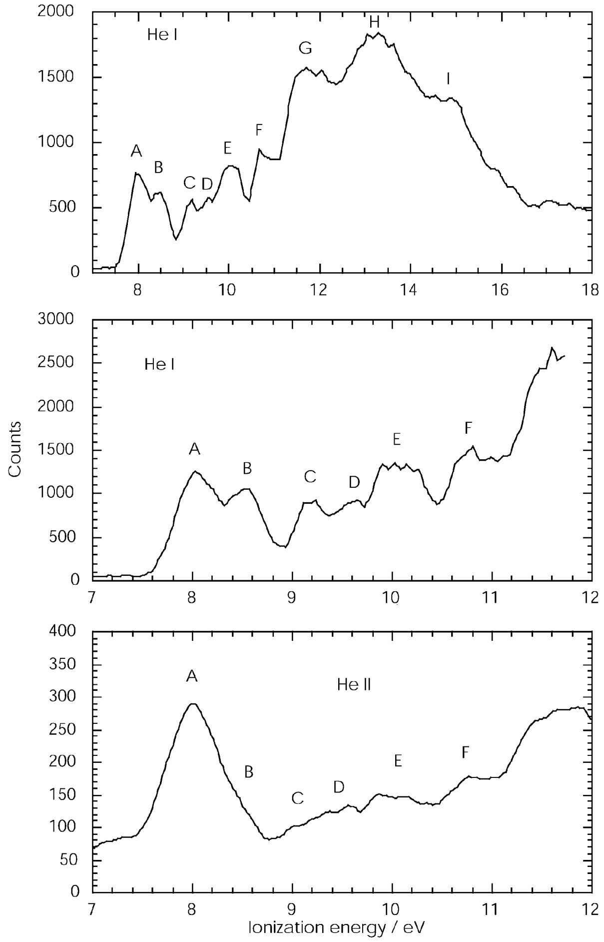

Fig. 2 He I and He II PE spectra of **1**.

The low IE region is more complex than that of the parent molecules [M(η-C_5H_5)(CO)$_3$] (M = Mn or Re), the PE spectra of which have extensively been studied.[5–10] Variable photon energy PES confirms the assignment of the lower IE bands to metal d ionisations.[9,10] [Mn(η-C_5H_5)(CO)$_3$] shows a band associated with the d electron ionisation which has a vertical IE of 8.05 eV and a shoulder at 8.40 eV. The relative intensity of the two features leads to assignment of the ground ion state as ^2E with the higher lying state being $^2A_1$. The 5d ionisation region in the PE spectrum of [Re(η-C_5H_5)(CO)$_3$] has three clear maxima at 8.13, 8.52 and 8.76 eV. The more complex structure is due to spin–orbit coupling of the ^2E ion state. The cyclopentadienyl upper π ionisations occur between 9.5 and 10.5 eV for [Mn(η-C_5H_5)(CO)$_3$] and 10 and 11 eV for [Re(η-C_5H_5)(CO)$_3$] the vertical IE being 9.90 and 10.18 eV respectively. These bands have a complex profile which has been attributed to the C_s symmetry of the molecules differentiating between the two upper π levels of the ring. We expect bands with similar IE in the spectra of **1** and **2**. In general the IEs of the rhenium compound are higher than those of the manganese compound.

PE spectra of compounds with metals bound to the $P_3C_2Bu^t_2$ ring have been obtained for Ti,[3] In,[4] Fe and Ru.[1] A general pattern has emerged for the ionisations which are principally ligand based. The two upper π levels show similar IE to those of the cyclopentadienyl analogues. Also three Pσ ionisations may generally be distinguished. One lies low in energy with IE close or coincidental with that of metal d bands. The other two have IE somewhat higher than those of the π bands.

These considerations suggest likely assignments for **1** and **2**. For **1** band A increases in relative intensity in the He II spectrum (Fig. 2) and may be associated with the 3d ionisations. Band B drops in intensity as the photon energy is increased and thus arises from a Pσ ionisation. The energy groupings of

Table 1 Orbital energies, calculated and experimental IEs and orbital compositions of **1** and **2**

		IE/eV		Orbital composition (>10%)	
Orbital	Orbital energy/eV	calc.	exp.	% $P_3C_2Bu^t_2$	% $M(CO)_3$
M = Mn					
34a′	−5.97	[a]	8.04 A	$P\sigma_3$ 36	a_1 35
33a′	−6.14	8.29		$P\sigma_3$ 14	1e 40, a_1 27
25a″	−6.19	8.3		π_3 14	1e 65, 2e 11
32a′	−6.27	8.38	8.54 B	$P\sigma_3$ 30, π_2 12	1e 23, a_1 17
24a″	−7.05	9.13	9.16 C	$P\sigma_2$ 36, π_3 36	1e 16
31a′	−7.5	[a]	9.59 D	π_2 44, $P\sigma_3$ 16	2e 14, 1e 14
23a″	−7.6	9.63	10.07 E	$P\sigma_2$ 61, π_3 18	
30a′	−7.67	9.64		$P\sigma_1$ 76	
M = Re					
38a′	−6.07	7.83	8.11 A	$P\sigma_3$ 31, π_2 19	1e 26, a_1 12
37a′	−6.19	7.96	8.47 B	$P\sigma_3$ 19	a_1 30, 1e 29
28a″	−6.25	7.96		π_3 22	1e 56, 2e 11
36a′	−6.43	8.2	8.74 C	$P\sigma_3$ 30	a_1 32, 1e 13
27a″	−7.21	8.91	9.54 D	$P\sigma_2$ 53, π_3 24	1e 17
26a″	−7.72	9.35	10.07 E_1	$P\sigma_2$ 42, π_3 27	1e 14
35a′	−7.74	9.34	10.21 E_2	π_2 37, $P\sigma_3$ 15	a_1 12, 1e 11
34a′	−7.76	9.45	10.38 E_3	$P\sigma_1$ 71	1e 11

[a] SCF convergence was not achieved for this ion state.

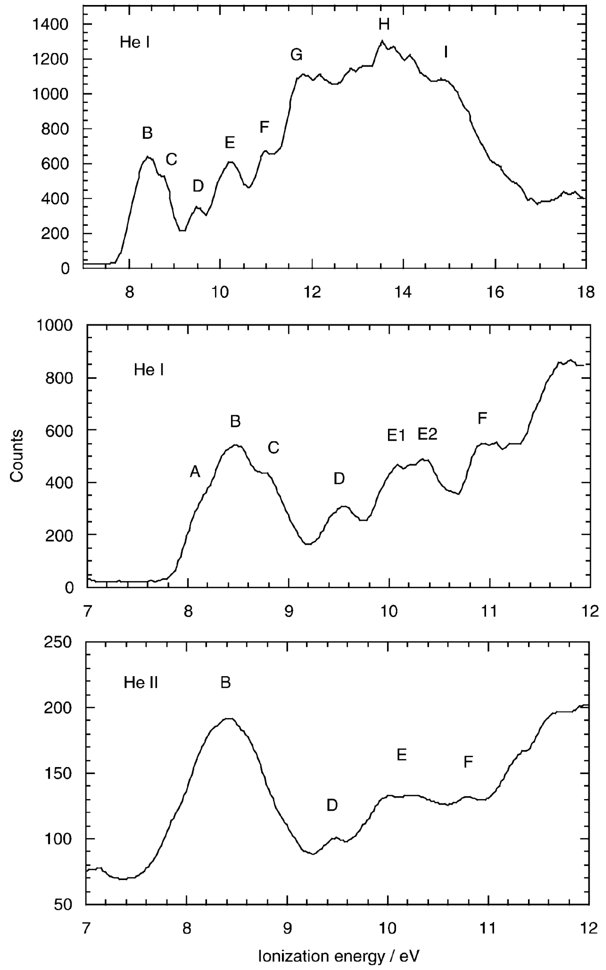

Fig. 3 He I and He II PE spectra of **2**.

bands C, D and E make assignment of E to the remaining Pσ ionisations most likely with C and D being the two ring π levels.

Assignment of the PE spectrum of **2** is less clear cut. The He II spectrum shows the first band A + B + C rising in relative intensity compared to the He II spectrum but the lower resolution in the He II spectrum precludes differentiation of the three features. Comparison with the cyclopentadienyl analogues suggests that band A is likely to arise from a d based spin–orbit component and that C is largely Pσ in character. Band E is assigned to the Pσ levels of the ring leaving only D as a π ionisation. Presumably the other π ionisation also lies under band E.

Given these assignments comparisons may be made between the IEs of **1** and **2** and their cyclopentadienyl analogues. If we compare the IE of the most intense feature of the d band the change of ring makes very little difference; for both categories of ligand the rhenium d IE are marginally greater than the manganese ones. Thus the inductive effect of two *tert*-butyl groups in the triphosphacyclopentadienyl ring is counteracted by the presence of the three P atoms. This is in accord with previous studies. With respect to the ligand π ionisations those of the triphosphacyclopentadienyl complexes lie at lower IE than of the cyclopentadienyl complexes. Thus, in this case ring modification and substitution raises the energy of the π electrons. A similar effect was observed when the PE spectrum of $[Mo(\eta\text{-}C_6H_3Bu^t_3)(CO)_3]$ was compared with that of $[Mo(\eta\text{-}C_3P_3Bu^t_3)(CO)_3]$.[2]

The π IE in the PE spectrum of **2** are significantly higher than those in the PE spectrum of **1**. The stabilisation of the π levels in the rhenium complex compared to that of Mn is greater than that found for the cyclopentadienyl complexes.

Electronic structure calculations

These qualitative assignments were examined by density functional calculations on **1** and **2**. The structures of **1** and **2** were optimised assuming C_s symmetry such that the *tert*-butyl groups were staggered with respect to the carbonyl ligands. Key distances are given in Table 2, where those for **2** are compared with the experimental values. The agreement between theory and experiment is very good.

The orbital structures of compounds **1** and **2** are conveniently analysed by considering combination of a $[M(CO)_3]$ fragment with the triphospholyl ring. Fragment calculations were carried out to obtain the composition of the frontier MOs of the molecules in terms of the MOs of such fragments. The results are included in Table 1 and an interaction diagram for **1** is given in Fig. 4. That for **2** is similar.

The fragment analysis presents a complex picture of the bonding. Though the primary contribution to the orbitals is in line with the PE assignment (assuming a Koopmans like ordering) there is substantial mixing between the π levels of the

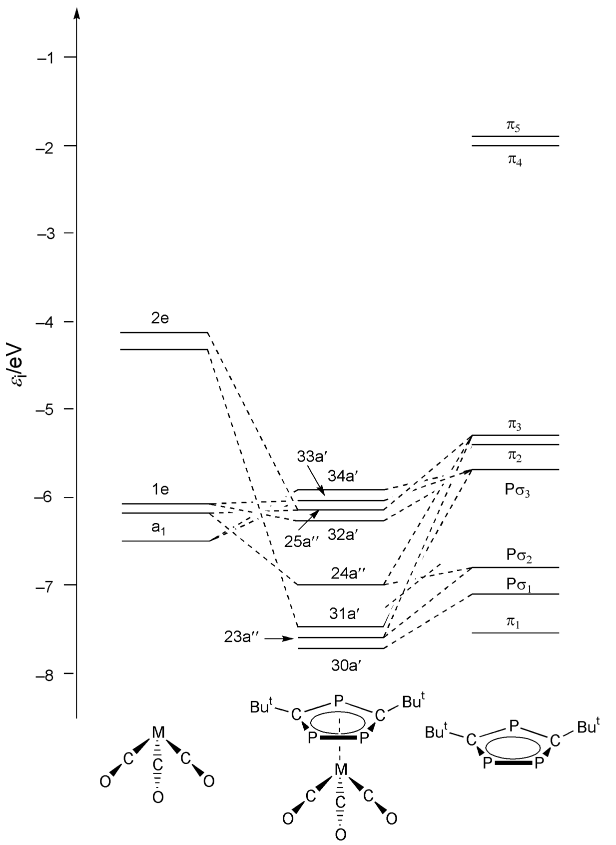

Fig. 4 Interaction diagram representing the formation of the MOs of **1** and **2** from a C_{3v} M(CO)$_3$ fragment and a $P_3C_2Bu^t_2$ ring.

Table 2 Calculated bond lengths (Å) and angles (°) for **1** and **2**

	M = Mn	M = Re
P2–P2′	2.16	2.16 (2.129(4))
P2–C3	1.78	1.79 (1.780(7))
P1–C3	1.77	1.78 (1.774(7))
M–P2	2.41	2.57 (2.557(2))
M–P1	2.37	2.52 (2.534(3))
M–C3	2.22	2.37 (2.395(7))
M–CO	1.76	1.91 (1.94 av.)
C–O	1.16	1.16 (1.13 av.)
C3–P2–P2′	98	99 (99.4(2))
C3–P1–C3′	98	98 (99.7(5))
P2–C3–P1	123	122 (120.7(4))

ring and the Pσ orbitals. The calculation places $P\sigma_3$ at a similar energy to that of the three d levels and it mixes with the two d levels of the same a′ symmetry. In **1** the fifth and sixth levels have as their major contributor the π_2 and π_3 orbitals but are mixed strongly with Pσ orbitals as well as donating to the metal fragment. In **2** the balance is reversed with Pσ making a greater contribution than π to the fifth and sixth levels. Similar σ–π mixing was found in DFT calculations on phosphaferrocenes.[1] The ability of the ring P atoms to rehybridise enhances their ability to bond to the metal.

The gross occupation of the fragment orbitals given in Table 3 presents a simpler picture. From this it may be seen that the Pσ orbitals are virtually fully occupied in the complex, as is π_1. Significant donation has occurred from π_2 and π_3 compared with the free anion but donation into π_4 and π_5 is small. Thus the interaction between the P_3C_2 ring is mainly donation from the ring to the metal fragment with very little back donation. This contrasts with the pattern found for the triphosphabenzene ring coordinated to Group 6 metal tricarbonyls where back donation was found to be more important than donation.

Table 3 Gross occupations of fragment orbitals in **1**, **2** and **3**

Fragment orbital	Occupancy		
Ring	**1** M = Mn	**2** M = Re	**3**
π_1	1.9	1.9	1.9
π_2	1.4	1.6	1.5
π_3	1.5	1.6	1.5
π_4	0.13	0.16	0.34
π_5	0.14	0.16	0.25
$P\sigma_1$	2.0	2.0	2.0
$P\sigma_2$	2.0	2.0	2.0
$P\sigma_3$	1.9	1.9	1.9
M(CO)$_3$			
a_1	2.0	1.9	
$1e_1$	1.8	1.8	
$2e_1$	0.6	0.4	

Table 4 Calculated and experimental distances (Å) and angle between the ring planes, *a* (°), found for **3** in the ^2A ground state

Parameter	Calc.	Exp.
P2–P3	2.18	2.131(2)
P1–C1	1.80	1.769(5)
P1–C2	1.80	1.762(6)
P2–C1	1.81	1.779(5)
P3–C2	1.80	1.774(5)
Mn–P1	2.40	2.363(2)
Mn–P2	2.42	2.3870(14)
Mn–P3	2.41	2.3906(14)
Mn–C1	2.24	2.214(5)
Mn–C2	2.27	2.219(5)
a	8.9	9.0(2)

Ionisation energies were calculated for both **1** and **2** (Table 1) though SCF convergence was not achieved for all ion states in the case of **1**. In spite of this the agreement between calculated and experimental values for **1** was very good. That for **2** was less exact, the calculated IE being on average about 0.6 eV too low. The agreement was better for the lower IE bands than the higher ones.

The holes in the ion states were well represented by their parent molecular orbitals which suggests that the qualitative assignment of the PE spectrum given above is too simple in the treatment of the orbital character, as σ–π mixing was not considered.

It is worth noting that for **1** coordination to a [Cr(CO)$_5$] moiety through one of the less sterically hindered P atoms, P2, has been achieved.[19] The presence of the $P\sigma_3$ orbital at a high energy comparable to that of the manganese d orbitals must in part be responsible for this basic behaviour.

[Mn(η^5-$P_3C_2Bu^t_2$)$_2$], 3. If we assume that the electronic structure of **3**, which has C_2 symmetry, resembles that of a perturbed D_5 metallocene, we may discuss the ^2A ground state in terms of the occupancy of the e_2, a_1 and e_1 d like orbitals. In [Mn(η^5-C_5H_5)$_2$] the ^6A ground state results from single occupancy of all five orbitals. For [Mn(η^5-C_5Me_5)$_2$] the ^2E ground state is consistent with an $e_2^3a_1^2$ configuration. The ESR spectrum of **3** is consistent with a ^2A ground state and near axially symmetry, which would correlate wth a $e_2^4a_1^1$ configuration.[19] The DFT calculations reported were fully consistent with this.[19] Though the symmetry is now C_2 the parent configuration is indicated to be $e_2^4a_1^1$ with the unpaired spin being in a metal centred d(z^2) like orbital with very small spin density on the ligands. Zenneck and co-workers attribute this to a reversal of ordering of the MOs with the e_2 lying below the a_1 in the P_6 manganocene.[19] They were unable to give a clear reason for this reversal. Given that we have found previously a strong metal–ring interaction of the e_2 type in [Ti(η^5-$P_3C_2Bu^t_2$)$_2$],[3] we have carried out DFT calculations on **3** in order to test

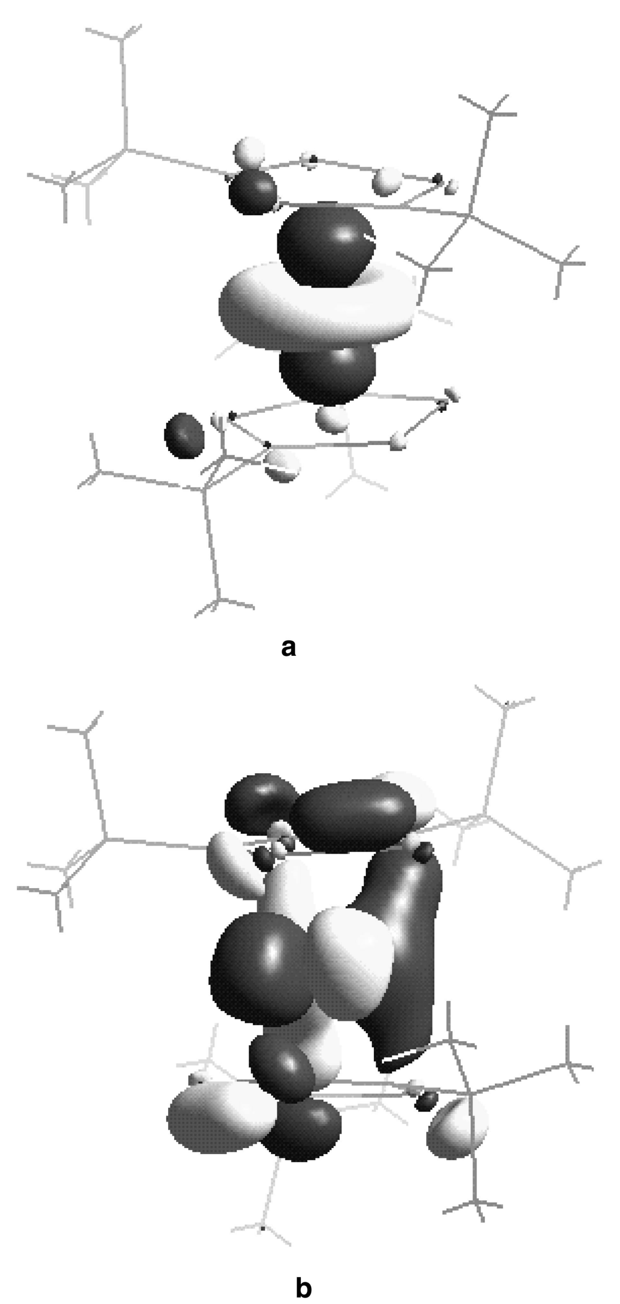

Fig. 5 Isosurfaces for MOs of **3**: (a) a symmetry representing orbital containing the unpaired spin density; (b) one of the metal localised b spin orbitals showing the metal–ligand δ interaction.

whether a similar interaction was present for the manganese analogue.

The geometry was optimised in C_2 symmetry to give a ^{2}A ground state with the geometric parameters given in Table 4. They compare well with the experimental values. The unpaired spin density was found to have a d(x^2) like distribution, shown in Fig. 5a; this is equivalent to an a_1 (d(z^2)) orbital in a D_5 metallocene. Gross populations of the fragment orbitals (Table 3) show that occupation of π_2 and π_3 is similar to that in **1** and **2**, but that occupation of π_4 and π_5 is double that found for **1** and **2**. This increased interaction corresponds to back donation from the e_2 like metal orbitals forming a δ bond with the P_3 ring. A representation of one of the orbitals involved is given in Fig. 5b, where a significant ring contribution is evident. It is the formation of this δ bond that stabilises the e_2 type level leading to a $e_2{}^4a_1{}^1$ type configuration and a ^{2}A ground state.

Conclusion

Density functional calculations give structural and electronic properties for **1**, **2** and **3** fully consistent with the experimental data. The cymantrene analogues, **1** and **2**, where the P_3C_2 ring is coordinated to an electron withdrawing $M(CO)_3$ group, show donation from the ring to the metal to be significantly more important than back donation from the metal to the ring. In contrast, the manganocene analogue, **3**, has significantly greater metal–ring back donation while maintaining comparable donation levels. The back donation results in stabilisation of the e_2 type levels and the formation of the unusual ^{2}A ground state.

Experimental

Photoelectron spectroscopy

He I and He II PE spectra of **1** and **2** were recorded in Oxford using a PES Laboratories Ltd. 0078 spectrometer interfaced with an Atari microprocessor. They were calibrated using He, Xe and N_2.

Computational methods

Calculations were performed using density functional methods of the Amsterdam Density Functional Package (versions 1999.02 and 2000.02).[27] Type IV basis sets were used with triple ζ accuracy sets of Slater type orbitals, with a single polarisation function added to the main group atoms. The cores of the atoms were frozen up to 2p for Mn, 4d for Re, 1s for C and O and 2p for P. First order relativistic corrections were made to the cores of the atoms. Quasi-relativistic corrections were included using the Pauli formalism for the manganese calculations and the ZORA (Zero Order Relativistic Approximation) method for the rhenium calculations. The generalised gradient approximation (GGA non-local) method was used, using Vosko, Wilk and Nusair's local density approximation[28] with non-local exchange corrections by Becke[29] and non-local correlation corrections by Perdew.[30] Ionisation energies were calculated by direct calculations on the molecular ions in their ground and appropriate excited states, and subtraction of the energy of the neutral molecule. The basis sets used for the ion state calculations were the MOs of the respective molecules. This not only assisted SCF convergence but enabled a check as to how well the hole in the ion was described by the ground state MO.

Preparations

[Mn(η^5-P$_3$C$_2$Bu^t$_2$)(CO)$_3$] 1. A solution of [K($P_3C_2Bu^t{}_2$)] (0.5 g, 1.8 mmol) and [Mn(MeCN)$_3$(CO)$_3$][PF$_6$] (0.74 g, 1.8 mmol) in 25 ml of THF was refluxed at 70 °C overnight, changing from yellow to red. The solvent was removed and the product extracted with hexane and purified by vacuum sublimation (80 °C, 0.05 mmHg). Yield 40% after sublimation. The structure of the compound was established by a single crystal X-ray diffraction study (see text) and by its NMR spectra (in $CDCl_3$, at r. t.), δP_A 111.8 (triplet), δP_B 114.1 (doublet), $^2JP_AP_B = 41.1$ Hz, δH Bu^t 1.3, which are in good agreement with previously published data.[19]

[Re(η^5-P$_3$C$_2$Bu^t$_2$)(CO)$_3$] 2. A solution of [Re(CO)$_5$Br] (0.75 g, 1.8 mmol) and of [K($P_3C_2Bu^t{}_2$)] (0.5 g, 1.8 mmol) in 20 ml of THF was refluxed at 70 °C overnight. The solvent was removed and the product extracted with hexane and further purified by recrystallisation from hexane at −20 °C. Yield 70% after crystallisation. Complex **2** which could be sublimed at 70 °C, 0.05 mmHg, was fully characterised by its ^{31}P-{^{1}H} and ^{1}H NMR, mass and IR spectra, elemental analysis and a single crystal X-ray diffraction study. NMR data: ^{31}P-{^{1}H}, δP_A 96.7 (triplet), δP_B 99.1 (doublet), $^2JP_AP_B = 41.6$ Hz; ^{1}H, δH Bu^t 1.13 (in C_6D_6, at r.t.); ^{13}C-{^{1}H}, δ(CO) 191.2, δC (ring) 158.9, $J_{AM} = 84.7$, $J_{AM} + J_{AX'} = 105.6$, $J_{XX'} \gg 100$, $\delta_X - \delta_Y = 0.026$, δC (^{t}Bu) 39.2, $J_{AM} = 16.8$, $J_{AX} + J_{AX'} = 12.6$, and δ C(Me) 37.8,

$J_{AM} = 8.7$, $J_{AX} + J_{AX'} = 8.4$ Hz (where P_M is the unique P ring atom and P_X and P_Y are the chemically equivalent, but magnetically non-equivalent, directly bonded P atoms). IR data: ν_{CO} 2031(s), 1952(b) cm^{-1}. Mass spectrum (EI): *m*/*z* [M] 502, [M − 2CO] 446, [M − 3CO] 418. Elemental analysis: Found C, 31.53%; H, 3.89%; $C_{13}H_{18}O_3P_3Re$ requires C, 31.14%, H, 3.62%.

Crystal structure determination

Crystal data for $C_{13}H_{18}O_3P_3Re$ 2. $M = 501.38$, orthorhombic, space group $Pn2_1m$ (no. 31), $a = 6.4454(4)$, $b = 6.8624(4)$, $c = 19.0731(11)$ Å, $U = 843.62(9)$ Å^3, $T = 173(2)$ K, $Z = 2$, λ(Mo-Kα) = 0.71073 Å. Data collection Kappa CCD. 4688 Reflections were measured, 1854 with $[I > 2\sigma(I)]$. Final R indices for $I > 2\sigma(I)$ with 1854 reflections were $R1 = 0.036$, $wR2 = 0.094$. The structure was refined by full-matrix least squares on F^2.

CCDC reference number 157828.

See http://www.rsc.org/suppdata/dt/b1/b101014j/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Atomic Energy commission of Syria, Damascus, P.O. Box 6091, for financial support (for M. A.-K.) and Dr Tony Avent (Sussex University) for the ^{13}C NMR spectrum simulation. Part of this work was carried out using the resources of the Oxford Super-Computing Centre and part the EPSRC Columbus cluster at the Rutherford laboratory.

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