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Electronic Structure of 2,4-Di-*tert*-butyl-η^4-1,3-diphosphacyclobutadiene Complexes with $Fe(CO)_3$ and η^5-C_5H_5Co. Photoelectron Spectra and Molecular Orbital Calculations

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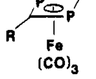
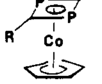
To understand the electronic structure of the 2,4-di-*tert*-butyl-η^4-1,3-diphosphacyclobutadiene complexes with $Fe(CO)_3$ (**1a**) and η^5-C_5H_5Co (**2a**), we have correlated the highest occupied MO's of **1a** and **2a** with those of $(C_4H_4)Fe(CO)_3$ (**3**), $(C_4H_4)Co(C_5H_5)$ (**4**), and related species. The highest occupied MO's of **1**–**4** were calculated by an INDO procedure. It is found that the interaction between the 1,3-diphosphacyclobutadiene ring and the metal fragment is considerably stronger than with the cyclobutadiene ligand and the metal part. This finding is supported by the He I PE spectra of **1a** and **2a**. The interpretation of these spectra is based on empirical correlations with related species and on INDO calculations, explicitly considering relaxation and correlation effects by Green's function technique.

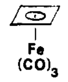
The synthesis of kinetically stabilized phosphaalkynes has opened a new door to phospha heterocycles.[1] Of particular interest have been cyclooligomerization reactions in the coordination sphere of a metal. Thus *tert*-butylphosphaacetylene can be dimerized to give the iron and cobalt complexes of 2,4-di-*tert*-butyl-1,3-diphosphacyclobutadiene (**1a** and **2a**).[3,4] These new heterocyclic systems are of interest with respect to their electronic structure and with respect to related systems like the cyclobutadiene congeners **3** and **4**. In this paper we report on the He I photoelectron (PE) spectra of **1a** and **2a**. For the interpretation of these spectra we will rely on PE results for **3**[5a] and calculations on **3** concerning the ionization energies[5b] as well as on results obtained in our laboratory for **4** and related species.



R=t-butyl **1a**
R=CH_3 **1b**



R=t-butyl **2a**
R=CH_3 **2b**



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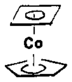

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Calculations

In the case of transition-metal compounds it has been found that Koopmans' theorem[6] is no longer applicable, even for the outer valence region.[7,8] Strongly localized metal 3d functions show considerably larger Koopmans defects in comparison with the reorganization energies of delocalized ligand orbitals. A very efficient way of calculating reorganization effects is Green's function formalism, where relaxation and correlation effects in the ground state and the cationic states are considered. A detailed description of the basic principles of Green's function approach is described in the literature.[9–11] In analogy to previous studies[8,12] we have adopted the following approximation for the self-energy part $\sum(\omega)$ in the inverse Dyson equation.[13]

$$\sum(\omega) = \sum{}^2(\omega) + D4 \qquad (1)$$

This expression contains second-order terms $\sum^2(\omega)$ to approximate the self-energy part and one third-order term, D4.[10] In the case of molecular orbital calculations that do not reach the HF limit exactly, D4 also has the character of a semiempirical correction term.[14] The jth vertical ionization energy, I^{GF2}, is related to the jth canonical MO energy, ϵ_j, according to (2) if the inverse Dyson equation

$$-I^{GF2}{}_{v,j} = \epsilon_j + \sum{}^2{}_{j,j}(\omega_j) + (D4)_{jj} \qquad (2)$$

is solved via a diagonal variant. The computational background is an improved INDO procedure[15] which has been developed to simulate the results of high-quality ab

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† Organisch-Chemisches Institut der Universität Heidelberg.
‡ Max-Planck-Institut für Kohlenforschung.
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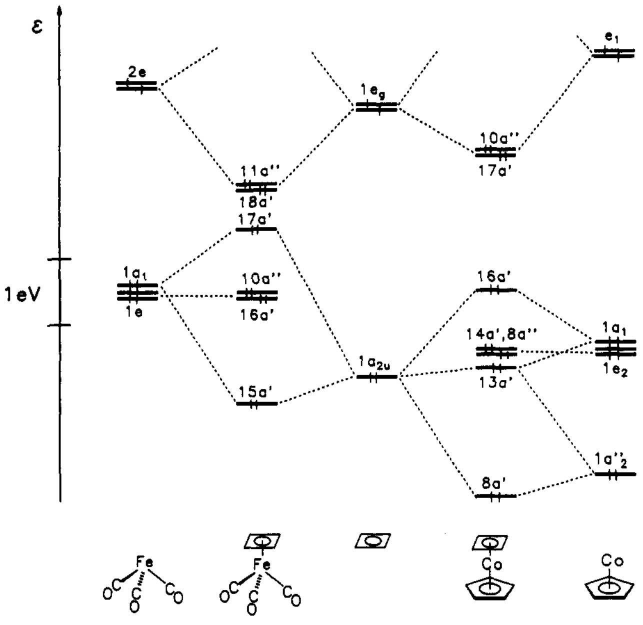


Figure 1. Qualitative diagram showing the interaction between the valence MO's of a cyclobutadiene unit (center) and the fragment orbitals of a Fe(CO)$_3$ unit (left) and a CpCo unit (right). For the fragment MO's of the CpCo, Cb, and Fe(CO)$_3$ units we adopted the irreducible representation of the local symmetry i.e. for CpCo (C_{5v}), Cb (D_{4h}), and Fe(CO)$_3$ (C_{3v}).

initio calculations on organometallic systems. In the summations of eq 2 we have used an array of 14 hole states and 10 particle functions.

It should be pointed out that the corrections given in eq 2 are only valid for the Hartree–Fock SCF-type of approach as the 0th approximation. In this case electronic relaxation processes will lead to a sizable reduction of the value of the ionization energy in comparison to the calculated orbital energies.[16] The energy shifts derived by the employed method correspond to a lower limit as a result of the adaption of "experimental" two-electron integrals. Ab initio calculations will lead to even larger effects.[17] Such differences between orbital energies and ionization energies will not be obtained in those procedures where the one-electron energies are of different physical meaning; examples include the Xα method[18] or the local density approximations.[19] The reorganization energies mentioned above, which are a result of the two-electron part of the Hamiltonian, are irrelevant in methods which are based on a one-electron Hamiltonian like the extended Hückel[20] or Fenske–Hall[21] method. For the INDO calculations, we have used the experimental X-ray data for 2,[3] 3,[22] and 4.[23] The geometrical parameters of **1b** have been extrapolated on the basis of the bond lengths and bond angles of **2** and **3**. For the distance from the Fe center to the P$_2$C$_2$ ring we assumed the value of 1.836 Å. The calculations were carried out on **1b** and **2b**. Standard bond lengths of 1.1 Å have been adopted for the CH bonds in all compounds.

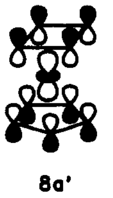
Table I. Valence Molecular Orbitals of 2,4-Dimethyl-η^4-λ^3-1,3-diphosphacyclobutadiene(ligand)iron Tricarbonyl (1b)

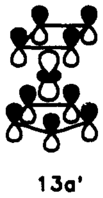
		population analysis, %			
SYM	ϵ_j, eV	Fe	L	CO	MO type[a]
14a''	−10.42	44	34	22	L 1a$_2$(π), d$_{yz}$
21a'	−11.79	59	21	20	d$_{z^2}$, L 1b$_1$(π)
20a'	−12.08	79	11	10	d$_{x^2-y^2}$, d$_{xz}$
13a''	−12.27	86	7	7	d$_{xy}$, d$_{yz}$
19a'	−12.79	22	62	16	L 2b$_1$(π)
18a'	−13.27	25	59	16	L 1b$_1$(π), d$_{z^2}$

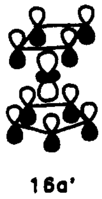
[a] For the MO's of the ligand (L) we adopted the irreducible representation of the local symmetry C_{2v}, with the z axis going through the heteroatoms.

Ground-State Properties of 1a and 2a

To elucidate the electronic structures of **1a** and **2a**, we will start by discussing briefly the electronic structures of the well-known complexes **3**[5,24] and **4**.[24,25] In Figure 1 is shown a simple diagram showing the interaction of the highest occupied π MO's of the cyclobutadiene ligand (center) with the fragment orbitals of a Fe(CO)$_3$ moiety (left) and the CpCo fragment (right).[24] The two highest occupied MO's of **3** (11a'', 18a') and **4** (10a'', 17a') originate from the interaction of the half-filled 1e$_g$ levels of the cyclobutadiene ligand with the half-filled e levels of the metal fragments. This interaction, shown in the upper part of Figure 1, leads to a considerable stabilization of the former e$_g$ MO's of the cyclobutadiene ring and to a transfer of electron density from the metal to the C$_4$H$_4$ part. The two highest filled MO's of **3** and **4** are followed by three MO's with appreciable 3d character (17a', 10a'', 16a' in the case of **3**, and 16a', 14a', 8a'' in the case of **4**). Two of them correlate with the 1e (d$_{xy}$, d$_{x^2-y^2}$) set of the metal fragment; the other results from the interaction of the 3d$_{z^2}$ AO with a$_{2u}$(π) of the cyclobutadiene part. In the case of **4** the interaction scheme is somewhat more complex (Figure 1 right) since there are two fragment orbitals (1a$_1$(d$_{z^2}$) and 1a''$_2$(π)) on the side of the CpCo part which are suited to interact with the 1a$_{2u}$(π) of the cyclobutadiene unit. The interaction between these three basis orbitals gives rise to 16a', 13a', and 8a'. The three resulting wave functions are shown.


8a'


13a'


16a'

It should be mentioned that we have omitted some σ MO's of the cyclobutadiene ring in Figure 1 for the sake of clarity. Additionally for **4**, we omitted two MO's (15a', 9a'') between 16a' and 14a' which can be described as linear combinations of the 1e$_1$''(π) set of the cyclopentadiene ring and of 3d$_{xz}$ and 3d$_{yz}$ of the metal, respectively.

To derive the orbital sequence of **1b** and **2b**, we must replace two opposite CH centers of the cyclobutadiene ring in **3** and **4** by two P atoms. The resulting correlations are shown in Figures 2 and 3. These correlations are based on INDO calculations on **3**, **4**, **1b**, and **2b**. The detailed results for **1b** and **2b** are listed in Tables I and II. A

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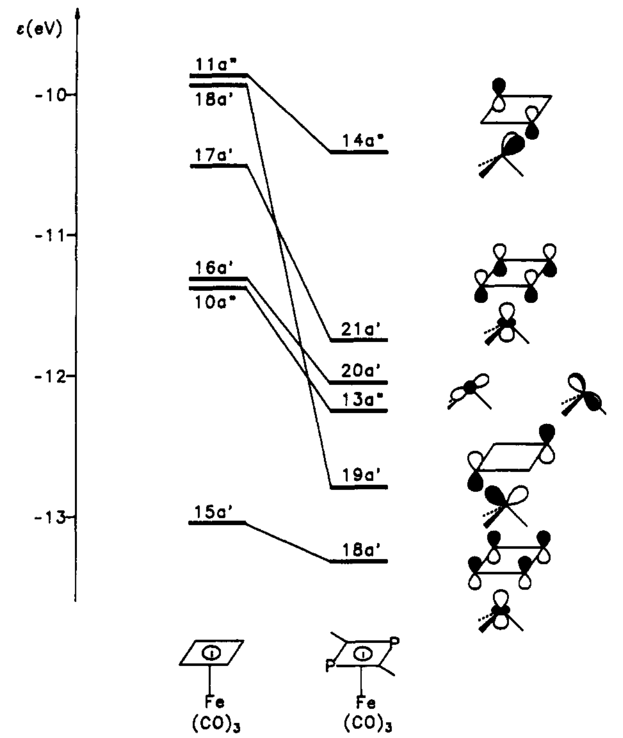


Figure 2. Correlation diagram between the valence orbitals of 3 (left) and **1b** (right). The energy levels were calculated with the INDO method.

Table II. Valence Molecular Orbitals of 2,4-Dimethyl-η^4-λ^3-1,3-diphosphacyclobutadiene(ligand)-η^5-cyclopentadienylcobalt (2b)

		population analysis, %			
SYM	ϵ_j, eV	Co	L	Cp	MO type[a]
13a″	-9.49	12	21	67	L $1a_2(\pi)$; Cp $1e_{1b}''(\pi)$
20a′	-10.86	27	2	71	Cp $1e_{1a}''(\pi)$; d_{xz}
19a′	-12.33	79	6	15	d_{z^2}
12a″	-12.41	49	8	43	Cp $1e_{1b}''(\pi)$; d_{yz}
18a′	-12.66	85	11	4	$d_{x^2-y^2}$
11a″	-12.79	96	2	2	d_{xy}
16a′	-13.28	20	43	37	L $1b_1(\pi)$; Cp $a_2''(\pi)$
17a′	-13.29	4	77	19	L $2b_1(\pi)$

[a] For the MO's of the ligand (L) we adopted the irreducible representation of the local symmetry C_{2v}, with the z axis going through the heteroatoms.

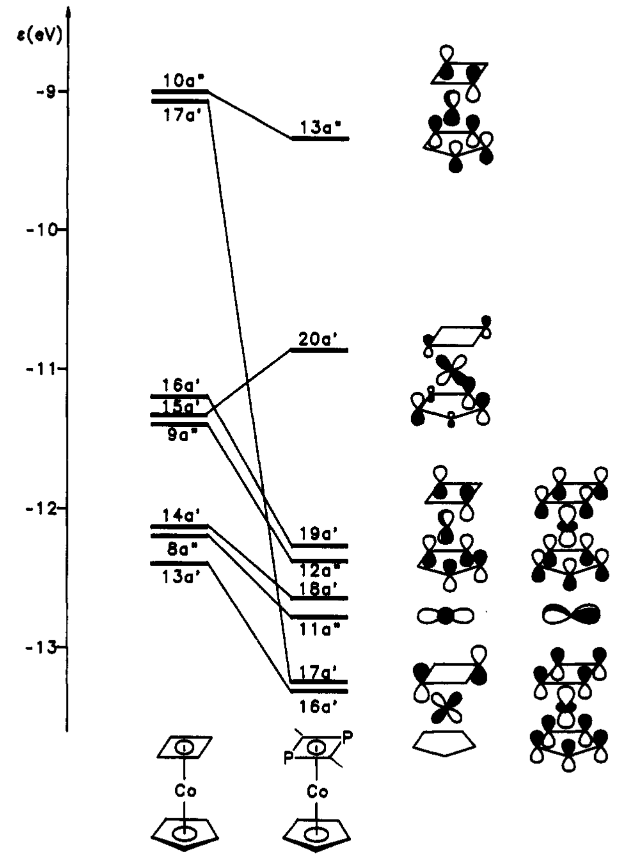


Figure 3. Correlation diagram between the valence orbitals of 4 (left) and **2b** (right). The energy levels were calculated with the INDO method.

comparison of the highest occupied MO's of 3 with those of **1b** (Figure 2) shows two effects: (i) a stabilization of all MO's on the order of 0.5–1.5 eV and (ii) a strong splitting of the former nearly degenerate pair 11a″, 18a′. The stabilization is to a small part due to the higher ionization energy used in our INDO version for 3p on P as compared to 2p on C. The main reason is, however, the better overlap between the P and metal AO's. The strong energy difference between 14a″ and 19a′ also originates in the stronger overlap between $3d_{xz}$ and the 3p AO's centered at the diphosphacyclobutadiene ligand as compared to the 2p AO's and $3d_{yz}$ of 14a″. For the later discussion one should keep in mind that in the case of 3 the calculation predicts two ligand orbitals (11a″, 18a′) on top of three "metal orbitals" (17a′, 10a″, 16a′), while in **1b** only one ligand orbital (14a″) is calculated to be on top of three metal orbitals (21a′, 20a′, 13a″).

The correlation of the highest occupied MO's of 4 and those of **2b**, shown in Figure 3, exhibits the same trends as already noted in Figure 2: a stabilization of the MO's when the CH unit is replaced by P, and a strong splitting of the near degenerate ligand levels 10a″, 17a′ and 15a′, 9a″, respectively.

Photoelectron Spectra of 1–5

Before we discuss the PE spectra of 1 and 2, we will briefly discuss those of 3 and 4—the more simple congeners. The PE spectrum of 3 was published some time ago.[5a] It shows two broad peaks at 8.4 and 9.2 eV. By means of ab initio calculations considering the various ionic states explicitly and by using intensity criteria of a He I and He II light source, it was concluded that the first peak must be due to the ionization from the three MO's with large 3d character (17a′, 16a′, 10a″). The second peak is assigned to the ionization from the two highest occupied MO's of 3, 11a″ and 18a′. The INDO method used in this paper reproduces this assignment very well (see Table III). The various methods of calculation predict large Koopmans' defects (2–3 eV) for the three 3d MO's and small ones (ca. 0.6 eV) for the ligand MO's of 3.

To our knowledge, the PE spectrum of 4 has not been published to date. It shows (Figure 4, Table III) three peaks below 10 eV. The ratio of the areas below the envelopes of these peaks amounts approximately to 1:4:2. From our previous experience with cobalt compounds[8] and the orbital sequence given in Figures 1 and 3, we expect large Koopmans' defects for the MO's 16a′, 14a′, and 8a″ and small defects for 10a″ and 17a′ as well as 15a′ and 9a″, the ligand π MO's. This and the intensity ratio mentioned above suggest that we assign the first two peaks to five ionic states and the third peak to two ionic states from the Cp ligand orbitals. In line with this assignment of the latter peak are the PE results obtained from the investigations of CpCo(η^4-cyclohexa-1,3-diene) and of CpCo(COD).[26] Here the ionic states corresponding to the

Table III. Comparison between Calculated IE^{GF}_{CALC} and Measured Vertical Ionization Energies (eV) IE^{EXP} for 1a, 2a, 3, and 4[a]

compd	assgnt	ΔI	IE^{GF}_{CALC}	IE^{EXP}	band
1a	13a″	3.80	8.47	8.3	1, 2
	20a′	3.26	8.82		
	21a′	2.78	9.01	8.7^{sh}	3
	14a″	1.19	9.23	9.4	4
	18a′	1.42	11.85	10.6	5
	19a′	0.78	12.01	10.8	
2a	11a″	4.92	7.87	7.4^{sh}	1–3
	19a′	4.09	8.24	7.8	
	18a′	4.40	8.26		
	13a″	0.52	8.97	8.4	4
	12a″	2.30	10.11	9.4	5
	20a′	0.55	10.31		6
	17a′	1.46	11.82	10.3	7
	16a′	0.58	12.71		
3	17a′	2.04	8.41	8.17^{sh}	1
	16a′	2.73	8.60	8.45	
	10a″	2.55	8.79		
	18a′	0.65	9.30	9.21	2
	11a″	0.66	9.28		
4	14a′	5.19	6.95	7.33	1
	8a″	5.10	7.10	7.7^{sh}	2–5
	16a′	3.87	7.48		
	10a″	0.11	9.03	8.1	
	17a′	0.11	9.03		
	15a′	1.40	9.98	9.33	6
	9a″	1.40	9.98		7

[a] The ionization energies were calculated by Green's function approach IE^{GF}_{CALC} for **1b**, **2b**, **3**, and **4**.

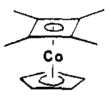
Table IV. Vertical Ionization Energies, $I_{v,j}$ (eV), of the PE Spectra of 5 and 6

band	$I_{v,j}$ (**5**)	$I_{v,j}$ (**6**)	assgnt[a]
1	6.74	6.70	16a′: Co d_{z^2}
2	7.14	7.10	14a′, 8a″: Co $d_{x^2-y^2}$, d_{xy}
3	7.39	7.30	10a″, 17a′: Cb $1e_g(\pi)$
4	8.84	8.70	15a′, 9a″: Cp $1e_1''(\pi)$

[a] We adopt the same notation as for **4** in Figure 1.

ionization from Cp π MO's are found at 9.27 and 9.11 eV, respectively. In agreement with our qualitative argument are MO calculations using the INDO method (see Table III). These calculations predict three states (14a′, 8a″, 16a′) mainly arising from 3d orbitals on top of two ionic states (10a″, 17a′) from the HOMO's and two states (15a′ and 9a″) from the cyclopentadiene ligands.

Further support of our assignment of the second peak of the PE spectrum of **4** is obtained when we compare the half-width of this peak (0.9 eV) with the half-width of the same peak in the PE spectra of **5** and **6** (0.75 eV). This



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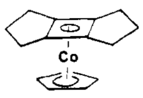

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indicates the anticipated stronger shift of the bands arising from the ligand orbitals localized at the cyclobutadiene ring as compared to the bands originating from the metal MO's. The first ionization energies of **5** and **6** are collected in Table IV.

The PE spectra of **1a** and **2a** (see Figure 4) are similar to that of **4**. One broad peak at low energy is followed by a small one at higher energy. To discuss both spectra qualitatively, we start with the correlation diagram in Figures 2 and 3 and assume large Koopmans' defects for the 3d MO's and small ones for the ligand MO's.

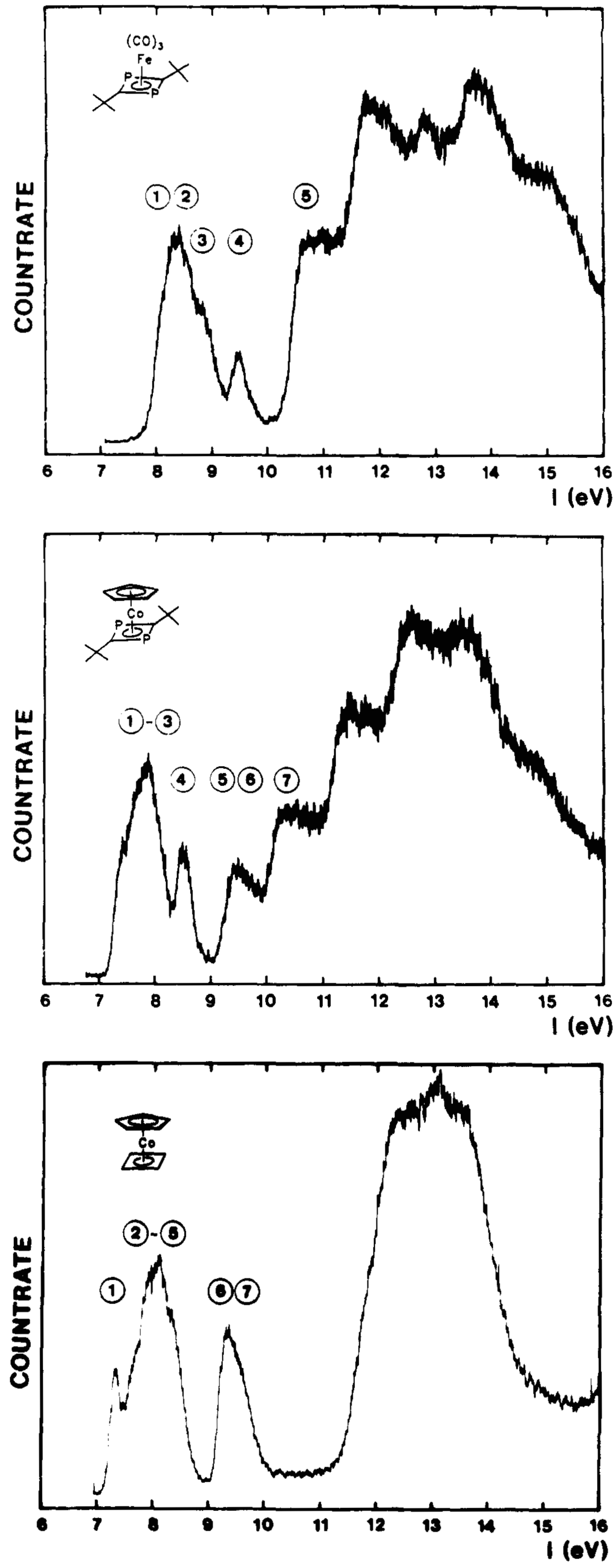

Figure 4. He I photoelectron spectra of **1a**, **2a**, and **4**.

From the difference of the orbital sequence between **1b** and **3** as discussed above, we estimate three ionic states for the first band in the PE spectrum of **1a** (21a′, 20a′, and 13a″) and one ionic state (14a″) for the band at 9.4 eV. The assignment of the first bands in the PE spectrum of **1a** is supported by a comparison of the band intensities

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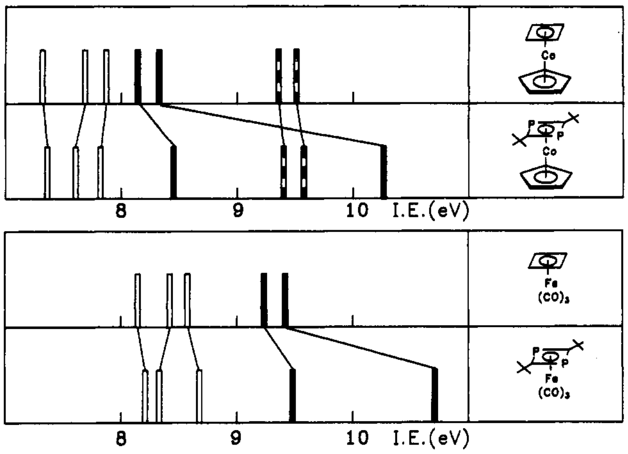

Figure 5. Correlation between the first bands in the PE spectra of **2a** and **4** (top) and **1a** and **3** (bottom). Full bars indicate bands that originate from ligand MO's; empty bars correspond to bands that originate from metal MO's.

of the He I PE spectra with those of the He II PE spectra making use of the observation that the PE cross sections of metal d orbitals and ligand MO's differ significantly.[27] In fact, a comparison of the He I and He II intensities for **1a** reveals an enhancement of the first peak (bands 1–3) with respect to bands 4 and 5. The relations of the intensities of the PE bands 1–3:4:5 expressed as percentages are as follows: He I (**1a**), 38:19:43; He II (**1a**), 55:14:31.

Similarly, we estimate three states for the first peak of the PE spectrum of **2a** (11a″, 19a′, and 18a′) and one for the second band (13a″). The position of the third peak (9.4 eV) is close in energy to the third peak (9.33 eV) in the PE spectrum of **4**. Therefore, we suggest an assignment of this band to the ionization from the Cp ligand orbitals 20a′ and 12a″.

The comparison with the INDO results confirms the qualitative assignments given (see Table III). The numerical agreement between experiment and calculation is good. The calculations predict rather large Koopmans' defects for the metal-centered MO's (3–5 eV) and small ones for the ligand MO's. In both cases, for the first broad peak three ionic states are predicted, while for the second peak one ionic state, the one arising from the HOMO, is predicted. Due to the different metal fragments $Fe(CO)_3$ vs CpCo the energies for both states vary considerably (9.4 vs 8.4 eV).

Concluding Remarks

The correlation between the PE spectra of **2a** and **4** and **1a** and **3**, respectively (see Figure 5), reveals a strong stabilization of one ionic state from the 4π ligand. It thus demonstrates a very strong interaction between the π ligand and the metal. This effect may also be responsible for the failure of all attempts to remove the metal fragment from **1a** and **2a**, respectively, by decomplexation. 2,4-Di-*tert*-butyl-1,3-λ^3-diphosphacyclobutadiene and its reactivity so far are still unknown. The comparison also shows a slight stabilization of the $a_2(\pi)$ level. In addition to thermodynamic and kinetic factors, the electronic effects just discussed may contribute to the high thermal stability of **1a** and **2a** as compared to **3** and **4**.

Experimental Section

Compounds **1a** and **2a** have been prepared recently.[2,3] The preparation of **4–6** has been described in the literature.[28–30] The photoelectron spectra of **1a**, **2a**, and **4–6** have been recorded with a PS 18 instrument from Perkin-Elmer (Beaconsfield). The He II PE spectrum of **1a** has been recorded on an instrument from Helectros Developments (Beaconsfield, England).[31] The recording temperatures were as follows: **1a**, 35 °C; **2a**, 85 °C; **4** and **5**, 28 °C; 70 °C. The calibration was done with Ar (15.76 and 15.94 eV) and Xe (12.13 and 13.44 eV). A resolution of 20 meV on the $^2P_{3/2}$ Ar line was obtained.

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Registry No. **1a**, 126859-53-8; **1b**, 137366-00-8; **2a**, 105267-82-1; **2b**, 137366-01-9; **3**, 12078-17-0; **4**, 12306-95-5; **5**, 12245-36-2; **6**, 112397-43-0.

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