phenyltin fluoride (126 mg, 0.341 mmol, 43.9% based on the formation of 2 mol/mol of stannane 11). Volatiles were removed from the supernatant by evaporation under reduced pressure, giving a residue which contained allyltriphenylmethane[20] and triphenylmethane (90% yield by NMR). These two compounds could not be separated by thin-layer chromatography under a variety of conditions, but careful molecular distillation at 65 °C (0.15 torr) yielded pure triphenylmethane (33.6 mg, 0.138 mmol, 35.6%). Further distillation at 85 °C (0.13 torr) yielded allyltriphenylmethane (32.8 mg, 0.120 mmol, 30.9%), which by NMR, IR, and mass spectrometry was identical with an authentic sample.[20,21]

Relative Rates of Reduction of Triphenylcarbenium Tetrafluoroborate by 2-[(Triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2) and 1,3-Propanediylbis[triphenylstannane] (11). A mixture of 2-[(triphenylstannyl)methyl]-1,3-propanediylbis[triphenylstannane] (2; 5.5 mg, 5.0 μmol) and diphenylmethane (3.4 mg, 20 μmol), added as an internal standard, was treated under Ar with a solution of triphenylcarbenium tetrafluoroborate in deuteriochloroform (0.80 mL, 0.074 M, 59 μmol). The resulting solution was kept at 25 °C, and the rate of formation of triphenylmethane was measured by NMR.

An analogous experiment yielded the rate of reduction of triphenylcarbenium tetrafluoroborate by 1,3-propanediylbis[triphenylstannane] (11).

Acknowledgment. This work was financially supported by Research Corp., the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Éducation du Québec. We are grateful to Mr. M. Evans and Dr. M. T. Phan Viet, who recorded our mass and high-field NMR spectra.

Registry No. 2, 87549-81-3; 3, 1871-57-4; 4, 3775-29-9; 5, 3513-81-3; 6, 87597-80-6; 7, 87597-81-7; 11, 86623-72-5; Ph_3SnLi, 4167-90-2; Ph_3SnH, 892-20-6; $Ph_3C^+PF_6^-$, 437-17-2; 1,3-dibromopropane, 109-64-8.

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He I and He II Photoelectron Spectroscopic Studies of the Bonding in Cobalt, Rhodium, and Iridium Cyclopentadienyl Diene Complexes

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He I and He II photoelectron spectra have been obtained for a series of cobalt, rhodium, and iridium complexes where the metal is bonded both to a cyclopentadienyl group and to a diene system, $M(\eta\text{-}C_5R_5)L_2$: M = Co, R = H, L_2 = (η^4-cycloocta-1,5-diene), IV, L_2 = (η^4-cyclohexa-1,3-diene), VI; M = Co, R_5 = Me_4Et, L_2 = (η^4-cycloocta-1,5-diene), IVa; M = Rh, R = H, L_2 = (η^4-buta-1,3-diene), I, L_2 = (η^4-cycloocta-1,5-diene), V, L_2 = (η^4-cyclohexa-1,3-diene), VII, L_2 = (η^4-cyclooctatetraene), VIII; M = Rh, R = Me, L_2 = (η^4-cycloocta-1,5-diene), Va, L = C_2H_4, IX; M = Ir, R = H, L_2 = (η^4-buta-1,3-diene), II, L_2 = (η^4-2-methylbuta-1,3-diene), III. Ionization energy trends and intensity patterns are used to assign the spectra on the basis of a qualitative MO scheme. The nature of the HOMO is found to vary markedly from the Co complexes to the Rh and Ir complexes. In the cobalt cases the HOMO is largely d in character, whereas for Rh and Ir substantial localization on the ligands is indicated. These differences in electronic structure can be correlated with differences in chemical behavior. The preference of the metal–cyclopentadienyl unit for bonding to nonconjugated dienes is discussed.

Introduction

There have been several investigations of the photoelectron spectra of dienes and diolefins bonded to transition metals.[1-9] Most of the studies of dienes were on complexes of the type $M(CO)_3L_2$, where M = Fe or Ru,[1-4,6-8] whereas that on the diolefins was of compounds of the type M(β-diketonate)L_2, where M = Rh or Ir.[9] There also exists a large class of volatile diene complexes of the type $M(\eta\text{-}C_5R_5)L_2$, where M = Co, Rh, and Ir, in which the metal center would be expected to be more

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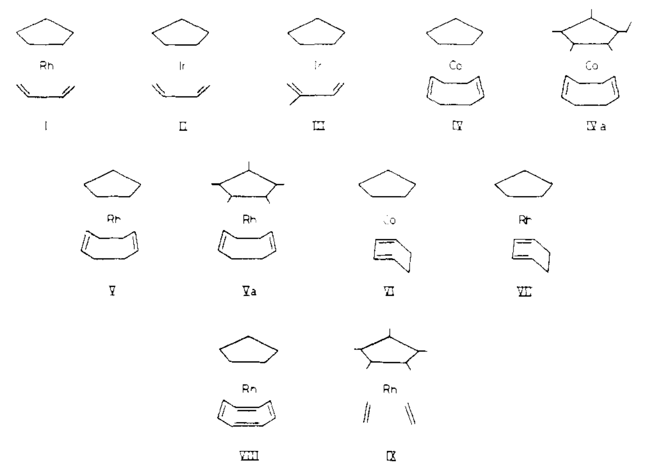
[9] van Dam, H.; Tepstra, A.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3448.

Chart I



electron donating than in either of the two former classes. The metal cyclopentadienyl unit sows a preference for bonding to nonconjugated dienes, for example, cycloocta-1,3-, cycloocta-1,4-, and cycloocta-1,5-dienes all react with $Rh_2(\eta\text{-}C_5Me_5)_2Cl_2$ to give a 1,5-diene complex.[10,11] However in the case of cyclohexa-1,4-diene, where steric constraints are greater, the 1,4-diene complex is first formed which then isomerizes to the 1,3-diene complex.[12] Cyclooctatetraene also coordinates in a 1,5 mode.[13] This behavior is in contrast to the $M(CO)_3$ system which shows a preference for coordination to conjugated dienes. The $M(CO)_3$ preference has been explained by Elian and Hoffmann[14] in terms of the donor and acceptor characteristics of the fragment.

We have therefore undertaken a study of the photoelectron spectra of a series of metal cyclopentadienyl diene complexes in order to obtain experimental information on their electronic structure.[15] The complexes studied are denoted in Chart I.

Experimental Section

Samples of some of the complexes were prepared and donated by Dr. D. M. P. Mingos (Va, IX), Dr. L. J. Russell (IV, Va, VII, VIII), and Dr. R. Pardy (IVa). All were purified prior to spectral measurement. The compounds II, III, V, and Va were prepared by the literature methods.[16-18]

(η^5-Cyclopentadienyl)(η^4-butadiene)rhodium, I, was prepared from bis(cyclooctene)rhodium chloride dimer (0.35 g) and liquid butadiene (3 mL). The resulting bis(butadiene)rhodium chloride was treated with thallium cyclopentadienide (0.269 g) in dry diethyl ether at room temperature, in the dark. After the mixture was stirred for about 30 min, thallium chloride was removed by filtration, leaving a yellow solution. The solvent was removed under reduced pressure to give yellow crystals of I. The yield was approximately quantitative.

(η^5-Cyclopentadienyl)(η^4-cyclohexa-1,3-diene)cobalt, VI, was prepared by a modification of the procedure described by King.[19] Cobalt cyclopentadienyl dicarbonyl (1 mL, 1.3 g), cyclohexa-1,3-diene (2 mL, 1.8 g), and ethylcyclohexane (5 mL) were refluxed (135 °C) for 12 h under a nitrogen atmosphere. The reaction mixture was chromatographed on alumina by using pentane as eluant. An orange band was collected, the pentane removed under reduced pressure, and the resulting oil recrystallized from pentane at low temperature.

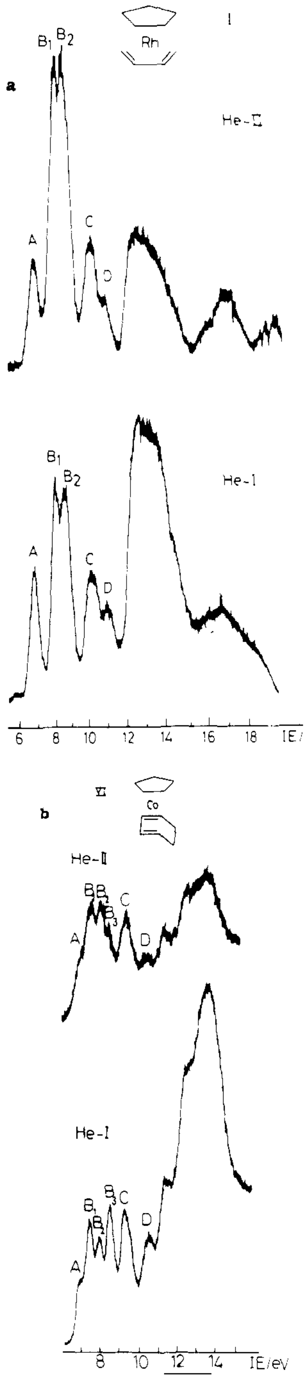


Figure 1. He I and He II spectra of I and VI.

Photoelectron spectra of the compounds I–IX were obtained by using a Perkin-Elmer PS 16/18 spectrometer fitted with a Helectros discharge lamp capable of producing both He I and He II radiation. He I and He II spectra were obtained, at least in duplicate, for each complex, and calibration was carried out using xenon, nitrogen, and the He self-ionization band. Relative intensities of bands were corrected by dividing by the kinetic energy of their electrons. Measurement conditions are given in Table I.

Results

Vertical ionization energies (IE) are given in Table II and band intensities in Table III.

As spectra show a main band centered around 13 eV and a higher band around 16.5 eV (see Figure 1) that are due

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Table I. Photoelectron Spectroscopic Measurement Conditions for Compounds I-IX

compd	temp, °C	He I, counts/s	He II, counts/s
I	45	4000	400
II	39	4000	400
III	41	4000	400
IV	38	4000	100
IVa	54	1000	100
V	57	4000	100
Va	80	4000	400
VI	41	4000	400
VII	56	4000	400
VIII	66	1000	100
IX	76	4000	400

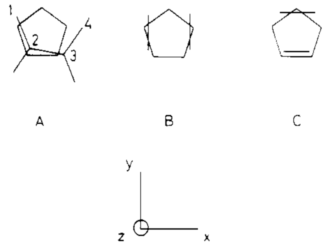

Figure 2. Projection of the structures in the *xy* plane: A, Rh(η-C_5H_5)(η^4-2-MeC_4H_5); B and C, alternative structures for nonconjugated diene complexes.

to ionization of the structure of the hydrocarbon ligands; these will not be discussed further. In the case of the peralkylated complexes IVa, Va, and IX there is an additional band at ca. 11.5 eV due to ionizations from the ring alkyl groups.[20] In the spectra of the rhodium and iridium complexes there is a striking intensity increase in some of the low-energy ionization bands in the He II spectra compared with the He I spectra. This is illustrated in Figure 1a. Although relative intensity changes are also found for the cobalt complexes, they are not so large (see Figure 1b).

Bonding Model

Although there are no literature reports on the structure of the complexes I-IX, there have been sufficient X-ray investigations of related species for the general structural features of such compounds to be well established.[21-27] The structure of (cyclopentadienyl)(2,3-dimethylbuta-1,3-diene)rhodium[21] (Figure 2A) shows small distortions from the idealized geometry of two parallel hydrocarbon units and a mirror plane for the molecule. The butadiene unit shows almost equal C-C distances, indicating significant occupation of the third π level in the complex. In the case of nonconjugated dienes, two structural types are found, parts B and C of Figure 2, differing in the orientation of the ring to the two parallel olefin groups.[22-27] However free rotation of the ring is observed even at very low temperatures[23] when the ring bears no electron-withdrawing substituents, showing the energy difference to be small. For the purposes of description of the bonding we will assume an idealized form of A and B, as the structural types, both possessing a mirror plane, *yz*.

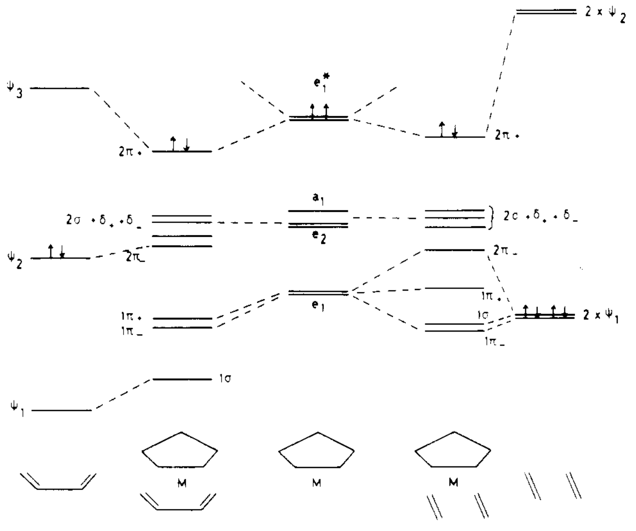

Figure 3. Molecular orbital schemes for a M(η-C_5H_5) fragment bonded to a conjugated and a non-conjugated diene.

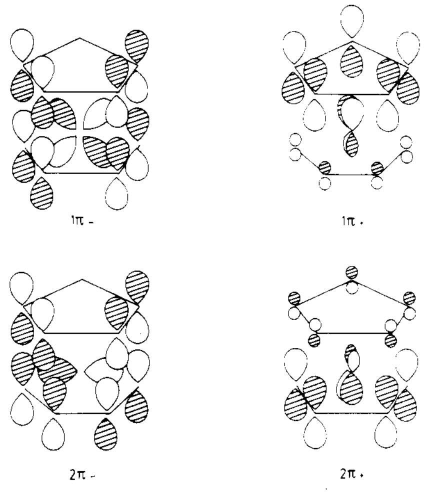

Figure 4. Diagrammatic representation of the orbitals $1\pi_+$, $1\pi_-$, $2\pi_+$, and $2\pi_-$.

In the assignment of the PE spectra we will be concerned principally with eight levels. These are 18-electron compounds, but the ionization band of the lowest π level of the cyclopentadienyl ring is obscured by the main hydrocarbon ionization band. We will label these eight levels, + or −, according to their reflection in the *yz* plane, and also σ, π, or δ, according to the number of angular nodes they possess on rotation about the *z* axis. This is not, of course, a $C_{\infty v}$ axis but does provide a clear basis for identifying orbitals and one which stresses their relationship to the MO of a metallocene.

In Figure 3 MO diagrams have been constructed by using a fragment approach[13] for a metal cyclopentadienyl unit bonded both to a conjugated diene and to two nonconjugated dienes. When M is Co, Rh, or Ir the antibonding e_1* orbital of the M(η-C_5H_5) unit will be occupied by two electrons. On interaction with the LUMO of the diene units, the degeneracy of the e_1* orbitals is split, resulting in a combined orbital, $2\pi_+$, in which these two electrons are paired. The $2\pi_+$ orbital is metal-diene bonding but metal-ring antibonding. This back-donation from the metal to the diene units is expected to be more

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Table II. Vertical Ionization Energies (eV) and Assignments of Bands for Compounds I-IX

band	I	II	III	VII	assignt	band	IX	assignt	V	assignt	Va	assignt
A	7.26	7.31	7.21	7.17	$2\pi_+$	A	7.03	$2\pi_+$	7.07	$2\pi_+$	6.36	$2\pi_+$
B_1	8.32	8.16	8.02	8.10	δ_+, δ_-	B_1	8.22	$2\sigma, \delta_+, \delta_-$	7.89		7.67	$2\sigma, \delta_+, \delta_-$
		8.41	8.29						8.12	$2\sigma, \delta_+, \delta_-$		
B_2	8.81	8.82	8.76	8.52	$2\sigma, 2\pi_-$	B_2	8.88	$2\pi_-$	8.57		8.16	$2\pi_-$
		9.16	9.08						8.84	$2\pi_-$		
C	10.17	10.58	10.50	9.88	$1\pi_+, 1\pi_-$	C	9.51	$1\pi_+$	9.27	1σ	9.11	$1\sigma, 1\pi_+, 1\pi_-$
D	10.99	10.99	10.50	10.43	1σ	D	10.22	$1\sigma, 1\pi_-$	9.82	$1\pi_+, 1\pi_-$		
other	13.0	12.7	12.7	11.5		other	11.6		10.7		10.2	
	16.8	13.3	16.8	12.3			12.6		11.1		12.1	
		16.8		13.3			13.7		12.3		13.5	
				16.5			16.5		13.5		16.3	
									16.4			

band	VI	assignt	band	IV	assignt	IVa	assignt	band	VIII	assignt
A	6.92	$2\pi_+$	A	6.96	$2\pi_+, 2\sigma$	6.63	$2\pi_+, 2\sigma$	A	7.13	$2\pi_+$
B_1	7.43	2σ	B	7.54	δ_-, δ_+	7.21	δ_-, δ_+	B	7.99	δ_+, δ_-
B_2	7.97	δ_+, δ_-						C	9.06	$2\sigma, 2\pi_-, a_1$(COT)
B_3	8.47	$2\pi_-$						D	9.94	e_+(COT)
C	9.27	$1\pi_+, 1\pi_-$	C	8.78	$2\pi_-, 1\sigma$	8.14	$2\pi_-, 1\pi_+$	E	10.78	$1\pi_+, 1\pi_-, b_2$(COT)
D	10.43	1σ	D	9.11	$1\pi_+, 1\pi_-$	8.81	$1\sigma, 1\pi_-$	other	12.3	
other	11.2		other	10.7		11.3			13.8	
	12.3			11.4		11.9				
	13.5			13.5		13.4				
	16.3									

Table III. Intensities of PE Bands Expressed as Percentages for Compounds I-IX

compd		A	B	C	D
I	He I	14	51	22	13
	He II	10	63	18	8
II	He I	13	54	22	11
	He II	10	63	19	8
III	He I	13	53	33	
	He II	12	61	27	
VII	He I	13	51	23	13
	He II	9	63	28	
IX	He I	15	53	10	21
	He II	10	61	12	18
V	He I	17	53	10	21
	He II	9	57	12	22
Va	He I	14	49	36	
	He II	10	57	33	
IV	He I	21	19	19	41
	He II	22	28	13	37
IVa	He I	21	21	19	38
	He II	24	27	19	29

compd		A	B_1	B_2	B_3	C	D
VI	He I	8	17	12	19	25	19
	He II	11	19	17	15	25	13

compd		A	B	C	D	E
VIII	He I	9	16	33	6	36
	He II	6	28	42	7	17

successful in the case of the conjugated dienes than the nonconjugated ones as the diene LUMO will lie lower in energy in the former case.[13]

A "molecules in molecules" approach to the interpretation of PE spectra[28] is most successful when the energies of interacting orbitals are sufficiently disparate for perturbations to be small. There is a possibility in the molecules under consideration here of strong delocalized interactions between the HOMO of the diene and the π_- component of the e_1 M–ring bonding orbitals. This is illustrated in Figure 4 where the analogy is drawn with metallocene bonding. The $1\pi_-$ combination of the ring and diene orbitals is stabilized by interaction with the metal d_{xz} orbital, while the $2\pi_-$ orbital can only interact with the metal p_z orbital and consequently lies higher in energy. The π_+ orbitals are also illustrated diagramatically. The diene contributor to this set is unoccupied and lies much higher in energy. Mixing between the ring and diene system is therefore expected to be less extensive. All four of these orbitals are occupied in the compounds studied and their ionization energies are expected to be a sensitive function of the metal and of the type of ligand.

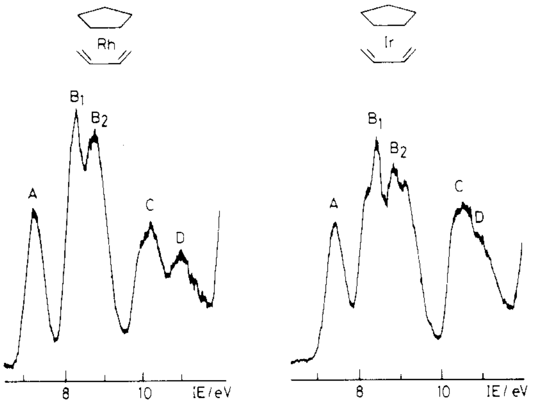

Figure 5. He I photoelectron spectra of the low-energy regions of I and II.

The orbitals 2σ, δ_+, and δ_- correlate with d_{z^2}, $d_{x^2-y^2}$, and d_{xy} respectively. They are all expected to be largely metal d in character: the lobes of the carbon $2p\pi$ orbitals closer to the metal tend to lie on the nodal cone of the d_{z^2} orbital and overlap is poor. The in phase combination of the carbon $2p\pi$ orbitals, ψ_1, will compete with the a_1 ring π orbital for the metal s orbital (and the p_z orbital).

Spectral Assignment

The procedure we have used for assigning the PE spectra of the compounds I–IX is first to take those cases where interpretation seems to us unambiguous, on the grounds of characteristic IE and intensity variations, and the proceed by analogy where assignment is less obvious.

Rhodium and Iridium Complexes with Conjugated Dienes, I, II, III, and VII. Representative spectra are shown in Figures 1, 5, and 7 and the assignments summarized in Table II. The lowest energy band, A, lies well separated from subsequent bands and shows a significant

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[28] Green, J. C.; Jackson, S. E.; Higginson, B. R. *J. Chem. Soc., Dalton Trans.* **1975**, 403.

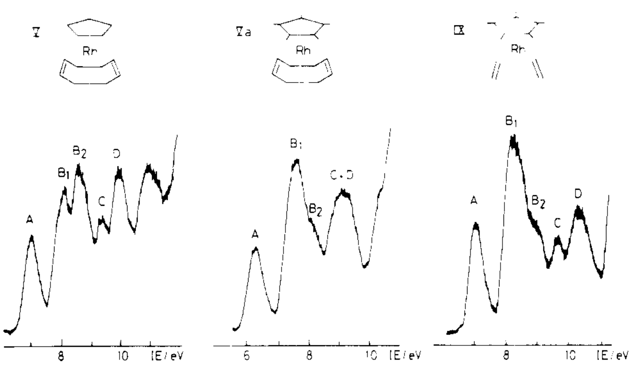

Figure 6. He I photoelectron spectra of the low-energy regions of V, Va, and IX.

decrease in relative intensity in the He II spectrum, indicating a high ligand character. All these properties are consistent with assignment to $2\pi_+$. The subsequent bands, B_1 and B_2, are shown in the iridium spectra to consist of four ionization processes and are consequently assigned to 2σ, δ_+, δ_-, and $2\pi_-$. Overall B shows relative increase in intensity in the He II spectra, indicating metal d character.

Both band C and band D have intensity characteristics of primarily ligand bands. Band C, which is double the intensity of band D in both the He I and He II spectra, is assigned to $1\pi_+$ and $1\pi_-$ and, band D to 1σ. It is noteworthy how consistent the intensity characteristics of the bands are within this set of compounds (Table III). We therefore feel justified in using the intensities found here as guidelines for the assignment of other Rh spectra.

Rhodium Compounds with Nonconjugated Dienes, V, Va, and IX. Whereas the relation between bands is clear for the series of butadiene derivatives discussed above, in this series the PE spectra have rather contrasting appearances (see Figure 6).

The first band A can be identified clearly by its separation from subsequent bands and its intensity characteristics and can be assigned to ionization of $2\pi_+$. In the case of IX, in which two ethylene molecules are bound to rhodium, the free olefin ionizes at 10.51 eV,[29] whereas with V and Va, where cycloocta-1,5-diene is the ligand, the free ligand shows only one π ionization band at 9.06 eV.[30] Cycloocta-1,5-diene shows a σ band at 10.7 eV so structure in this region in the spectrum of V can be attributed to ligand ionizations.

For V and IX band C is approximately half the intensity of band D so it seems reasonable to assume, given the actual percentage areas and their correspondences to those of the previous set of compounds, that band C comprises one ionization and band D two. If we now look first at IX we assign band D to 1σ and $1\pi_-$ and band C to $1\pi_+$. The high-energy shoulder of B (at 8.88 eV) is then assigned to $2\pi_-$. This shoulder is relatively less intense in the He II spectrum. The main part of B is assigned to 2σ, δ_+, and δ_-. The IE separation of $1\pi_-$ and $2\pi_-$ is 1.34 eV of comparable magnitude to the $e_{1u} - e_{1g}$ separation in ruthenocene[31] (e_{1u}, 8.51 eV; e_{1g}, 9.93 eV; $e_{1g} - e_{1u} = 1.42$ eV).

For V, a more reasonable assignment of 1σ is to band C, suggesting assignment of D to $1\pi_+$ and $1\pi_-$ and the high-energy shoulder of B_2 (8.84 eV) to $2\pi_-$. From the IE of the parent olefins it seems reasonable to infer that the character of the $1\pi_-$ orbital changes between IX and V in the proportion of cyclopentadienyl and diene contribution. In IX $1\pi_-$ should contain a relatively high proportion of diene character and $2\pi_-$ consequently a lower proportion, whereas the reverse should be true of V. The two bands comprising B_1 and the maximum of B_2 are assigned to the d ionizations 2σ, δ_+, and δ_-.

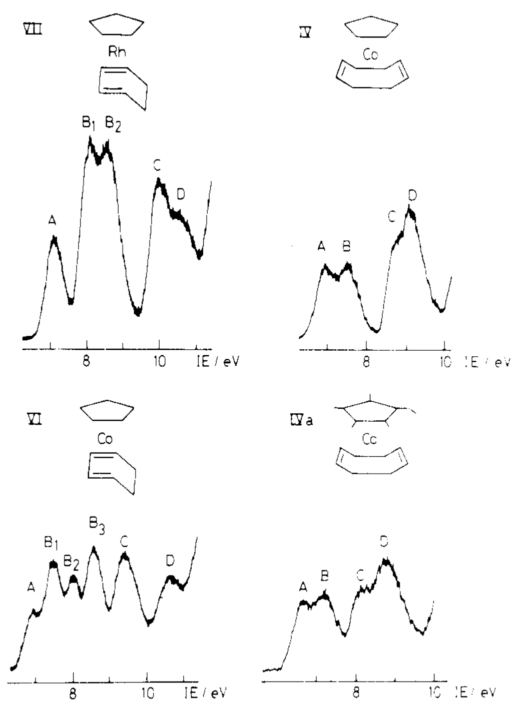

Figure 7. He I photoelectron spectra of the low-energy regions of VII, VI, IV, and IVa.

In Va, which differs from V by permethylation of the cyclopentadienyl ring, band D appears to merge with band C. On our assignment of V one would expect this, as 1σ should be less sensitive to the substitution than $1\pi_+$ and $1\pi_-$. Band B_2 is assigned to $2\pi_-$ and B_1 to 2σ, δ_+, and δ_-.

The Cobalt Compounds VI, IV, and IVa. In all cases we have a rhodium compound with which the cobalt compound may be compared directly, VI with VII, IV with V, and IVa with Va. The He I spectra of VI, VII, IV, and IVa are shown in Figure 7. The most striking difference is the absence of a band in the cobalt spectra with the characteristics of band A.

In the He II spectrum of VI, bands A, B_1, and B_2 undergo a relative increase in intensity, with A undergoing marginally less of an increase than B_1 or B_2 (see Figure 1b). It therefore seems reasonable to assign A to $2\pi_+$ and B_1 and B_2 to δ_+, δ_-, and 2σ but to conclude that $2\pi_+$ has very much more metal d character in the cobalt compounds than in the rhodium or iridium compounds.

Band B_3 shows a relative decrease in intensity in the He II spectrum and occurs at a very similar IE (8.47 eV) to the $2\pi_-$ band in the spectrum of VII (8.52 eV) as does D (10.43 eV) and the 1σ band in the spectrum of VII (10.43 eV); we thus assign B_3 to $2\pi_-$ and D to 1σ. This leaves band C unassigned; it is rather more intense than D and is assigned to the $1\pi_+$ and $1\pi_-$ ionizations. C has a rather lower IE (9.27 eV) than the corresponding band in VII (9.88 eV): a similar variation is found in the e_{1g} ionization of ferrocene (9.14 eV) and ruthenocene (9.93 eV).

The spectra of the cobalt complexes with nonconjugated dienes, IV and IVa, show rather fewer bands. In the case of IV the intensity and ionization energy pattern suggest the assignment of A and B to $2\pi_+$, δ_+, δ_-, and 2σ, C to $2\pi_-$ and 1σ, and D to $1\pi_+$ and $1\pi_-$, the two latter ionizations

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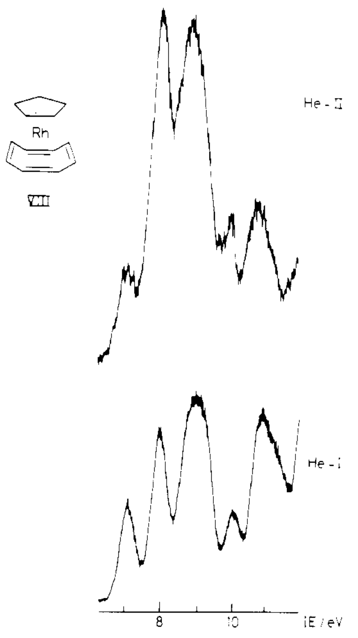

Figure 8. He I and He II photoelectron spectra of VIII.

being 0.71 eV lower in IE than the corresponding bands in the rhodium analogue V. In the case of IVa the assignment of A and B is similar. Extrapolation from Va suggests that the 1σ ionization may lie under D together with $1\pi_-$, whereas extrapolation from IV would put $1\pi_+$ under C together with $2\pi_-$.

We can make an interesting comparison of the shift of band A on peralkylation of the ring. In the case of the rhodium compounds V and Va, the shift on permethylation of the $2\pi_+$ band is 0.71 eV; between the cobalt compounds IV and IVa the shift is much less, 0.36 eV. This observation reinforces the proposition that the $2\pi_+$ orbital is of different character in the cobalt compounds compared with the rhodium compounds, the greater shift in the rhodium cases being a consequence of the greater localization of the ionizing electrons on the ring, as it is well documented, for example in the case of metallocenes,[20] that ring orbitals are more sensitive to peralkylation than metal-localized orbitals.

Cyclopentadienyl(cyclooctatetraene)rhodium, VIII. The compound VIII has been shown by NMR and IR studies[12] to contain the C_8H_8 ring bonded to the metal is an η^4 mode through C_1, C_2, C_5, and C_6. The free ligand adopts the boat conformation, a very similar geometry to that envisaged for the bound ligand. The PE spectrum of the free ligant[30] shows three π ionization bands: a_1, 8.42 eV; e, 9.78 eV; b_2, 11.5 eV. On binding to the metal, the degeneracy of the e pair will be lifted, the e_- component participating in the $1\pi_-$ and $2\pi_-$ MO, whereas the e_+ component is located on the carbon atoms uncoordinated to the metal and should remain relatively unperturbed. Band D in the spectrum at 9.44 eV is a good candidate for the e_+ (COT) ionization. Otherwise a reasonable assignment would be band A to $2\pi_+$, band B and part of band C to 2σ, δ_+, and δ_-, the remaining part of band C to $2\pi_-$ and a_1 (COT), and E to $1\pi_+$, $1\pi_-$, and b_2 (COT).

The d Bands. In the assignments above, we have been able to identify three bands which have been assigned to δ_+, δ_-, and 2σ but have made no attempt to distinguish between them. There is a fairly constant pattern in the Rh and Ir complex spectra of two of these bands having a rather lower ionization energy than the other one. The separation is about 0.5 eV. We have no experimental grounds for preferring any particular assignment of these bands. Theoretically there seems more cause for a significant $\delta - \sigma$ separation, on the grounds of pseudosymmetry, than a $\delta_+ - \delta_-$ separation, as the latter orbitals are distinguished only by differential backdonation.

Discussion

The most interesting feature of these spectra is the $2\pi_+$ ionization band. There is a marked contrast between its properties in the cobalt spectra and in the rhodium and iridium spectra. In the former cases, the $2\pi_+$ band has the characteristics of ionization from an orbital largely metal d in character and its IE is only ca. 0.5 eV lower than the average of the other three d bands which can be regarded as largely nonbonding. To use a fairly crude description, the cobalt complexes behave in accord with their formal oxidation state of I as d^8 compounds.

In contrast, the rhodium and iridium complexes give rise to a $2\pi_+$ band which has all the characteristics of ionization from a largely ligand-based orbital with rather low metal d character, though possibly metal p character. The band drops in relative intensity in the He II spectrum, is very sensitive to permethylation of the ring, and is separated by ca 1.2 eV from the average IE of the three d bands. The behavior of the rhodium and iridium compounds therefore approximate to a d^6 or M(III) formalism, with the HOMO being a ligand-based orbital.

The origin of this difference lies in the strong covalent interaction of rhodium and iridium d orbitals with the π orbitals of the cyclopentadienyl ring and the diene. This gives rise to stable low-lying $1\pi_+$ and $1\pi_-$ orbitals, as is found, for example, with ruthenocene and osmocene, and in the case of the π_+ interactions, where the diene contributor is the LUMO of the free ligand and antibonding, a high-lying antibonding $2\pi_+$ partner.

The difference of the HOMO of the cobalt and rhodium complexes should have significant implications for their chemical reactivity. In the analogous compounds, $\mathrm{M}(\eta\text{-}\mathrm{C_5H_5})\mathrm{L_2}$, where L represent phosphines, phosphites, or CO, differences have been found in the behavior of the one-electron oxidation products.[32-35] One-electron oxidation of $\mathrm{Co}(\eta\text{-}\mathrm{C_5H_5})\mathrm{L_2}$ compounds give rise to stable 17-electron cations,[35] whereas analogous treatment of rhodium compounds lead to dimerization through the cyclopentadienyl rings to a difulvalene product, e.g. $[\mathrm{Rh_2L_4}(\eta^5,\eta^5\text{-}\mathrm{C_{10}H_8})]^{2+}$,[33-35] though in the case of $\mathrm{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})$ and silver ions as an oxidant an adduct is first formed, $[\mathrm{Ag\{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})\}_2]^+$. This will act as a source of the unstable cation $[\mathrm{Rh(CO)(PPh_3)}(\eta\text{-}\mathrm{C_5H_5})]^+$.[35] Semiempirical MO calculations[34] show the HOMO to contain a contribution from a carbon p orbital in the cyclopentadienyl group, but did not lead to a prediction of difference in behaviour between rhodium and cobalt.

Though these compounds differ from those under study here in their L_2 ligands, the nature of the b_1 HOMO is controlled primarily by the metal–ring interaction and similar localization and antibonding character is to be expected.

It also seems likely that the Rh and Ir derivatives would show a greater tendency to form 16-electron systems than the cobalt derivatives, a type of behavior which is well established for second and third transition series group 8 metals.

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The $M(\eta\text{-}C_5H_5)$ unit, where M = Rh and Ir, shows a preference for complexing to non-conjugated dienes rather than conjugated dienes;[10-12,36-38] in the case of cobalt, however, this preference is not paticularly marked. Thus 1,3,5-cyclooctatriene can bond either as a 1,2,5,6 or a 1–4 ligand to $Co(\eta\text{-}C_5H_5)$.[39] This behavior contrasts with that of the $M(CO)_3$ unit of Fe, Ru, and Os and CoL_3^+; These d^8 ML_3 fragments prefer to bind conjugated dienes.[40] Elian and Hoffman[14] have discussed the preference of the $M(CO)_3$ unit and concluded that the frontier orbitals consist of an empty σ acceptor orbital and two π orbitals occupied by two electrons. The conjugated diene provides a good donor orbital, ψ_2, of the right symmetry to interact with one of the π components and a good acceptor orbital, ψ_3, to interact with the other. In a nonconjugated diene both the donor and acceptor properties would be expected to be poorer. As the $M(\eta\text{-}C_5H_5)$ fragment is claimed to be isolobal with $M(CO)_3$ and in the case of Co, Rh, and Ir the electron occupancy is similar to that described above, the absence of preference for conjugated dienes is rather surprising.

It is difficult to ascertain from our studies whether the ionization energy data bear out the relative acceptor properties of the two types of diene. The ionization energy of the $2\pi_+$ band is very sensitive to substituent effects, for example, it shifts 0.1 eV to lower IE on the introduction of one methyl group on the diene (II and III) and 0.7 eV on permethylation of the ring (V and Va). Comparable substituent effects might be envisaged for VII and V, and in these cases the nonconjugated diene complex V does show a lower (0.1 eV) $2\pi_+$ band than the conjugated diene complex VII. However the difference is not striking.

What is apparent from the ionization energy pattern, is that there appears to be substantially more mixing in the $1\pi_-$ and $2\pi_-$ orbitals in the nonconjugated diene complexes than the conjugated diene complexes. This is because the π_- orbital of the nonconjugated dienes lies closer in energy to the metal–ring e_1 orbital. It may well be that the resulting delocalization of electrons is the important stabilizing force.

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Registry No. I, 51232-43-0; II, 87871-01-0; III, 87871-02-1; IV, 12184-35-9; IVa, 71251-98-4; V, 32610-45-0; Va, 55787-63-8; VI, 38959-22-7; VII, 37685-50-0; VIII, 55480-71-2; IX, 32613-78-8; bis(cyclooctene)rhodium chloride dimer, 12279-09-3; thallium cyclopentadienide, 34822-90-7; cobalt cyclopentadienyl dicarbonyl, 12078-25-0; butadiene, 106-99-0; cyclohexa-1,3-diene, 592-57-4.

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Reactions of Coordinatively Unsaturated Cobalt–Alkene Complexes Generated by Metal Atom Condensation Techniques

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The cocondensation of cobalt atoms with ethylene at 77 K generates a labile cobalt–ethylene complex. Addition of either acetaldehyde or formaldehyde to this complex brings about insertion of the ethylene into the aldehydic C–H bond and reduction of the aldehyde. Thus, the products of the reaction of acetaldehyde with the $Co–C_2H_4$ complex are 2-butanone, 2-butanol, ethanol, ethyl acetate, and methane. Addition of CO and H_2 to the $Co–C_2H_4$ complex results in the hydroformylation of the ethylene and reduction of the CO. Substitution of propylene for ethylene generates a complex that mainly effects reduction of the added aldehyde.

Introduction

There have been numerous investigations of the cocondensation of metal atoms with organic ligands in which coordinatively unsaturated organometallic intermediates have been implicated chemically[1] and identified spectroscopically.[2] An interesting example of the latter is the low-temperature matrix reaction of metal atoms with ethylene in which the formation of mono-, bis-, and tris(ethylene) complexes of general formula $M_n(C_2H_4)_m$ (n, m = 1, 2, 3, 4; M = Co, Ni, Pd, Cu) have been reported.[2,3] In the case of cobalt, complexes of the formula $Co_n(C_2H_4)_m$ (n, m = 1, 2, 3, or 4) have been observed spectroscopically either in an inert argon matrix or in a pure ethylene matrix.[3a] In analogy with other unsaturated organometallic intermediates, it is expected that species generated in this manner should be capable of effecting novel transformations of added substrates. In this connection, we report the reaction of the coordinatively unsaturated cobalt–ethylene intermediates, which have been observed spectroscopically,[3a] with simple aldehydes. The result of this

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