He I and He II Photoelectron Spectra of Open-chain Pentadienyl Complexes of Manganese and Rhenium *

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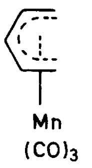
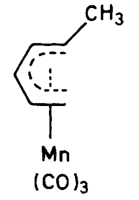
The He I and He II photoelectron spectra of some open-chain pentadienyl complexes of manganese and of rhenium, [M(η^5-C_5H_7)(CO)$_3$] (M = Mn or Re), [Mn(η^5-C_5H_6Me)(CO)$_3$], [Mn(η^5-C_5H_7)(CO)$_2${P(OMe)$_3$}], and [Mn(η^3-C_5H_7)(CO)$_3$(PMe$_3$)] are reported. The spectra are assigned by comparison of the ionization energies with those of similar complexes and from intensity patterns, and are related to a qualitative molecular-orbital scheme. The bonding of η^5-C_5H_7 is compared with that of η^5-C_5H_5.

The photoelectron (p.e.) spectra of the cyclopentadienyltricarbonyl complexes of manganese and rhenium and of several derivatives have been reported.[1-5] There has also been a study of some related η^5-dienyl complexes including cyclohexadienyl- and cycloheptadienyl-tricarbonylmanganese.[6] Recently open-chain pentadienyl complexes [M(η^5-C_5H_7)(CO)$_3$] (M = Mn or Re) have been prepared[7,8] and some of their reactions explored.[9] In contrast to [Mn(η-C_5H_5)(CO)$_3$], the open-chain pentadienyl is readily converted into η^3-pentadienyl derivatives [Mn(η^3-C_5H_7)(CO)$_3$L] by addition of a ligand L such as trimethylphosphine. We have recorded the He I and He II p.e. spectra of some of these open-chain pentadienyls in order to obtain experimental information about their electronic structure. The complexes studied are shown below.



(1)



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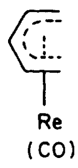

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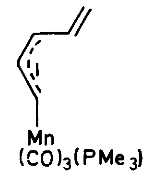

(5)

Experimental

The complexes were prepared as already described.[7-9] They were purified by sublimation *in vacuo* prior to measurement of the spectra.

Photoelectron spectra of compounds (1)—(5) 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 self-ionization band of helium. Relative intensities of bands were corrected by dividing by the kinetic energy of their electrons.

Results and Discussion

Vertical ionization energies (i.e.) are given in Table 1 and relative band intensities in Table 2. All spectra show a main band centred around 14—15 eV with a broad shoulder at about 12—13 eV (see Figure 1). These bands are assigned to ionization from the σ orbitals of the hydrocarbon and carbonyl ligands and are not discussed further.

Although the structures of complexes (1)—(4) have not been reported, there have been several studies of related compounds[10-12] so that a good estimate of the correct structures can be made. For example in tricarbonylcyclohexadienylmanganese[10] the η-bonded five-carbon fragment of the organic ligand is essentially planar, with the methylene group bent away from the manganese atom by 43° from this plane. Barriers to rotation of the M(CO)$_3$ group about the z axis have been found

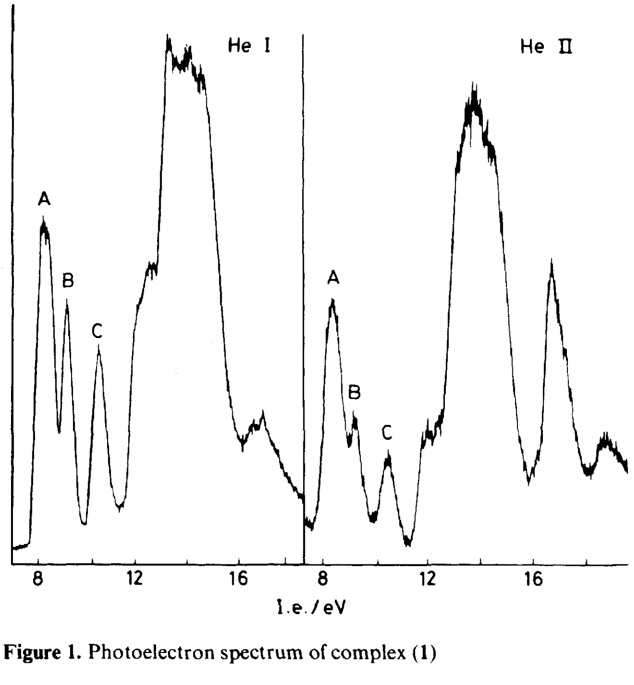

Figure 1. Photoelectron spectrum of complex (1)

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* *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

Table 1. He I ionization data[a] for the complexes $[M(\eta^5\text{-}C_5H_6R)(CO)_2L]$

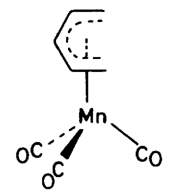
	Type of orbital			
		π Ligand		
Complex	Non-bonding metal Band A	Band B	Band C	Ref.
(**1**) $[Mn(\eta^5\text{-}C_5H_7)(CO)_3]$	8.07	9.02	10.39	This work
(**2**) $[Mn(\eta^5\text{-}C_5H_6Me)(CO)_3]$	7.77, 8.0	8.72	10.11	This work
(**3**) $[Re(\eta^5\text{-}C_5H_7)(CO)_3]$	8.05, 8.36, 8.67	9.25	10.70	This work
(**4**) $[Mn(\eta^5\text{-}C_5H_7)(CO)_2\{P(OMe)_3\}]$	7.16, 7.59	8.42	9.94	This work
(**5**) $[Mn(\eta^3\text{-}C_5H_7)(CO)_3(PMe_3)]$	8.06	8.59	10.25	6
(**6**) $[Mn(\eta^5\text{-}C_7H_9)(CO)_3]$	7.86, 8.10	8.67	9.97	6
(**7**) $[Mn(\eta^5\text{-}C_5H_5)(CO)_3]$	8.05, 8.40[b]	9.90	10.29	1, 2
(**8**) $[Re(\eta^5\text{-}C_5H_5)(CO)_3]$	8.13, 8.52, 8.76	10.18	10.59	1
	8.05, 8.44, 8.72	10.11	10.54	2

[a] Ionization energies in eV. [b] Two i.e.s obtained by curve fitting.

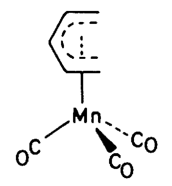
Table 2. Relative band intensities for $[M(\eta^5\text{-}C_5H_6R)(CO)_2L]$

		He I		He II	
Complex	Band	Distribution (%)	Relative area*	Distribution (%)	Relative area*
$[Mn(\eta^5\text{-}C_5H_7)(CO)_3]$	A	48.1	1	54.2	1
	B	25.0	0.52	24.6	0.45
	C	26.9	0.56	21.2	0.39
$[Mn(\eta^5\text{-}C_5H_6Me)(CO)_3]$	A	46.2	1	53.3	1
	B	27.4	0.59	22.8	0.43
	C	26.4	0.57	23.9	0.45
$[Re(\eta^5\text{-}C_5H_7)(CO)_3]$	A	51.72	1	57.40	1
	B	26.30	0.51	26.62	0.46
	C	21.98	0.43	15.98	0.28
$[Mn(\eta^5\text{-}C_5H_7)(CO)_2\{P(OMe)_3\}]$	A	34.89	1	45.32	1
	B	25.53	0.73	26.45	0.58
	C	39.57	1.13	28.22	0.62

* Relative to the lowest ionization potential.



(**A**)



(**B**)

experimentally[13] and estimated theoretically.[14,15] Conformation (**A**) is preferred over (**B**) by about 50 kJ mol^{-1}. Molecular-orbital (m.o.) calculations using a Fenske-Hall semiempirical method were used to aid assignment of the p.e. spectra of $[Mn(\eta^5\text{-}C_6H_7)(CO)_3]$, $[Mn(\eta^5\text{-}C_7H_9)(CO)_3]$, and $[Mn(\eta^5\text{-}C_7H_7)(CO)_3]$.[16] A similar m.o. description of such molecules has been proposed on the basis of fragment analysis.[14,17–19] A diagram showing the interaction of a pentadienyl fragment with $M(CO)_3$ in conformation (**A**) ($M = Mn$ or Fe^+) is shown in Figure 2. The major interactions are of the $2e_s$ orbital with the $\pi_3(s)$ orbital and of the $2e_a$ orbital with the $\pi_2(a)$ orbital. The description assumes a planar pentadienyl ligand. This is unlikely to be the conformation adopted on account of the considerable $H_{endo}\cdots H_{endo}$ repulsion which would arise. An *X*-ray diffraction study on $[Ru(\eta^5\text{-}2,3,4\text{-}Me_3C_5H_4)_2]$[20] indicates that the H_{exo} hydrogen atoms are bent towards the metal by about 17° and the H_{endo} hydrogens are tilted away from the metal by about 45°. This is supported by similar results on the iron analogue $[Fe(\eta^5\text{-}2,4\text{-}Me_2C_5H_5)_2]$[21] and by m.o. calculations.[22] The tilting of the CH_2 groups enhances the interaction of the π-atomic orbitals of carbon with the metal $3d_{xy}$ orbital.

The energy-level diagram shown is similar to that derived by Whitesides *et al.*[16] On the basis of semiempirical calculations, they argue that within a series of similar compounds the ordering of ionizations is strictly comparable. Orbital reorganization, however, has been shown to be significant in the theoretical analysis of u.v. p.e. spectra of organometallic molecules.[23] In the case of electrons ejected from strongly localized $3d$ m.o.s, Koopmans' theorem cannot be assumed. Böhm[24] has studied a series of tricarbonylmetal complexes by means of semiempirical INDO calculations and many-body perturbation theory based on the Green's function formalism. By this method he was able to reproduce vertical ionization potentials for several organotransition-metal complexes,[25,26] whereas ΔSCF *ab initio* results often do not agree with experiment.

Assignment of the Spectra.—The first ionization band A occurs at 8.07 eV (Table 1) for complex (**1**). The corresponding band in the spectrum of the 1-methylpentadienyl derivative (**2**) (Figure 3) is split into two distinct ionizations A_1 and A_2 at 7.77 and 8.00 eV. By analogy with the cyclic analogues, vertical ionization energies of which are also listed, this band is assigned to ionization from predominantly metal-based levels. The second band B at 9.02 eV [compound (**1**)] or 8.72 eV [compound (**2**)] is associated with the orbital $2a'$ derived from the bonding interaction between the symmetrical $\pi_3(s)$ ligand

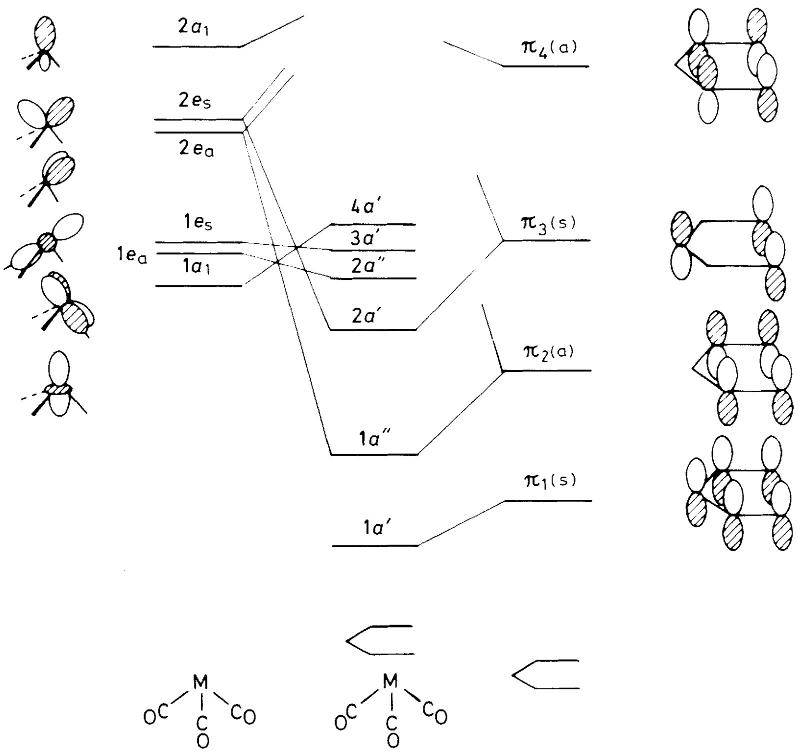


Figure 2. Schematic energy-level diagram showing the allowed interactions between a pentadienyl fragment and a $M(CO)_3$ unit. The scheme is based on refs. 14 and 16—19 with the levels for the complex adjusted to correspond to the ionization-energy ordering

Table 3. Areas under some bands of $[Mn(\eta^3\text{-}C_5H_7)(CO)_3(PMe_3)]$

	A				
	$A_1 + A_2$	A_3	B	C	D
I.e./eV	(7.17, 7.50)	(7.86)	(9.59)	(10.10)	(10.82)
He I distribution (%)	29.65	27.58	12.09	16.72	13.96
Area relative to $A_1 + A_2$	1	0.93	0.41	0.56	0.47
He II distribution (%)	36.25	29.48	10.49	14.78	9.00
Area relative to $A_1 + A_2$	1	0.81	0.29	0.41	0.25

orbital and the metal d_{xz} ($2e_s$) orbital. A marked increase in the intensity of band A relative to band B when the ionizing radiation is changed from He I to He II supports these assignments. The third band C, at a little above 10 eV, represents ionization from the 1a'' orbital, which is derived from the ligand π_2(a) orbital.

The He I and He II spectra of tricarbonylpentadienylrhenium, (**3**) (Figure 4), have the same general features as those of the manganese analogue, except for the considerable splitting observed in the lowest-energy ionization band (A_1, A_2, A_3). A similar pattern has been observed in the spectrum of tricarbonylcyclopentadienylrhenium,[1,2] where it was attributed to spin–orbit coupling in the third transition-series element. This explanation is not necessarily the case for complex (**2**) on account of its lower molecular symmetry, though second-order spin–orbit effects may still be present. Böhm and Gleiter,[27] however, have observed that ionization bands associated with orbitals localized at the metal atom split and become sharper when a 3d metal is replaced by a 4d or a 5d element. Covalent interaction between the nd orbitals of the metal and the orbitals

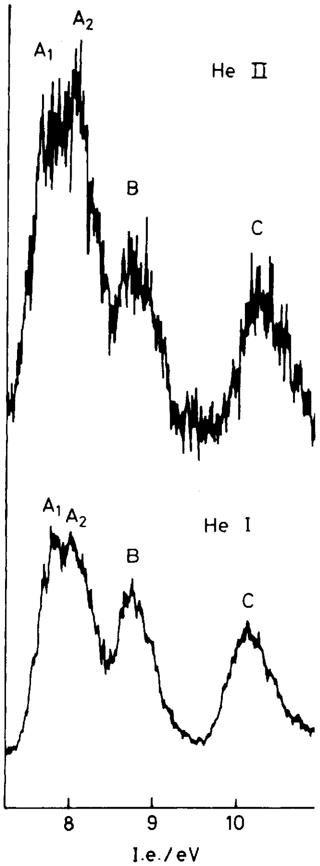


Figure 3. Low-energy region of the p.e. spectrum of complex (**2**)

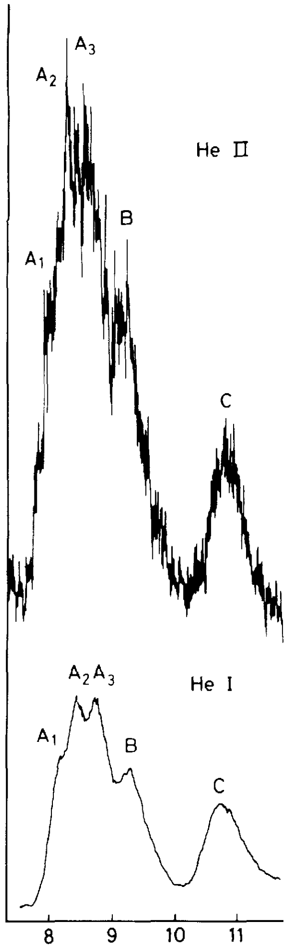


Figure 4. Low-energy region of the p.e. spectrum of complex (3)

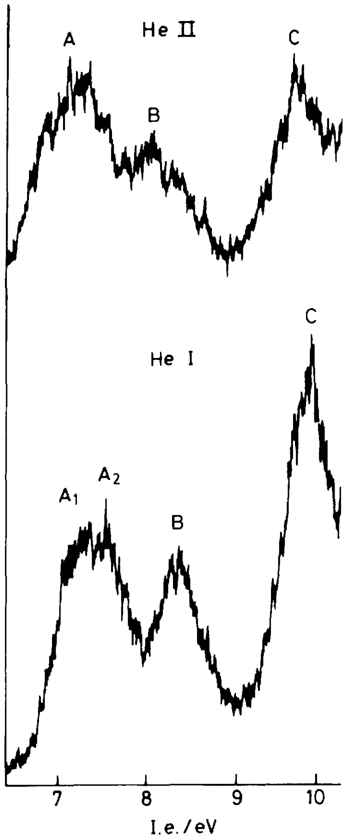


Figure 5. Low-energy region of the p.e. spectrum of complex (4)

of the organic ligand becomes greater at higher principal quantum numbers of the metal. Hence slight differences in covalent interaction are enhanced.

Interestingly, band B for the rhenium compound does not show the relative intensity decrease expected in the He II spectrum for a band of high ligand content whereas band C does. This may well indicate greater covalency on the part of rhenium in the 2*a*′ interaction.

Assuming that no appreciable change is expected from the decrease in symmetry from $Mn(CO)_3$ to the dicarbonyl fragment $Mn(CO)_2\{P(OMe)_3\}$, we have assigned the p.e. spectra of complex (**4**) in a similar way to those of the parent compound (**1**) (Figure 5). Replacement of CO by $P(OMe)_3$ raises the energies of the metal-centred orbitals and this is reflected in the lower vertical ionization energies of the complex. The first band, which has two components A_1 and A_2, is assigned to ionization from metal *d* levels. The next two bands B and C are associated, as before, with 2*a*′ and 1*a*′ respectively. The band C, however, has a much greater intensity than the corresponding bands for similar complexes. This suggests that it has two overlapping components, ionization from phosphorus as well as from 1*a*″.

The u.v. p.e. spectra of the η^3-pentadienyl derivative $[Mn(\eta^3\text{-}C_5H_7)(CO)_3(PMe_3)]$, (**5**), were also measured (Table 3). In the crystal this molecule has a pseudo-octahedral geometry in which the three carbonyl groups adopt a facial stereochemistry and the phosphine ligand is *trans* to one of the carbonyl groups.[9] The spectrum is interpreted qualitatively using the interaction diagram derived by Elian and Hoffmann [19] between the $Mn(CO)_4$ unit and an allyl fragment.[17] A similar m.o. energy diagram has been derived from INDO calculations.[28]

The p.e. spectra of $[Mn(\eta^3\text{-}C_3H_5)(CO)_4]$ and its 2-methyl derivative have been measured and discussed by Worley *et al.*[29] These workers and others [28] assign the lowest-energy bands at 8.04 and 8.40 eV in the parent complex to ionizations from predominantly metal orbitals. The next two bands at 9.04 and 11.10 eV are attributed to ionization from 1*a*″ (π_2) and 1*a*′ (π_1) respectively. These assignments are supported by work on the rhenium derivative $[Re(\eta^3\text{-}C_3H_5)(CO)_4]$.

In the spectrum of compound (**5**) (Figure 6) the first main ionization band is resolved into three components A_1, A_2, and A_3. The first two components are assigned to ionizations from the predominantly metal-based orbitals 2*a*′, 3*a*′, and 2*a*″. Comparison between the He I and He II spectra supports this assignment. The next ionization at 7.86 eV (A_3) is assigned to the perturbed π_2 orbitals on the pentadienyl fragment, considered as an allyl. Bands B (9.59 eV) and C (10.10 eV) probably correspond to electron loss from the uncomplexed double bond and from the perturbed π_1 orbital of the ligand. It is difficult to distinguish between these with certainty. Some interaction between the metal-bound fragment of the η^3-pentadienyl system and the uncomplexed double bond would be expected, which suggests that the ionization from the latter would be at lower energy than that in a free alkene (*cf.* C_2H_4, 10.51 eV).[17] Moreover, comparison between the He I p.e. spectrum of $[Mn(\eta^3\text{-}C_3H_5)(CO)_4]$ [28,29] and that of (**5**) suggests that we may assign the band at 10.10 eV to ionization from the π_1 m.o. of the η^3-pentadienyl fragment, on account of the similar separation (2.24 eV) between π_1 and π_2 in this system and the allyl (2.10 eV). As the fourth band D at 10.82 eV

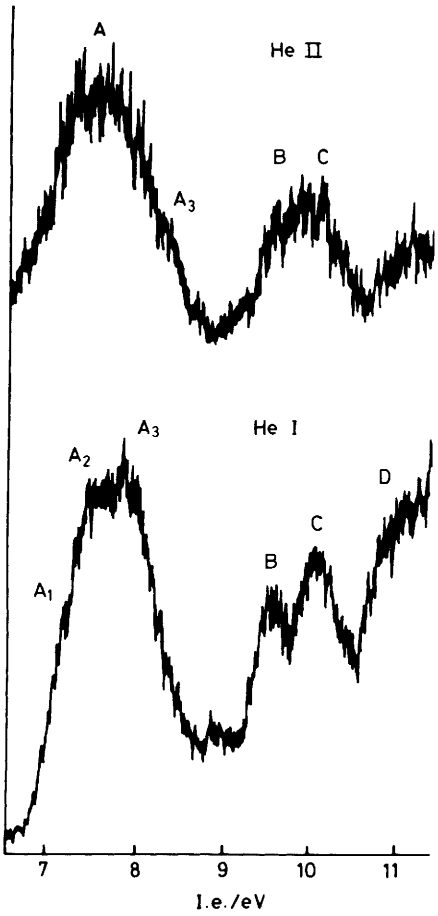


Figure 6. Low-energy region of the p.e. spectrum of complex (**5**)

decreases in relative intensity from the He I to the He II spectrum, it is assigned to the phosphorus ionization.

Conclusions

The measurement and assignment of the p.e. spectra of complexes (**1**) and (**2**) enable us to carry out a comparison of i.e. data between the open pentadienyl complexes $[M(\eta^5\text{-}C_5H_7)(CO)_3]$ and cyclopentadienyl analogue $[M(\eta^5\text{-}C_5H_5)(CO)_3]$. The i.e. data for the latter where M = Mn (**7**) or Re (**8**) are given in Table 1. The principal contrast is in the i.e. associated with the upper ligand levels. Band C for complexes (**1**) and (**3**) has a higher i.e. than the C_5H_5 ionization of (**7**) and (**8**), whereas the i.e.s of band B are substantially lower in energy. This may be attributed directly to the modification of the bonding properties of π_2 and π_3 on opening the ring.

However, the consequent effect of the modification of ligand-bonding levels on the metal ionization is small. There are no differences between the i.e. of the substantial *d* levels of complexes (**1**) and (**2**) and (**7**) and (**8**). This is in marked contrast to the changes found on going from $[Fe(\eta^5\text{-}C_5H_5)_2]$ to $[Fe(\eta^5\text{-}C_5H_7)_2]$.[22] Here, although the i.e. of the d_{z^2} and $d_{x^2-y^2}$ orbitals are largely unchanged on opening of the ring, the d_{xy} i.e. increases by *ca.* 1.4 eV. This increase is shown by m.o. calculations to be attributable to mixing with the d_{xz} orbital and an interaction with the symmetric combination of the π_2 orbitals on both rings. The interaction is enhanced by means of a rotation of the terminal CH_2 groups in such a way that the π atomic orbitals point towards the iron centre, simultaneously relieving steric repulsion between the *endo*-H atoms at C^1 and C^5. In the case of $[M(\eta^5\text{-}C_5H_7)(CO)_3]$, the tilting of the d_{xy} orbital (by mixing with d_{xz}) to enhance this interaction would be disfavoured. The d_{xy} orbital is involved in profitable back donation to the CO groups of the $M(CO)_3$ fragment which would be lessened by such a tilt.

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