He(I) Photoelectron Spectra of Tetracarbonyliron Complexes of Group 5 Ligands and of Olefinic Ligands

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The photoelectron spectra of some five-co-ordinate trigonal-bipyramidal complexes $[Fe(CO)_4L]$ (L = PMe_3, PPh_3, $AsPh_3$, or pyridine in an axial position, or $CH_2=CH-CN$ and $CH_2=CH-CHO$ in the equatorial plane) have been measured. The spectra have been assigned by comparing them with one another and with those available for $[Fe(CO)_5]$ and $[Fe(CO)_4(\eta-C_2H_4)]$. CNDO calculations carried out for $[Fe(CO)_4(py)]$ and $[Fe(CO)_4(\eta^2-CH_2=CH-CN)]$ are of only limited help in making assignments. The substituent effect on the stability of the Fe–L bond is discussed. The stability order obtained is the same as that found previously *via* kinetic studies.

RECENTLY some of us reported the reactivity of some five-co-ordinate trigonal-bipyramidal complexes of the type $[Fe(CO)_4L]$ having L in an equatorial (olefinic ligands, *e.g.* $CH_2=CH-CN$, $CH_2=CH-CHO$ [1-3]) or axial position [Group 5 ligands, *e.g.* pyridine (py) [4] and other N-bonding ligands [5]]. From a study of the rates and mechanism of reaction with ligands MR_3 (M = P, As, or Sb) it was possible to obtain quantitative information on the thermodynamic stability of the complexes. We now present the results of an ultraviolet photoelectron (p.e.) spectroscopic study of the electronic structure of the complexes $[Fe(CO)_4L]$ (L = PPh_3, PMe_3, $AsPh_3$, or py

at an axial position of the trigonal bipyramid or $CH_2=CH-CN$ or $CH_2=CH-CHO$ in the equatorial plane). These complexes have not previously been studied by this technique. The aim was to obtain information on the nature and stability of the Fe–L bond and compare this with the kinetic results.

Few p.e. spectra of five-co-ordinate iron(0) complexes have been reported, despite the fact that this is the preferred mode of co-ordination for Fe^0 {*e.g.* $[Fe(CO)_5]$,[6] $[Fe(CO)_4(\eta-C_2H_4)]$,[7] $[Fe(CO)_3(\eta-C_4H_6)]$,[8] and, recently, $[Fe(CO)_3(\eta^4\text{-cyclic diene})]$ [9]}. Apart from the novelty of

p.e. spectra for $[Fe(CO)_4L]$ having axial L, we feel that the results reported here are also useful in unequivocally assigning the electronic structure of complexes in which L is equatorial. Only a single such complex, with L = C_2H_4, is described in the literature.[7] Indeed, no p.e. spectrum of any of the olefin complexes described previously shows the two bands due to ionisation of the iron *d* orbitals well separated from the bands due to ionisation of the ' mobile ' electrons of the olefin. Although this situation occurs for one of our complexes, $[Fe(CO)_4(\eta^2-CH_2=CH-CHO)]$ it does not for the analogue $[Fe(CO)_4(\eta^2-CH_2=CH-CN)]$.

Experimental vertical ionisation potentials (eV) and proposed assignment for $[Fe(CO)_4L]$ complexes. The ionisation potentials of $[Fe(CO)_5]$,$[Fe(CO)_4(\eta-C_2H_4)]$, and of the ligand L are given for comparison

	$[Fe(CO)_5]$	$[Fe(CO)_4(PMe_3)]$	PMe_3[15]	$[Fe(CO)_4(PPh_3)]$	PPh_3[16]	$[Fe(CO)_4(AsPh_3)]$	$AsPh_3$[16]	$[Fe(CO)_4(py)]$	py[17]	$[Fe(CO)_4(\eta^2-CH_2=CH-CN)]$	$CH_2=CH-CN$[18]	$[Fe(CO)_4(\eta^2-CH_2=CH-CHO)]$	$CH_2=CH-CHO$[17]	$[Fe(CO)_4(\eta^2-C_2H_4)]$[7]	C_2H_4[7]
(i) Metal															
8.6 (x^2-y^2, xy)	8.6	7.77 a		7.55		7.50 b		7.65		8.90		9.35		8.40	9.2
										9.05		9.45(sh)			
9.9 (xx, yz)	9.9	8.85 a		8.45		8.40 b		8.65		9.70		9.55(sh)		9.6	9.8
								8.90		9.90(sh)		9.85(sh)		9.8	
(ii) Ligands															
		10.45 (nP)	8.60	9.10(sh) (nP)	7.88	9.15(sh) (nAs)	7.95			10.65 [π(C–O)]	10.91	9.24 c (no)	10.11 c		
				9.40	9.25	9.40	8.90	10.53	9.5		12.36				
		10.70	10.90	10.60			10.40	11.50	10.5	11.85 [π(C–N)]		11.43 c [π(C–C)]	10.93 c		
								11.80 (π)	12.5 (π)						
				11.40 (nPh)		11.10 (nPh)								10.5 [π(C–C)]	10.5
		12.27 [σ(P–C)]	11.34	12.08 [σ(P–C)]		11.90 [σ(As–C)]				12.35 (nN)	13.04	12.33 [π(C–O)]	13.20		

a Average value of the maxima of the band split by the Jahn–Teller effect. *b* Broad. *c* Adiabatic ionisation potential.

The assignment of the spectra is based on considerations of energy and intensity changes, and on comparison with literature data on the ligands and on the complexes $[Fe(CO)_5]$ and $[Fe(CO)_4(\eta-C_2H_4)]$. We have also carried out a CNDO molecular-orbital (m.o.) calculation on some of these molecules, but the result was of little use for assignment purposes because this calculation gave the first ionisation potentials due to ligand orbitals.

EXPERIMENTAL

The complex $[Fe(CO)_4(\eta^2-CH_2=CH-CN)]$ was prepared and purified as described in ref. 10; $[Fe(CO)_4(\eta^2-CH_2=CH-CHO)]$

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(ref. 11) was prepared by treating [Fe$_2$(CO)$_9$] with CH$_2$=CH–CHO at room temperature and purified by sublimation *in vacuo*; [Fe(CO)$_4$(PPh$_3$)] was prepared as described in ref. 12 and purified by sublimation *in vacuo*. The complex [Fe(CO)$_4$(AsPh$_3$)] was prepared from equimolar quantities of [Fe$_2$(CO)$_9$] and AsPh$_3$, in benzene at room temperature and purified by crystallisation from CH$_2$Cl$_2$–*n*-hexane. The complex [Fe(CO)$_4$(py)] was prepared by the reaction of [Fe$_2$(CO)$_9$] with pyridine (excess) in benzene at 10 °C. The solid residue obtained on heating the solution to dryness was sublimed. The complex obtained corresponded to that obtained in ref. 13. [Fe(CO)$_4$(PMe$_3$)] was kindly supplied by B. Chaudret.

The p.e. spectra were recorded on a Perkin-Elmer PS 18 instrument, keeping the complexes at temperatures lower than 40 °C in order to avoid decomposition. In spite of this precaution, the spectrum of [Fe(CO)$_4$(py)] shows a weak band at 9.80 eV,* due to decomposition; on increasing the temperature the intensity of this band increases and the characteristic bands of free CO appear. The complexes [Fe(CO)$_4$(PPh$_3$)] and [Fe(CO)$_4$(AsPh$_3$)] were introduced into the spectrometer at 130 °C. It was not possible to obtain an intense spectrum for [Fe(CO)$_4$(AsPh$_3$)] since it decomposes at above 130 °C and gives the spectrum of AsPh$_3$. The calibration was made with inert gases (Ar or Xe) and MeI. The spectral resolution was *ca.* 50 meV at an ionisation potential of 15.75 eV.

Description of the Spectra and Assignment.—The most significant part of the spectra is that at ionisation energy $\leqslant 13$ eV. Above this value the ionisation potentials of the CO σ and π orbitals and of the C–C and C–H σ orbitals give rise to a very broad band (present in all the spectra) which defies analysis. In addition, this part of the spectrum is relatively insensitive to changes in L in the series [Fe(CO)$_4$L] because L interacts mainly with the metal orbitals. From a comparison with the spectra of the free ligands, the bands of which shift to lower energy or remain more or less constant (see Table), the rest of the spectrum may be divided into two clear regions {with the exception of [Fe(CO)$_4$(η^2-CH$_2$=CH–CHO)]}. The first region contains the bands due to the metal and the second, at higher ionisation energy, those due to the ligands.

Metal bands. For all the complexes except [Fe(CO)$_4$(η^2-CH$_2$=CH–CHO)] the first two bands may be assigned to the metal. These bands are doublets (Figures 1 and 2), in some cases split because of the operation of a Jahn–Teller effect and in others because of low symmetry. These bands are similar for all the complexes studied, in both shape and intensity (half-height amplitude *ca.* 0.7 eV) and in energy separation (*ca.* 1 eV). We assign the first band to the $d_{x^2-y^2}$, d_{xy} orbitals and the second to the d_{xz},d_{yz} orbitals, as for [Fe(CO)$_5$].[14] In agreement with this, substitution of a CO by another ligand may alter the separation between the d orbitals but not their order. The doubling of these bands is clearly visible for [Fe(CO)$_4$(PMe$_3$)] (Jahn–Teller effect) [Figure 1(d)] and for [Fe(CO)$_4$(η^2-CH$_2$=CH–CN)] (low symmetry) [Figure 2(b)]. The complex [Fe(CO)$_4$(py)] shows

the doubling of the second band (low symmetry) [Figure 1(a)]; this splitting supports the assignment to the d_{xz} and

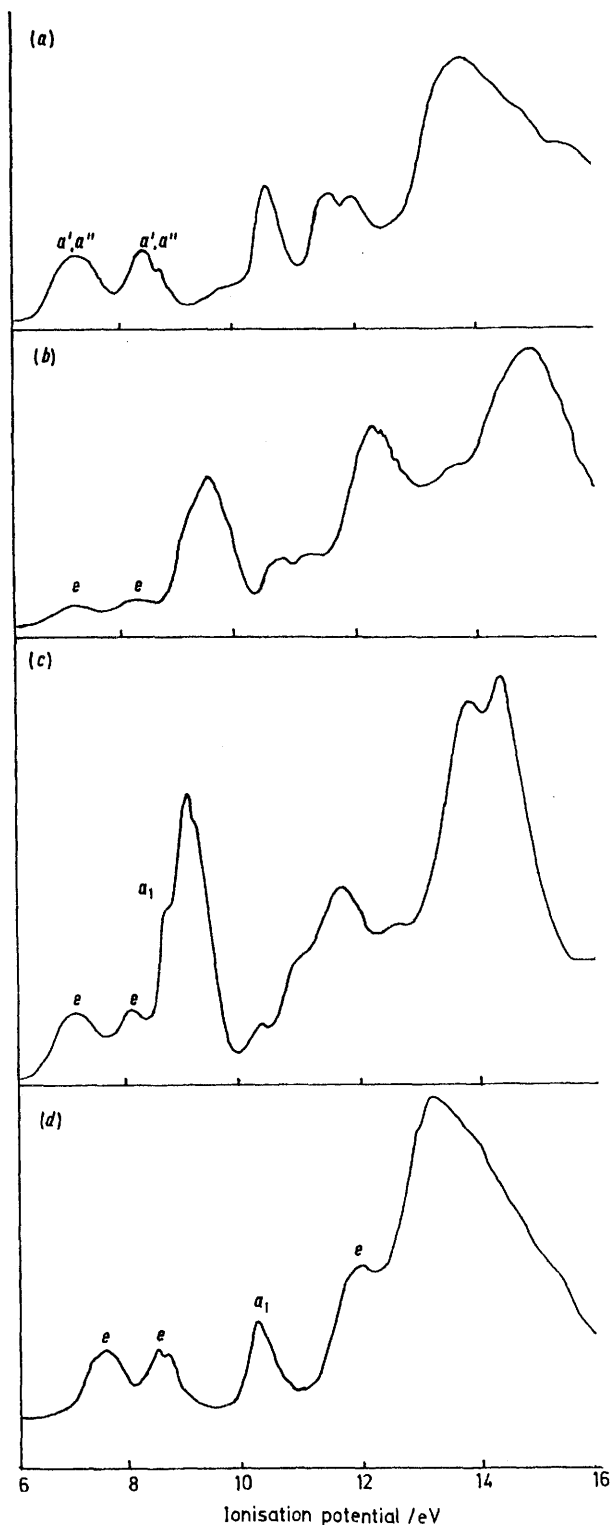FIGURE 1   He(I) Photoelectron spectra of [Fe(CO)$_4$L]: L = py (a), AsPh$_3$ (b), PPh$_3$ (c), and PMe$_3$ (d)

d_{yz} orbitals, with which the pyridine interacts to a greater extent than the $d_{x^2-y^2}$ and d_{xy} orbitals, which give rise to the

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* Throughout this paper: 1 eV $\approx$ 1.60 $\times$ 10^{-19} J.

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two unresolved ion states associated with the first band. It is not surprising that the splitting is not resolved in the other two cases in which the Jahn–Teller effect operates {i.e. C_{3v} [Fe(CO)$_4$(PPh$_3$)] and [Fe(CO)$_4$(AsPh$_3$)], Figure 1(c) and 1(b)} because of the difference between PMe$_3$, PPh$_3$, or AsPh$_3$.[15]

For the olefinic complexes and [Fe(CO)$_5$] the second band lies at about the same energy. This is also the case for [Fe(CO)$_4$(η-C$_2$H$_4$)] (Table) and [Fe(CO)$_3$(η-C$_4$H$_6$)] in which
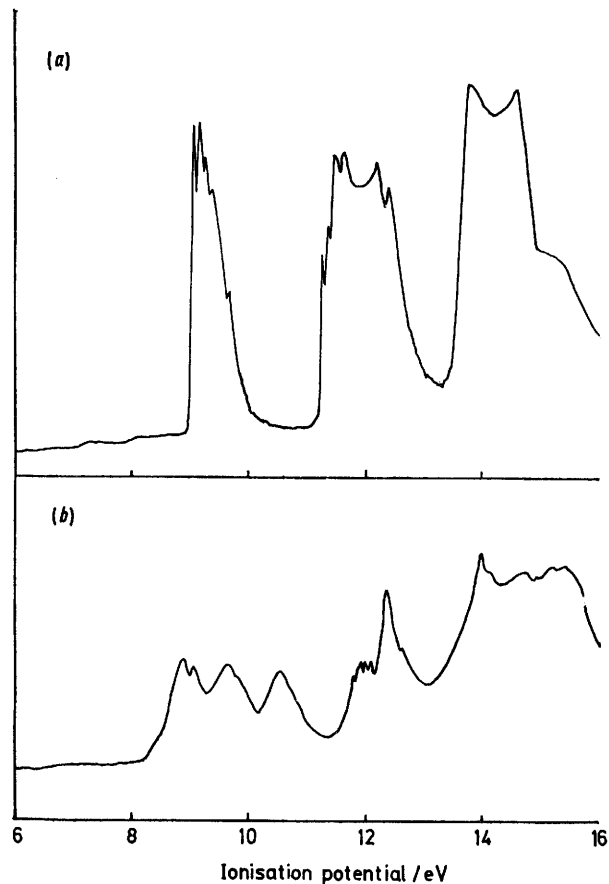
FIGURE 2 He(I) Photoelectron spectra of [Fe(CO)$_4$L]: L = CH$_2$=CH–CHO (a) and CH$_2$=CH–CN (b)

the iron d orbitals have an ionisation energy which varies from 8.82 to 9.93 eV. However, the first band is more sensitive to changes in L. Thus, although the energy of the first band of [Fe(CO)$_4$(η-C$_2$H$_4$)] is still similar to that of [Fe(CO)$_5$], as found previously,[7] in the other cases it is close to that of the second band. Indeed, for [Fe(CO)$_4$(η^2-CH$_2$=CH–CHO)] these two first bands have very similar energy (which varies between 9.3 and 9.8 eV) and are partially obscured by a more intense band derived from the ionisation of the oxygen lone pair (n_O) [Figure 2(a)].

Ligand bands. After the first two bands due to the metal, in each molecule two or more bands may be identified at ionisation energies $\leqslant 13$ eV; these are due to the ligands. Given the differences in the ligands L, these bands are discussed one by one.

[Fe(CO)$_4$(PMe$_3$)]. Two bands are clearly identified, the

second (at 12.27 eV) twice as intense as the first. This suggests a doublet (i.e. of e symmetry) due to the ionisation of two σ(P–C) orbitals, which lie at 11.34 eV in the free ligand.[15] The first band is due to the phosphorus lone pair (a_1).

[Fe(CO)$_4$(PPh$_3$)] *and* [Fe(CO)$_4$(AsPh$_3$)]. The spectra of these two complexes are very similar; five ionisation potentials in the range 9—13 eV are clearly observable. A comparison with the spectrum of [Fe(CO)$_4$(PMe$_3$)] allows assignment of the band due to the degenerate (e) σ(M–C) orbital at 12.08 (M = P) and 11.90 eV (M = As). The other bands are due to the phenyl orbitals (at least seven orbitals gave an ionisation energy in this range, as for the free ligands [16]), sometimes grouped together to give multiplets, and the lone pair (a_1) of the donor atom. The assignment of the a_1 orbital is the most important for our purposes. A comparison with the spectra of the free ligands, as regards both the ionisation energy and the band shape, allows the lone pair to be assigned, to the band appearing as a shoulder on the more intense band at 9.10 (P) and 9.15 eV (As).

The phenyl bands are derived from the orbitals, of which at least four are grouped together in the more intense band at 9.40 (P) and 9.55 (As) eV and a further three in the two remaining bands. The latter bands are much less intense than the former {the spectrum of [Fe(CO)$_4$(AsPh$_3$)] in this region is much less clear and of low intensity; see Experimental section}.

[Fe(CO)$_4$(py)]. Three bands, having ionisation energies at 10.53, 11.50, and 11.80 eV, are apparent; the first band, because of its asymmetric shape, is a doublet, corresponding to the first band of free pyridine at 9.5 eV (ref. 17) and due to two orbitals. Two other orbitals of pyridine are expected to fall in this energy region (between 9.5 and 12.5 eV) and these can be assigned to the bands at 11.50 and 11.80 eV. We are not in a position to assign the band arising from the nitrogen lone pair because of the mixing of this orbital with other π orbitals, due to the low symmetry of the complex (C_s); similar behaviour is found in free pyridine, although the higher symmetry (C_{2v}) allows a possible assignment of this orbital to the narrowest band at 10.5 eV.[17] We note, however, that the shift of the n_N orbital of pyridine in the complex will be not more than 1 eV.

[Fe(CO)$_4$(η^2-CH$_2$=CH–CN)]. Three bands are observed, which originate from the ionisation of the orbitals π(C–C), π(C–N), and n_N. These are assigned in the same order as in the free ligand, since olefinic ligands, like all π-type ligands, are little influenced by co-ordination, even as regards the ionisation energy of the orbital directly involved in the co-ordination. The nitrogen n orbital give rise to a narrow, readily identified, band, which obscures another band, perhaps that due to the second orbital of the CN group. The band at 11.85 eV shows a similar vibrational structure to that of the free ligand.[18]

[Fe(CO)$_4$(η^2-CH$_2$=CH–CHO)]. The ligand orbitals that may be ionised at potentials < 13 eV are π(C–C), π(C–O), and n_O. Three bands are, indeed, observed for the complex, of which the first corresponds to the n_O orbital (adiabatic and vertical potentials coincide, as do those of the free ligand [17]). As mentioned above, this band partially obscures those due

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to the metal. The other two bands may be assigned in the same order as in the free ligand [*i.e.* $\pi(C-C) < \pi(C-O)$].

DISCUSSION

A comparison of the ionisation potentials of iron in $[Fe(CO)_5]$ and in $[Fe(CO)_4L]$ allows the overall effect caused by substitution of a CO group by L to be identified. For complexes having axial L the ionisation potential of the metal (Table) decreases with respect to that in $[Fe(CO)_5]$ and this decrease occurs for both of the bands observed, since the charge is donated to the metal through the d_{z^2} orbital, which has a density different from zero in all three planes (xy, xz, and yz). This decrease indicates that the $\sigma(L{\rightarrow}M)$ effect predominates in these complexes. An estimate of this effect may be obtained *via* the stabilisation of the donor orbital, which follows the order: $PMe_3 > PPh_3 > AsPh_3 > py$.

The separation between the iron d orbitals remains more or less constant. Nevertheless, there are slight differences within the series and also when the complexes are compared with $[Fe(CO)_5]$. The latter has the largest separation (*ca.* 1.3 eV) followed by py (1.12 eV), PMe_3 (1.07 eV), PPh_3 (0.9 eV), and $AsPh_3$. This separation may be taken as a measure of the π-acceptor strength of L and the stabilisation of the second group of orbitals (d_{xz}, d_{yz}). It may be concluded that the ligands L studied are weaker π acceptors than CO.[19]

The strength of the Fe-L bond is the resultant of two effects, $\sigma(L{\rightarrow}M)$ and $\pi(M{\rightarrow}L)$, of which the first predominates. The relatively strong π-acceptor effect of pyridine does not change the position of this ligand in the Fe-L bond-strength order since py is a weak σ donor. Nevertheless, the p.e. spectrum does give some indication of the π-acceptor strength of pyridine, which results in the stability of the complex $[Fe(CO)_4(py)]$ {*cf.* other N-donor ligands, *e.g.* amines, which, lacking the stabilising $\pi(M{\rightarrow}L)$ affect, do not form $[Fe(CO)_4L]$ complexes.[20] The stability order obtained from the p.e. measurements is the same as that deduced from kinetic measurements,[4,5,21,22] *i.e.* $PMe_3 > PPh_3 > AsPh_3 > py$.

In complexes containing equatorial L (olefins) the acceptor effect predominates, since the ionisation potentials of the iron are larger than in $[Fe(CO)_5]$ (*i.e.* this is a bonding effect). We note that the ionisation potential of the first group of orbitals ($d_{x^2-y^2}$) increases, whilst that of the second group remains more or less constant; the separation between the two groups therefore tends to decrease compared with that in

$[Fe(CO)_5]$. This decrease may be taken as a measure of the π-acceptor strength of the olefin, which follows the order $CH_2{=}CH{-}CHO > CH_2{=}CH{-}CN > C_2H_4$. In the two substituted-olefin complexes studied here, both of the iron orbitals in the equatorial plane are stabilised by back donation and the separation between them is therefore small. In contrast, in $[Fe(CO)_4(\eta{-}C_2H_4)]$ this separation is very large.

Unfortunately, an estimate of the $\pi(L{\rightarrow}M)$ effect is not possible because the extra charge on the ligand destabilises the orbitals, given that the $\pi(M{\rightarrow}L)$ effect predominates. This means that the $\pi(C-C)$ orbital remains roughly constant in energy or is shifted by only a fraction of an electronvolt compared to that in the free ligand. Consequently, for these complexes, the predominant effect on the bond stability is due to the π-acceptor strength of the olefin, as revealed by the kinetic results which allowed a measurement of the thermodynamic stability of a series of complexes $[Fe(CO)_4(\eta^2{-}olefin)]$.[11,12]

Calculations.—We have carried out CNDO-2 approximate SCF molecular-orbital calculations, extended to the transition elements,[23] on $[Fe(CO)_4(py)]$ and $[Fe(CO)_4(\eta^2{-}CH_2{=}CH{-}CN)]$ of known crystal structure.[24,25] In both cases the molecular orbitals in which the metal d orbitals participate are not those last occupied, but are preceded by the six ligand orbitals. In $[Fe(CO)_4(py)]$ the molecular orbitals having d participation have energies in the range 14.97—15.61 eV, and in $[Fe(CO)_4(\eta^2{-}CH_2{=}CH{-}CN)]$ between 16.79 and 17.11 eV. The calculations thus reproduce the observed shift (*ca.* 1.2 eV) of these orbitals in both cases, and also indicate that this shift may be due to a charge variation on the iron (which is more positive by 0.09 units when L $=$ $CH_2{=}CH{-}CN$).

These results obviously show that, within the calculation approximation, Koopmans' theorem is not valid for this series and that deviations from the theorem are constant throughout the series. Consequently, the changes in orbital energies (as deduced from the p.e. spectra and based on the validity of Koopmans' theorem) on which the discussion of the co-ordinative strength of the ligands and the thermodynamic stability of the Fe-L bond is based still have a relative meaning along the series.

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