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CARBON-13 NMR SPECTRA OF SOME GROUP VIB AND VIIB TRANSITION METAL CHALCOCARBONYL COMPLEXES*

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Summary

The ^{13}C NMR spectra of the five series of chalcocarbonyl complexes, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$, $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CX)$, $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CX)$, $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(CX)$ and $(\eta^5\text{-}C_5H_5)Re(CO)_2(CX)$ (X = O, S, Se), and some of their derivatives including several ^{13}C-enriched species have been investigated at −30 to −50°C. The chemical shift variations observed with changes in the CX ligand suggest that the π-acceptor/σ-donor capacity of these ligands increases in the order CO < CS < CSe. Changes in the nuclear charge and in the electronic density at the central metal atom affect $\delta(^{13}CS)$

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and $\delta(^{13}CO)$ in the same manner. The increased downfield chemical shift for $\delta(^{13}CX)$ in the chromium and manganese series on changing X from O to S and Se is in the direction expected from considerations of Pople's paramagnetic shielding expression.

Introduction

Unlike CO and CS, the related carbon monoselenide molecule, CSe, has thus far eluded isolation even at very low temperature [2], although some data have been reported for its electronic spectrum [3]. Recently, however, it has been discovered that CSe can be stabilized by coordination to transition metals in complexes such as (Ring)M$(CO)_2$(CSe) (M = Cr, Ring = η^6-$C_6H_5CO_2Me$; M = Mn, Re, Ring = η^5-C_5H_5), cis-$RuCl_2(CO)(CSe)(PPh_3)_2$, and $Cr(CO)_5(CSe)$ [4]. It is now possible, therefore, to compare the bonding properties of the CSe ligand with those of the isoelectronic CO and CS species, and one way to approach this problem is through the use of ^{13}C NMR spectroscopy.

Some comparative work on the ^{13}C NMR chemical shifts of the C=O and C=S groups in ketones and thioketones has been reported in the literature [5]. In one particular study [6], the $\delta(^{13}C{=}O)/\delta(^{13}C{=}S)$ ratio for analogous molecules was shown to be principally dependent on the average energy term, ΔE_{av}, of the paramagnetic shielding expression derived by Pople [7] for the ^{13}C NMR chemical shifts of unsaturated, multiple bonded centers such as the C=O group in formaldehyde.

$$\sigma_p^{AB} = -\frac{\text{const.}}{\Delta E_{av}} \cdot \frac{1}{\langle r^3 \rangle_{2p}} [Q_{AA} + \sum_B Q_{AB}] \qquad [1]$$

The terms, Q_{AA} and Q_{AB} depend on the atomic charge density and molecular bond order matrix elements, while $\langle r^3 \rangle_{2p}$ is the mean inverse cube radius for carbon 2p orbitals and ΔE_{av} is the average electronic excitation energy.

Equation 1 has also been used to explain the CO chemical shifts in transition metal carbonyls [8]. For example, Mahnke et al. [9] have attributed the large downfield CO shift (10-30 ppm) upon complexation of CO to transition metals to the ΔE_{av} term in the chemical shielding expression. Similarly, the same ΔE_{av} term has been used to account for the downfield shifts observed in metal carbonyl complexes as the electronic charge on the metallic center is increased [10]. Moreover, the value of ΔE_{av} can, for all practical purposes, be equated to the energy difference between the π (HOMO) and π^* (LUMO) molecular orbitals [7]. Therefore, the extent of metal stabilization of the CO ligands is reflected in the CO chemical shift values and it perhaps not unreasonable to expect similar effects for the isoelectronic CS and CSe ligands in analogous complexes.

In this paper, we report the results of a ^{13}C NMR study of the related chalcocarbonyls, (Ring)M$(CO)_2$(CX) [Ring = η^6-C_6H_6 and η^6-$C_6H_5CO_2Me$, M = Cr(0); Ring = η^5-C_5H_5, M = Mn(I), Re(I) and Fe(II); Ring = η^5-C_5H_4Me, M = Mn(I); X = O, S and Se], and several of their derivatives including some ^{13}C-enriched species.

Experimental

The manganese complexes, (η^5-C_5H_5)Mn$(CO)_3$ and (η^5-C_5H_4Me)Mn$(CO)_3$, were gifts from Ethyl Corp. The other parent tricarbonyls were either purchased from Strem Chemical Co. or were prepared by the standard literature procedures [11,12]. The methods used to synthesize the thiocarbonyl and selenocarbonyl complexes have been described elsewhere [13,14]. The details for preparing the ^{13}C-enriched species will be published shortly [15]. The derivatives, (η^5-C_5H_5)Re$(CO)_2$L (L = PPh_3, $AsPh_3$, C_8H_{14}) and (η^5-C_5H_4Me)Mn(CO)(CS)(PPh_3), were synthesized by UV irradiation of the appropriate tricarbonyl complex in tetrahydrofuran solution followed by addition of L [16]. All new compounds gave satisfactory elemental analyses and molecular weights (from mass spectral data). The ionic complexes, $[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]PF_6$ [17] and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$ [18], were obtained by the literature methods indicated.

The ^{13}C NMR spectra were recorded on a Bruker WH90, 22.6 MHz pulse Fourier transform instrument equipped with a 16K, 20 bit core memory, Nicolet B-NC-12 minicomputer. Spectral widths of 9090 or 6024 Hz and pulse intervals of 2.0-5.0 sec were used. Saturated solutions of the complexes containing 10% (v/v) Me_4Si as internal standard (δ = 0.00 ppm) and the paramagnetic relaxation agent, $Cr(acac)_3$ (0.1-0.2 M) [19], were placed in 10-mm NMR tubes. For the liquid complexes, the frequency stabilizing lock solvent, D_2O or d_8-toluene, was placed in a 5-mm tube. All the spectra were proton decoupled (0-9 ppm region) with modulated wideband rf (5 W). In general, the spectra were recorded at -30 to -50°C since the signal-to-noise ratios and the band widths of the CX resonances were markedly improved at low temperatures, especially in the case of the Group VIIB complexes*. The chemical shifts reported are considered to be accurate to ±0.1 ppm.

Results and Discussion

The observed resonances for the various chalcocarbonyl complexes are given in Table 1, together with the proposed assignments. The spectra of some of the tricarbonyl and monothiocarbonyl complexes have been reported previously [20].

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*At room temperature, the Group VIIB complexes display very weak and broad CX signals (∿50 Hz half-height band widths) due to the long T_1 relaxation times and extensive quadrupolar spin coupling to the metal atoms [^{55}Mn, I = 5/2 (100%); ^{185}Re, I = 5/2 (37%); ^{187}Re, I = 5/2 (63%)].

These spectra were remeasured in the present study from the point of view of internal consistency. Several of the assignments proposed earlier were substantiated by the spectra of the ^{13}C-enriched species.

Previous ^{13}C NMR studies on $(\eta^5\text{-}C_5H_4R)Mn(CO)_2L$ (R = H or Me; L = 2e$^-$ donor ligand) have revealed that increasing electron density at the manganese atom causes an upfield chemical shift of the ring carbons [10,21,22]. However, in the present work, replacement of one CO group in $(Ring)M(CO)_3$ by CS or CSe produces a downfield shift of the ring carbons relative to those of the original tricarbonyls. The data indicate that there is a reduction in electron density at the metal centers and that the net electron withdrawing power increases in the order CO<CS<CSe. The same effect is observed on further CO replacement in $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(CS)$ by CS to give $(\eta^5\text{-}C_5H_4Me)Mn(CO)(CS)_2$, i.e., there is a downfield shift in the positions of the ring carbons of about 1 ppm. Carbonyl replacement in $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ by NO$^+$ to give the cationic species, $[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]^+$, produces an even greater downfield chemical shift (12 ppm) in the ring carbons in accord with the lower electron density expected on the manganese atom due to the presence of the positive charge. In the case of $(\eta^5\text{-}C_5H_5)Re(CO)_2L$ (L = PPh_3, $AsPh_3$, C_8H_{14}), the ring carbon resonances are displaced upfield relative to that for $(\eta^5\text{-}C_5H_5)Re(CO)_3$, as observed for the related manganese derivatives. The above results also parallel the ^{1}H nmr shift trend found for the $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CX)$ complexes [14].

All the chalcocarbonyl complexes investigated exhibit resonances characteristic of the CX ligands and the integrated intensities of these signals are in complete accord with the proposed assignments, as are the data for the ^{13}C-enriched species. The resonances for the CO ligands appear in the

195-234 ppm region, in agreement with previous studies for CO groups bonded to transition metals [8]. The lower field resonances are attributed to the CS or CSe ligands, the observed ranges being 288-349 and 308-368 ppm, respectively. The CS resonances appear within the currently accepted range for $\delta(^{13}CS)$ in metal thiocarbonyls, viz., 286-352 ppm [4]. In the case of the selenocarbonyl complexes, no really meaningful comparisons can be made since there are no data available even for selenoketones. The chemical shifts for the carbon atoms bonded

TABLE 1

^{13}C NMR DATA FOR THE GROUP VIB AND VIIB TRANSITION METAL CHALCOCARBONYL COMPLEXES INVESTIGATED[a]

Complex	Solvent[b]	$\delta(^{13}C)$, ppm		
		Ring	CO	CX
$(\eta^6\text{-}C_6H_6)Cr(CO)_3$[c]	A	93.7	233.4	
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CS)$	A	99.3	231.5[d]	346.4[e]
$(\eta^6\text{-}C_6H_6)Cr(CO)_2(CSe)$	A	100.9	229.0	363.7[f]
$(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_3$	A	g	232.1	
$(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CS)$	A	h	230.3	347.6
$(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$	A	i	228.4	368.0
$(\eta^5\text{-}C_5H_5)Mn(CO)_3$	B	83.0	224.5	
$(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$	B	86.3	224.0	335.4
$(\eta^5\text{-}C_5H_5)Mn(CO)_2(CSe)$	B	86.9	223.1	357.2
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$	C	j	224.5	
$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2(CS)$	C	k	223.9	336.6
$(\eta^5\text{-}C_5H_4Me(Mn(CO)_2(CSe)$	C	ℓ	223.0	358.8
$(\eta^5\text{-}C_5H_5)Re(CO)_3$	D	85.9	195.0	

Continued

TABLE 1 Continued

$(\eta^5\text{-}C_5H_5)Re(CO)_2(CS)$	D	88.4	196.4	288.7
$(\eta^5\text{-}C_5H_5)Re(CO)_2(CSe)$	D	89.7	196.4	308.0
$(\eta^5\text{-}C_5H_4Me)Mn(CO)(CS)_2$	C	m	222.7	337.7
$(\eta^5\text{-}C_5H_4Me)Mn(CO)(CS)(PPh_3)$	C	n	233.4[o]	340.2[p]
$[(\eta^5\text{-}C_5H_5)Mn(CO(CS)(NO)]PF_6$	E	98.3	210.5	323.4
$[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CS)]PF_6$	D	92.0	198.4	307.5
$(\eta^5\text{-}C_5H_5)Re(CO)_2(C_8H_{14})$	F	84.3	205.2	
$(\eta^5\text{-}C_5H_5)Re(CO)_2(PPh_3)$[q]	F	84.7	202.8	
$(\eta^5\text{-}C_5H_5)Re(CO)_2(AsPh_3)$	G	84.7	200.9	

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[a] The chemical shifts are quoted downfield positive relative to Me_4Si (δ = 0.00 ppm).

[b] A = CH_2Cl_2; B = $CS_2/(CD_3)_2CO$; C = neat liquid; D = $(CD_3)_2CO$; E = $MeCN/(CD_3)_2CO$; F = C_4H_8O/C_6D_6; G = CH_2Cl_2/C_6D_6.

[c] No ^{13}C coupling to ring observed in $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_3$.

[d] In $(\eta^6\text{-}C_6H_6)Cr(CO)_2(^{13}CS)$, this peak appears as a 1:1 doublet with $^2J(^{13}CO,^{13}CS)$ = 11.0 Hz,

[e] In $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_2(CS)$, this peak appears as an approximate 1:2:1 triplet with $^2J(^{13}CO,^{13}CS)$ = ~10 Hz.

[f] In $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_2(CSe)$, this peak appears as an approximate 1:2:1 triplet with $^2J(^{13}CO,^{13}CSe)$ = ~10 Hz.

[g] $\delta C(1,3,5)$, 91.0; $\delta C(2,6)$, 95.9; $\delta C(4)$, 96.2; $\delta(CO_2)$, 166.4 ppm.

[h] $\delta C(1,3,5)$, 96.6; $\delta C(2,6)$, 100.4; $\delta C(4)$, 100.8; $\delta(CO_2)$, 165.7 ppm.

[i] $\delta C(1,3,5)$, 98.2; $\delta C(2,6)$, 101.5; $\delta C(4)$, 102.0; $\delta(CO_2)$, 165.0 ppm.

[j] $\delta C(1)$, 102.7; $\delta C(2,5)$, 82.4; $\delta C(3,4)$, 82.0; $\delta(Me)$, 13.3 ppm.

[k] $\delta C(1)$, 104.4; $\delta C(2.5)$, 85.5; $\delta C(3,4)$, 84.4; $\delta(Me)$, 13.3 ppm.

[ℓ] $\delta C(1)$, 105.5; $\delta C(2,5)$, 86.8; $\delta C(3,4)$, 85.5; $\delta(Me)$, 13.0 ppm.

[m] $\delta C(1)$, 105.6; $\delta C(2,5)$, 87.8; $\delta C(3,4)$, 86.7; $\delta(Me)$, 12.8 ppm.

[n] $\delta C(1)$, 101.9; $\delta C(2,5)$, 87.9; $\delta C(3,4)$, 85.4; $\delta(Me)$, 13.5 ppm.

[o] Doublet, $^2J(^{13}CO,^{31}P)$ = 29.0 Hz.

[p] Doublet, $^2J(^{13}CO,^{31}P)$ = 29.0 Hz.

[q] No ^{31}P coupling observed to either the ring or the CO groups.

to selenium in X—C_6H_4—Se—CH═CH_2 (X = H, NH_2, OMe, Me, etc.) fall in the range 127–147 ppm [23]. It is clear, however, that $\delta(^{13}CSe)$ for selenocarbonyl complexes appear at extremely low fields; in fact, the 368.0 ppm value for $\delta(^{13}CSe)$ in $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CSe)$ is one of the lowest field ^{13}C resonances ever observed for a diamagnetic species.

One of the reasons for studying the ^{13}C NMR spectra of the ^{13}C-enriched species, $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_3$, $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_2(CS)$, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(^{13}CS)$ and $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_2(CSe)$, was to see if any carbon-carbon coupling constants could be measured for these systems. In no case was any CO, CS or CSe coupling with the C_6H_6 ring carbons detected. The CS resonance in $(\eta^6\text{-}C_6H_6)Cr(^{13}CO)_2(CS)$ exhibits a poorly resolved triplet centered at 346.4 ppm $[^2J(^{13}CO,^{13}CS) = \sim 10\ Hz]$. A more accurate value for this particular coupling constant is obtained from the spectrum of $(\eta^6\text{-}C_6H_6)Cr(CO)_2(^{13}CS)$; the CO resonance at 232.5 ppm is split into a 1:1 doublet $[^2J(^{13}CO,^{13}CS) = 11.0\ Hz]$. This coupling constant can be taken as the value expected for the coupling between CS and the cis CO groups in octahedral complexes of the type fac-$Cr(CO)_2(CS)L_3$ because the bond angles for the $Cr(CO)_2(CS)$ moiety in the related methylbenzoate complex, $(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CS)$, are approximately 90° [24].

The $\delta(^{13}CX)$ values given in Table 1 show that there is a downfield shift for each series of complexes in the order $\delta(^{13}CO) < \delta(^{13}CS) < \delta(^{13}CSe)$. This trend can be explained by considering eq. 1 given in the Introduction. Molecular orbital calculations and photoelectronic studies [25] have demonstrated that the π-π^* molecular orbital energy difference in the free diatomic species and in transition metal complexes is smaller for CS than for CO. Unfortunately, no such information is available for CSe. However, the smaller $^1\Pi \rightarrow {}^1\Sigma$ electronic transition energy for CSe compared to that for CO and CS [3] suggests that the $\pi-\pi^*$ energy difference may also be smaller. So, assuming that ΔE_{av} in eq. 1 is approximately equal to the $\pi-\pi^*$ energy difference, the $\delta(^{13}CX)$ chemical shifts would follow the observed order because σ_p^{AB} is inversely proportional to ΔE_{av} and negative.

The CX chemical shifts exhibit a linear correlation ($\bar{r} = 0.92$) with the CX stretching force constants [$\delta(^{13}CX) = -13k_{CX} + 443$] (Fig. 1). This slope of this line (-13 ppm $mdyne^{-1}$ A) is

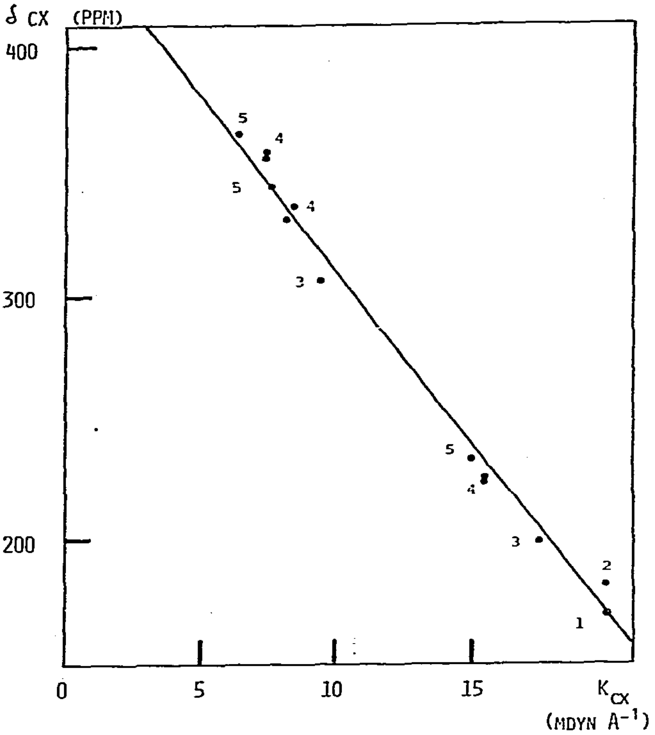

Fig. 1. Plot of the ^{13}C NMR chemical shifts (δCX) <u>vs</u>. the primary stretching force constants (k_{CX}) for the CX (X = O, S, Se) bonds in various chalcocarbonyl species. Note that k_{CX} decreases in the order, $k_{CO} > k_{CS} > k_{CSe}$. For details on the force constant data, see Ref. 28. 1 = $[Cu(CO)]^+$; 2 = CO gas; 3 = $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CX)]PF_6$ (X = O, S); 4 = $(\eta^5\text{-}C_5H_4R)Mn(CO)_2(CX)$ (R = H, Me; X = O, S, Se); 5 = $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = O, S, Se).

appreciably different from that found for related $\delta(^{13}CO)$ plots for other metal carbonyl complexes (-7 ppm mdyne^{-1} A) [10,26]. A possible explanation for the difference lies in the increased size of the carbon 2p atomic orbitals participating in the π molecular framework as the extent of metal-CO backbonding increases, i.e., as downfield chemical shifts are induced. This would affect the paramagnetic shielding throught the $\langle r^3 \rangle_{2p}$ term by adding a contrary shift to the downfield shift resulting from ΔE_{av}. This in turn would lead to shallower slopes for the $\delta(^{13}CO)$ vs. k_{CO} correlations, as is observed.

For the manganese and chromium complexes of the type, (Ring)M(CO)$_2$(CX), the $\delta(^{13}CO)$ values move upfield with changes in CX as CO<CS<CSe, i.e. in the opposite direction to that observed for other Lewis base substitutions of metal carbonyl groups. A similar observation has been noted for the arene derivatives, $(\eta^6\text{-}C_6H_{6-n}R_n)Cr(CO)_2(CX)$ (R = Me,CO$_2$Me etc.; X = O,S) [20]. It has now been well established by various physicochemical studies that CS and CSe are strongly bonded to metals than is CO on account of the greater net electron withdrawing capacity of these ligands [4]. In view of this, we attribute the $\delta(^{13}CO)$ behavior for these series of complexes to the increased π-acceptor/σ-donor capacity after CS and CSe ligands compared to CO. Moreover, this π/σ ratio apparently increases in the order CO<CS<CSe. The rhenium complexes, $(\eta^5\text{-}C_5H_5)Re(CO)_2(CX)$, do not appear to follow this trend because, unlike the analogous manganese complexes, the CO resonances in the thiocarbonyl and selenocarbonyl derivatives are shifted downfield by 1.4 ppm. While this behavior is not understood at present, it may be due to a change in the Re-CO rather than the Re-CX bonding interactions because the ring carbon ^{13}C resonances do follow the π/σ trend mentioned above.

The thiocarbonyl and selenocarbonyl ^{13}C chemical shifts parallel those for the carbonyl groups in sensitivity to changes in electron density on the metal. Both $\delta(^{13}CO)$ and $\delta(^{13}CS)$ shift downfield in $(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(PPh_3)$ relative to the values for $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$. There is a 12–14 ppm upfield shift for the CO and CS resonances on going from $(\eta^5\text{-}C_5H_5)Mn(CO)_2(CS)$ to $[(\eta^5\text{-}C_5H_5)Mn(CO)(CS)(NO)]^+$. On descending the group from Mn to Re in the $(\eta^5\text{-}C_5H_5)M(CO)_2(CX)$ series, there is a stepwise upfield shift for all the CX resonances. This is another example of the so-called "metal triad effect" [8]. Also, a change in the Ring in all five (Ring)$M(CO)_2(CX)$ series in Table 1 shows a relatively uniform shift for both the ^{13}CO and ^{13}CX (X = S,Se) resonances with each change. Mann [27] has attributed this ^{13}C chemical shift behavior in transition metal carbonyl complexes to a decrease in π-backdonation from the metal d orbitals to the carbonyl π^* orbitals as the nuclear charge on the metal increases. In view of the comparable bonding properties of the isoelectronic CS and CSe ligands, it seems likely that a similar explanation is true for these ligands as well.

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