

CATIONIC DI- AND MONO-CARBONYL COMPLEXES OF MANGANESE(I)

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Summary

The complexes *fac*-O₃ClOMn(CO)₃(NN) (NN = 1,10-phenantroline (phen) or 2,2'-bipyridine (bipy)) react with an excess of the ligands L [L = P(OR)₃ or P(OR)₂Ph, R = Me or Et] in refluxing ethanol to give *cis-trans*-[Mn(CO)₂(NN)L₂]ClO₄, or the more highly substituted [Mn(CO)(NN)L₃]ClO₄ if the reaction is carried out under UV irradiation. Carbonylation at normal pressure of the latter complexes results in the formation of *cis-cis*-[Mn(CO)₂(NN)L₂]ClO₄, which undergo isomerization to the *cis-trans* isomer when heated in acetone.

Treatment of *fac*-O₃ClOMn(CO)₃(dpe) (dpe = 1,2-bis(diphenylphosphino)ethane] with bipy or phen in refluxing ethanol gives the corresponding *cis*-[Mn(CO)₂(NN)(dpe)]ClO₄ complexes, and irradiation of these with UV in the presence of an excess of P(OR)₃ (R = Ph, Et or Me) gives the monocarbonyls [Mn(CO)(NN)(dpe)L]ClO₄.

Introduction

Most of the known octahedral carbonylmanganese derivatives [1–8] are pentacarbonyls [3,4,6,8], tetracarbonyls [5,9,10], and tricarbonyls [2–5,7]. If species other than octahedral are excluded, dicarbonyl complexes are scarcer [2,4,5,7,11], and only a few cationic monocarbonyls, all of them containing isocyanide ligands, have been reported [12–14].

Replacement of CO by Lewis bases (L) in both the neutral Mn(CO)_{5-n}L_nX or cationic [Mn(CO)_{6-n}L_n]⁺ species is increasingly difficult as *n* is increased. Thus, highly substituted derivatives have been obtained only by using strong π -acceptor ligands [2,4,7,15,16,17], or bidentate phosphorous donor ligands such as diphosphines [11,14,18,19], difluorophosphines [20] and others [21,22]; it has been pointed out that the chelate effect make these ligands analogous to the phosphites in CO substitution [23]. Some *cis*-labilizing ligands

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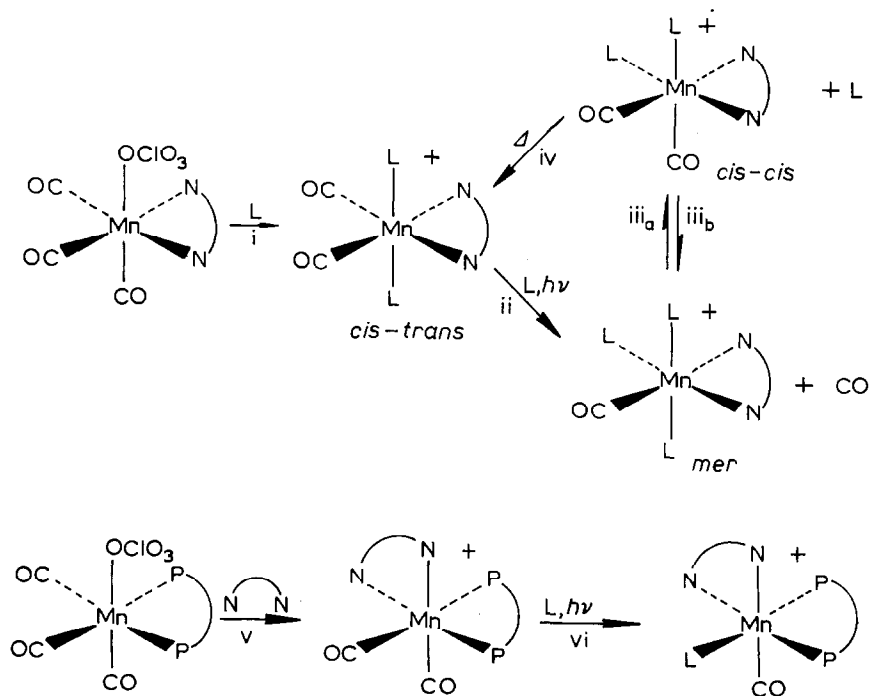
[24,25], such as bipy or phen, may also enhance CO substitution; thus, some salts *cis-trans*-[Mn(CO)₂(NN)L₂]ClO₄ (L = P(OR)₃ or PR₃) can be prepared by treating *fac*-[Mn(CO)₃(NN)L]ClO₄ with L under relatively mild conditions [5].

These considerations led us to investigate the possibility of synthesizing highly substituted cationic complexes of manganese(I) by using bipy or phen as ligands. Thus, we have prepared the dicarbonyls *cis-trans*- and *cis-cis*-[Mn(CO)₂(NN)L₂]⁺ and *cis*-[Mn(CO)₂(NN)(dpe)]⁺, and, as expected, there were found to give the highly substituted [Mn(CO)(NN)L₃]⁺ and [Mn(CO)(NN)(dpe)L]⁺, respectively, where L represents a phosphite or phosphonite ligand.

Results and discussion

The reaction between *fac*-O₃ClOMn(CO)₃(NN) (NN = bipy or phen) and one monodentate ligand L = P(OR)₃ or P(OR)₂Ph (R = Me or Et) in refluxing ethanol and in the absence of light (i in Scheme 1) gave the salts *cis-trans*-

SCHEME 1



[Mn(CO)₂(NN)L₂]ClO₄ (I–VI). (We previously made some of these complexes by treating *fac*-[Mn(CO)₃(NN)(Me₂CO)]ClO₄ with L = phosphines in refluxing acetone [5]). The $\bar{\nu}(\text{CO})$ IR spectra of these complexes showed two strong bands (Table 1), typical of an octahedral *cis*-dicarbonyl. As discussed in the earlier report [5], the *cis-trans* stereochemistry depicted in the scheme seemed likely in view the *cis*-labilizing effect of the chelating ligand NN, and this structure was recently confirmed by an X-ray diffraction crystal structure determination [29].

By virtue of the *cis*-labilizing nature of the NN ligand it seemed likely that further CO replacement in the above cationic dicarbonyls could be achieved. This proved to be the case and the highly substituted cations $[\text{Mn}(\text{CO})(\text{NN})\text{L}_3]^+$ were isolated as the perchlorate salts (VII–XIV) by treating the *cis-trans*- $[\text{Mn}(\text{CO})_2(\text{NN})\text{L}_2]\text{ClO}_4$ with an excess of the ligand $\text{L} = \text{P}(\text{OR})_3$ or $\text{P}(\text{OR})_2\text{Ph}$ ($\text{R} = \text{Et}$ or Me) in acetone under UV irradiation (ii in the scheme). Transitory monocarbonyl species were detected by IR in solution when $\text{L} = \text{P}(\text{OPh})_3$, $\text{P}(\text{OEt})\text{Ph}_2$ and PMePh_2 , but could not be isolated due to extensive decomposition. The complexes VII, VIII, IX and XII were also prepared, in much lower yield, by refluxing an acetone solution of *fac*- $\text{O}_3\text{ClO}_4\text{Mn}(\text{CO})_3(\text{NN})$ and a large excess of L. Under these conditions long reaction times (ca. 250 h) were required and decomposition took place. The IR spectra of the compounds VII–XIV showed one strong $\bar{\nu}(\text{CO})$ absorption (Table 1), but the (*fac*- or *mer*-) stereochemistry of the phosphite ligands (see below) could not be unambiguously assigned on the basis of the IR data only. The replacement of CO in reaction ii can take place with or without rearrangement of the ligands, depending on electronic and steric effects [26].

The UV irradiation of an acetone solution of the $[\text{Mn}(\text{CO})(\text{NN})\text{L}_3]\text{ClO}_4$ in the presence of CO (1 atm) (iiia in the scheme) led to the displacement of one molecule of L and to the formation of new dicarbonyl species, which were isolated and characterized as their salts *cis-cis*- $[\text{Mn}(\text{CO})_2(\text{NN})\text{L}_2]\text{ClO}_4$ (XV–XXII). They exhibit two $\bar{\nu}(\text{CO})$ bands in the IR at higher frequencies than those for their *cis-trans* isomers (Table 1). The *cis-cis* stereochemistry has been confirmed for *cis-cis*- $[\text{Mn}(\text{CO})_2(\text{phen})(\text{P}(\text{OMe})_3)_2]\text{ClO}_4$ by an X-ray single crystal structure determination [29]. The carbonylation iiia was only accomplished, however, when the free ligand formed was removed from the solution (see Experimental part), suggesting the equilibrium $\text{iiia} \rightleftharpoons \text{iiib}$ shown in Scheme 1. Process iiib occurred when acetone solutions of the *cis-cis* dicarbonyls were treated with L under UV irradiation, the precursor monocarbonyl being reformed.

We have reported that cationic complexes of the types *fac*- $[\text{Mn}(\text{CO})_3\text{L}_3]\text{ClO}_4$ [4], *fac*- $[\text{Mn}(\text{CO})_3(\text{diphos})\text{L}]\text{ClO}_4$ [7] and *cis*- $[\text{Mn}(\text{CO})_2\text{L}_4]\text{ClO}_4$ [4], where L is a phosphine or phosphite, isomerize upon heating to the *mer* or *trans* isomers, respectively. Similarly, the *cis-cis*- $[\text{Mn}(\text{CO})_2(\text{NN})\text{L}_2]\text{ClO}_4$ complexes isomerize in refluxing acetone in the absence of light to the *cis-trans* derivatives (iv in the scheme), while the monocarbonyl complexes decomposed under the same conditions. Conversely, UV irradiation of an acetone solution of the *cis-cis* dicarbonyls leads to decomposition with formation of some monocarbonyl; no isomerization to the *cis-trans* was observed.

As noted above, both cationic dicarbonyls *cis-trans*- and *cis-cis*- $[\text{Mn}(\text{CO})_2(\text{NN})\text{L}_2]\text{ClO}_4$ gave the same monocarbonyl derivative when irradiated with UV light in the presence of L; thus, the tentative *mer* stereochemistry assumed in the scheme may be proposed for the monocarbonyls on the basis of the *cis*-labilizing effect of the NN ligand (see iiib) and the assumption that the ligand L enters the position of the departing CO (see ref. 26 for general discussion). The carbonylation of the monocarbonyls to the *cis-cis* dicarbonyls also supports the *mer* stereochemistry of the former if we again assume that the CO enters the position of the departing L. However, in the absence of an X-ray structure determination the stereochemistry of the monocarbonyls cannot be unambiguously assigned.

TABLE 1
MELTING POINTS, CONDUCTIVITY, ANALYTICAL DATA AND $\nu(\text{CO})$ FREQUENCIES FOR COMPLEXES PREPARED

Compound	m.p. ($^{\circ}\text{C}$) ^c	ΔM ^a	Analysis found (calcd.) (%)			$\nu(\text{CO})$ ^b (cm^{-1})
			C	N	H	
I	179	137	49.4 (49.3)	3.9 (3.8)	4.2 (4.1)	1963, 1986
II	180	130	51.3 (51.9)	3.6 (3.6)	4.8 (4.8)	1959, 1891
III	239	127	35.6 (35.2)	4.5 (4.6)	4.2 (4.2)	1966, 1895
IV	244	132	41.4 (41.2)	4.1 (4.0)	5.5 (5.5)	1961, 1889
V	135	119	47.8 (47.6)	4.0 (4.0)	4.3 (4.3)	1960, 1892
VI	119	128	50.1 (50.4)	3.6 (3.7)	5.1 (5.0)	1958, 1890
VII	162	133	36.1 (35.9)	3.9 (3.8)	4.9 (4.8)	1871(br)
VIII	171	126	43.5 (43.2)	3.4 (3.2)	6.0 (6.2)	1873(br)
IX	156	121	50.9 (50.9)	3.4 (3.2)	4.8 (4.7)	1868(br)
X	145	130	54.2 (54.0)	3.1 (2.9)	5.7 (5.6)	1865(br)
XI	174	132	33.9 (33.8)	4.0 (3.9)	4.9 (5.0)	1871(br)
XII	182	129	41.8 (41.6)	3.8 (3.9)	6.3 (6.2)	1866(br)
XIII	149	139	49.6 (49.5)	3.2 (3.3)	5.0 (4.9)	1866(br)
XIV	155	128	52.6	3.1	5.2	1864(br)

XV	<i>cis-cis</i> -[Mn(CO) ₂ (phen)(P(OMe) ₃) ₂]ClO ₄	124	132	37.9 (37.6)	4.5 (4.4)	4.1 (4.1)	1984, 1905
XVI	<i>cis-cis</i> -[Mn(CO) ₂ (phen)(P(OEt) ₃) ₂]ClO ₄	237	124	43.0 (43.2)	3.8 (3.9)	5.2 (5.3)	1977, 1900
XVII	<i>cis-cis</i> -[Mn(CO) ₂ (phen)(P(OMe) ₂ Ph) ₂]ClO ₄	133	127	49.5 (49.3)	3.7 (3.8)	4.2 (4.1)	1978, 1904
XVIII	<i>cis-cis</i> -[Mn(CO) ₂ (phen)(P(OEt) ₂ Ph) ₂]ClO ₄	156	134	52.1 (51.9)	3.6 (3.6)	5.2 (4.9)	1976, 1904
XIX	<i>cis-cis</i> -[Mn(CO) ₂ (bipy)(P(OMe) ₃) ₂]ClO ₄	104	129	35.1 (35.2)	4.7 (4.6)	4.1 (4.2)	1982, 1903
XX	<i>cis-cis</i> -[Mn(CO) ₂ (bipy)(P(OEt) ₃) ₂]ClO ₄	96	131	41.1 (41.2)	3.9 (4.0)	5.1 (5.5)	1978, 1899
XXI	<i>cis-cis</i> -[Mn(CO) ₂ (bipy)(P(OMe) ₂ Ph) ₂]ClO ₄	122	128	47.3 (47.6)	3.8 (4.0)	4.3 (4.8)	1978, 1904
XXII	<i>cis-cis</i> -[Mn(CO) ₂ (bipy)(P(OEt) ₂ Ph) ₂]ClO ₄	128	126	50.2 (50.4)	3.6 (3.7)	4.9 (5.0)	1973, 1904
XXIII	<i>cis</i> -[Mn(CO) ₂ (bipy)(dpe)]ClO ₄	218	138	60.3 (59.7)	3.6 (3.7)	4.2 (4.2)	1957, 1887
XXIV	<i>cis</i> -[Mn(CO) ₂ (phen)(dpe)]ClO ₄	166	132	60.6 (60.8)	3.5 (3.5)	4.1 (4.0)	1957, 1887
XXV	[Mn(CO)(phen)(dpe)(P(OPh) ₃)]ClO ₄	170	145	63.1 (63.9)	2.5 (2.6)	4.4 (4.4)	1866(br)
XXVI	[Mn(CO)(phen)(dpe)(P(OEt) ₃)]ClO ₄	193	141	58.5 (58.2)	3.0 (3.0)	5.2 (5.1)	1855(br)
XXVII	[Mn(CO)(phen)(dpe)(P(OMe) ₃)]ClO ₄	183	148	56.9 (56.9)	2.7 (3.1)	4.3 (4.6)	1853(br)
XXVIII	[Mn(CO)(bipy)(dpe)(P(OPh) ₃)]ClO ₄	167	131	62.4 (63.1)	2.6 (2.6)	4.3 (4.5)	1864(br)
XXIX	[Mn(CO)(bipy)(dpe)(P(OEt) ₃)]ClO ₄	151	136	57.0 (57.1)	3.2 (3.1)	5.3 (5.2)	1852(br)
XXX	[Mn(CO)(bipy)(dpe)(P(OMe) ₃)]ClO ₄	165	138	55.3 (55.8)	3.1 (3.2)	4.9 (4.8)	1853(br)

^a Molar conductivity in 8 cm² mol⁻¹ of a 5 X 10⁻⁴ M acetone solution at 25°C. ^b The IR spectra were recorded in dichloromethane solution. All bands are strong.
^c All melted with decomposition.

The *cis-cis* to *cis-trans* isomerization of the dicarbonyls might be regarded as thermodynamically controlled, and it would be of interest to carry out a kinetic study in order to establish the mechanism of this process.

Treatment of *fac*-O₃ClOMn(CO)₃(NN) with the bidentate ligands NN or dpe failed to produce more substituted cationic complexes. Thus, the reaction between these neutral perchlorates and dpe in refluxing ethanol gave the known [27] *fac*-[Mn(CO)₃(NN)(dpe)]ClO₄ (in which the diphosphine is tentatively assumed to be monodentate), followed by slow decomposition. Finally, only slow decomposition took place when a mixture of *fac*-O₃ClOMn(CO)₃(NN) and the ligand NN was heated under reflux in ethanol or toluene.

As a possible alternative synthesis of cationic di- and monocarbonyls analogous to those discussed above, but containing diphosphines as ligands, we investigated the reactions of the neutral complexes *fac*-O₃ClOMn(CO)₃(diphos) (diphos = Ph₂(CH₂)_nPPh₂, *n* = 1 (dpm), 2 (dpe) and 3 (dpp)) with bipy or phen. The reactions were complex, and the final product(s) was dependent on the diphosphine, the solvent and on the temperature. Satisfactory results were only obtained by refluxing a 1 : 1 molar mixture of *fac*-O₃ClOMn(CO)₃(dpe) and the ligand NN in ethanol for 1 h, or for 4 h when the reaction was carried out in the absence of light. The red *cis*-[Mn(CO)₂(NN)(dpe)]ClO₄ for NN = bipy (XXIII) or phen (XXIV) were prepared in this way in good yields (*v* in the scheme). The two strong bands of almost the same intensity in the carbonyl region IR spectra of the complexes clearly indicate that the two CO's are *cis* to each other, and the examination of the full range solid state IR (bands at 840 (NN = phen), 770 (NN = bipy) and 1060s(br) and 630m cm⁻¹ (ClO₄⁻) also supported the formulation of the complexes as XXIII and XXIV, analogous to compounds XV–XXII. Complex decompositions were observed in reaction *v* when heating was prolonged beyond the time required for the formation of the cationic *cis* dicarbonyls, especially in the presence of light; from their $\bar{\nu}(\text{CO})$ bands the complexes *trans*-[Mn(CO)₂(dpe)₂]⁺ [11] and HMn(CO)₃(dpe) [28] were detected among the decomposition products. On the other hand, the complex *fac*-O₃ClOMn(CO)₃(dpm) reacted with bipy or phen in a variety of solvents giving a mixture of products, one of them being the *cis* dicarbonyl analogous to that, previously mentioned, containing dpe. The reactions between *fac*-O₃ClOMn(CO)₃(dpp) and bipy led (even at room temperature) to the cationic *cis* dicarbonyl analogous to XXIII, but the complex [Mn(CO)₄(dpp)]⁺ (characterized by its $\bar{\nu}(\text{CO})$ bands [7]) was also formed. The tetracarbonyl species were also formed when the perchlorate complexes containing dpm and dpe were treated with bipy or phen in solvents other than ethanol.

As in the case of their analogous *cis-cis* dicarbonyls previously described, the presence of two nitrogen atoms in the *cis*-[Mn(CO)₂(NN)(dpe)]ClO₄ suggested that further CO substitution might be achieved, and again this proved to be the case. Thus, UV irradiation of a dichloromethane solution of *cis*-[Mn(CO)₂(NN)(dpe)]ClO₄ (NN = bipy or phen) in the presence of one aryl or alkyl phosphite L, gave the deep red salts [Mn(CO)(NN)(dpe)L]ClO₄ (XXV–XXX), the IR spectra of which in the $\bar{\nu}(\text{CO})$ region showed a single broad absorption near 1860–1850 cm⁻¹ (Table 1). Depending upon the nature of the entering ligand L, varying amounts of the *trans*-[Mn(CO)₂(dpe)₂]ClO₄ were formed along with the monocarbonyl derivative, showing that complex decomposition

processes also took place during reaction vi. Furthermore, as in reaction ii, the decomposition prevailed when L was a poorer π -acceptor than the phosphites, e.g. $P(OMe)_2Ph$, PPh_3 etc, but, even in those cases, the monocarbonyls were formed, as shown by their $\bar{\nu}(CO)$ bands. Although three stereochemistries are consistent with the formulation $[Mn(CO)(NN)(dpe)L]ClO_4$, we believe, on the basis of the *cis*-labilizing effect of the NN ligand and assuming kinetic control for reaction vi, that the most likely structure is that shown in the scheme, but as noted above for the analogous $[Mn(CO)(NN)L_3]ClO_4$, an X-ray structural determination would be required for unambiguous assignment of the stereochemistry.

Experimental

All reactions were carried out under nitrogen. The complexes *fac*- $O_3ClOMn(CO)_3(NN)$ (NN = bipy or phen) [5] and *fac*- $O_3ClOMn(CO)_3(diphos)$ (diphos = dpm, dpe and dpp) [7] were prepared by published methods. IR spectra were recorded using a Perkin-Elmer 599 spectrophotometer and calibrated against the 1602 cm^{-1} polystyrene absorption. Analyses were performed with a Perkin-Elmer 240 microanalyzer.

Preparation of cis-trans $[Mn(CO)_2(NN)L_2]ClO_4$ (I–VI)

The complex *fac*- $O_3ClOMn(CO)_3(NN)$ (1 mmol) and the ligand L (5 mmol) were refluxed in ethanol (40 ml) for 2 h in the absence of light. The solution was evaporated to dryness and the residue was washed with diethyl ether. Recrystallization was from dichloromethane/ethanol. Yields 70–80%.

Preparation of $[Mn(CO)(NN)L_3]ClO_4$ (VII–XIV)

A solution of *cis-trans*- $[Mn(CO)_2(NN)L_2]ClO_4$ (1 mmol) and the ligand L (3 mmol) in acetone (40 ml) was exposed to the UV irradiation until the $\bar{\nu}(CO)$ absorptions of the starting complex could no longer be observed. The resulting deep red solution was evaporated to dryness, the residue was washed with diethyl ether, and the product recrystallized from dichloromethane/ethanol. Yields 60–70%. The reaction times were; 4 h (VII, VIII), 6.5 h (IX, X), 6 h (XI, XII), 7.5 h (XIII, XIV).

The compounds VII–XIV were similarly prepared in 70–80% yields from *cis-cis*- $[Mn(CO)_2(NN)L_2]ClO_4$. The reaction times were: 2 h (VII, VIII), 4 h (IX), 4.5 h (X), 3 h (XI), 3.5 h (XII), 4.5 h (XIII) and 5 h (XIV).

Preparation of cis-cis $[Mn(CO)_2(NN)L_2]ClO_4$ (XV–XXII)

Carbon monoxide (1 atm) was bubbled for 1 h through a solution of $[Mn(CO)(NN)L_3]ClO_4$ (0.5 mmol) in acetone (50 ml) exposed to UV light. The solution was evaporated to dryness and the residue was washed with diethyl ether to remove the free ligand. Acetone (50 ml) was added and the treatment was restarted. The procedure was repeated every 1/2 h until the $\bar{\nu}(CO)$ IR spectrum of the resulting solid no longer showed bands of the starting material. Ethanol (20 ml) was added and the solvents were evaporated under reduced pressure to leave a solid. Yields 60–70%.

Preparation of cis-[Mn(CO)₂(NN)(dpe)]ClO₄ (XXIII–XXIV)

The complex *fac*-O₃ClOMn(CO)₃(dpe) (0.63 g, 1 mmol) and bipy (0.19 g, 1.2 mmol) or phen · H₂O (0.23 g, 1.2 mmol) were refluxed for 1 h under UV irradiation (or 4 h in the absence of light) in ethanol (20 ml). The deep red solution was filtered and the solvent removed under reduced pressure. The residue was washed with diethyl ether and recrystallized from dichloromethane/ethanol. Yield 80%.

Preparation of [Mn(CO)(NN)(dpe)L]ClO₄ (XXV–XXX)

A solution of *cis*-[Mn(CO)₂(NN)(dpe)]ClO₄ (0.5 mmol) and the ligand L (2.5 mmol) in dichloromethane (20 ml) was irradiated with UV light at 0°C until the IR spectrum of the solution no longer showed the bands of the starting complex. The solvent was removed in vacuo and the resulting dark precipitate was washed with diethyl ether until free of the ligand. The residue was dissolved in dichloromethane, ethanol was added, and the solution was allowed to evaporate slowly to give dark red crystals of [Mn(CO)(NN)(dpe)L]ClO₄, mixed with other yellow crystals of *trans*-[Mn(CO)₂(dpe)₂]ClO₄. Most of the latter were removed manually and the residue was recrystallized from dichloromethane/ethanol. The yields were small (10–40%).

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