

REACTIVITIES OF LEWIS ACID ADDUCTS OF $\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Y}$ (Y = SPh, SO₂Ph, AND PPh₂) WITH NUCLEOPHILES

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Summary

Complexes of the type $\text{CpFe(CO)}_2\text{Y}$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, Y = SPh (I), Y = PPh₂ (II), Y = SO₂Ph (III)) and $\text{Cp}'\text{Fe(CO)}_2\text{SPh}$ ($\text{Cp}' = \eta^5\text{-C}_5(\text{CH}_3)_5$ (IV)), form adducts with the Lewis acids AlMe_3 , AlMe_2Cl or AlBr_3 . All of the Lewis acid adducts of I react with one or more of the nucleophiles L (L = PBu_3 , PPh_3 , P(OEt)_3 , cyclohexene) to form ionic products of the type $[\text{CpFe(CO)}_2(\text{L})][\text{PhS(AlR}_3)_2]$. The cation of each product has been isolated as the PF_6^- salt and characterized. One of the proposed anions, $[\text{PhS(AlMe}_3)_2]^-$, has been synthesized by an independent method and characterized as the lithium salt. The Lewis acid adducts of II, and III do not undergo substitution reactions with the same nucleophiles, whereas adducts of IV react only with PBu_3 in low yield. The AlMe_2Cl and AlBr_3 adducts of $\text{CpFe(CO)(PPh}_3\text{)SPh}$ (V) react with PPh_3 to form the halides, $\text{CpFe(CO)(PPh}_3\text{)X}$ (X = Cl^- and Br^- respectively), but the AlMe_3 adduct is unreactive.

Introduction

Lewis acid promoted substitution or insertion reactions have been reported for a variety of transition metal carbonyl complexes [1]. In most cases, adduct formation occurs at a carbonyl ligand or the metal center. In the complexes $\text{CpFe(CO)}_2\text{Y}$ (Y = SPh, SO₂Me, and PPh₂) however, adduct formation with both organometallic and inorganic Lewis acids has been shown to occur at the ligand Y [2]. We have prepared the AlMe_3 , AlMe_2Cl or AlBr_3 adducts of thiolate, sulfonyl and phosphide complexes to determine the effect adduct formation, at a site other than a carbonyl or the metal center, has on substitution reactions. The adducts of $\text{Cp}'\text{Fe(CO)}_2\text{SPh}$ and $\text{CpFe(CO)(PPh}_3\text{)SPh}$ were also prepared and allowed to react with nucleophiles to determine if methylation of Cp or substitution of a phosphine ligand for a carbonyl plays a significant role in the substitution reactions [3].

Experimental

All reactions were carried out in dried, degassed solvents under Ar, using Schlenk apparatus. IR spectra were recorded on a Perkin–Elmer 421 grating spectrometer and ^1H NMR were measured on a Perkin–Elmer, R-12, 60 MHz instrument using TMS as an internal reference. The complexes I [4], III [5], and IV [6] were prepared according to literature methods. Complex V, prepared using the method of Treichel [6], gave satisfactory elemental analysis [7].

Preparation of adducts of $\text{CpFe}(\text{CO})_2\text{SPh}$, $\text{Cp}'\text{Fe}(\text{CO})_2\text{SPh}$, and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}$

The Lewis acids AlMe_3 , AlMe_2Cl , or AlBr_3 , in CH_2Cl_2 , were added to equimolar amounts of a thiolate complex in 20 ml of the same solvent. Immediate quantitative formation of the adducts $\text{CpFe}(\text{CO})_2\text{SPh}(\text{AlMe}_3)$ (IA), $\text{CpFe}(\text{CO})_2\text{SPh}(\text{AlMe}_2\text{Cl})$ (IB), $\text{CpFe}(\text{CO})_2\text{SPh}(\text{AlBr}_3)$ (IC), $\text{Cp}'\text{Fe}(\text{CO})_2\text{SPh}(\text{AlMe}_3)$ (IVA), $\text{Cp}'\text{Fe}(\text{CO})_2\text{SPh}(\text{AlBr}_3)$ (IVC), $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}(\text{AlMe}_3)$ (VA), $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}(\text{AlMe}_2\text{Cl})$ (VB), and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}(\text{AlBr}_3)$ (VC) was indicated in the IR spectrum by the shifting of the carbonyl stretching bands of complexes I, IV, and V to higher frequencies (Table 1). The adducts IA–IC, isolated by concentrating the sample under vacuum, cooling and adding hexane, formed highly air sensitive oils which resisted crystallization attempts. The integration of the Cp and Al–Me resonances in the ^1H NMR spectra of the Cp derivatives indicated 1/1 adduct formation (Table 1).

Preparation of $[\text{PhS}(\text{AlMe}_3)_2]\text{Li}$

A suspension of $\text{PhS}^- \text{Li}^+$ (10 mmol) was prepared by slowly adding n-BuLi (4.0

TABLE 1
SPECTROSCOPIC DATA FOR COMPLEXES AND THEIR ADDUCTS

Complex	Lewis acid	$\nu(\text{CO}) (\text{cm}^{-1})$ ^a	$^1\text{H NMR}(\delta)$ ^f
$\text{CpFe}(\text{CO})_2\text{SPh}$	I	–	4.85s, Cp: 7.20m, Ph
	IA	AlMe_3	2049, 2005 – 0.45s, Me: 5.00s, Cp: 7.25m, Ph
	IB	AlMe_2Cl	2051, 2012 – 0.40s, Me: 5.15s, Cp: 7.25m, Ph
	IC	AlBr_3	2065, 2025 5.55s, Cp: 7.25m, Ph
$\text{CpFe}(\text{CO})_2\text{PPh}_2$	II	–	2010, 1966 ^d ^e
	IIA	AlMe_3	2040, 2000 ^d ^e
	IIC	AlBr_3	2055, 2013 ^d ^e
$\text{CpFe}(\text{CO})_2\text{SO}_2\text{Ph}$	III	–	2060, 2015 ^b ^e
	IIIC	AlBr_3	2080, 2040 ^c ^e
$\text{Cp}'\text{Fe}(\text{CO})_2\text{SPh}$	IV	–	2005, 1956 7.30–6.80m, Ph: 1.76s, Me
	IVA	AlMe_3	2025, 1985 – 0.40s, AlMe: 1.75s, Me: 7.30–6.90m, Ph
	IVC	AlBr_3	2038, 1996 ^e
$\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}$	V	–	1965 4.35d, Cp: 7.20m, Ph
	VA	AlMe_3	1965 – 0.40s, Me: 4.60d, Cp: 7.25m, Ph
	VB	AlMe_2Cl	1971 – 0.40s, Me: 4.85d, Cp: 7.25m, Ph
	VC	AlBr_3	1985 ^e
$[\text{PhS}(\text{AlMe}_3)_2]\text{Li}$	VIII	–	– – 0.80s, Me: 7.35m, Ph

^a In CH_2Cl_2 . ^b $\nu(\text{SO})$ 1190, 1160, 1030 cm^{-1} in CH_2Cl_2 . ^c $\nu(\text{SO})$ 1170, 1125, 1010 cm^{-1} in CH_2Cl_2 .

^d In benzene. ^e Not measured. ^f In CS_2 .

ml of 2.5 *M* solution in hexane, 10 mmol) to PhSH (1.1 g, 10 mmol) in 100 ml of toluene. The mixture was stirred at room temperature and AlMe₃ (1.8 g, 25 mmol) was added via a syringe. The mixture was then refluxed 1 h and filtered while hot. The compound [PhS(AlMe₃)₂Li] (VIII) was collected as a white powder from the filter and dried under vacuum. Yield 81%. An active alkyl analysis on this material indicated a 1.96/1 ratio of AlMe₃ to PhS⁻ for the adduct. Al Anal. Found: Al, 20.43. C₁₂H₂₃Al₂LiS calcd.: Al, 20.77%.

Preparation of adducts of CpFe(CO)₂PPh₂

Solid sodium methoxide (0.25 g, 4.6 mmol) was added, in one portion, to 2.0 mmol (0.89 g) of [CpFe(CO)₂(PPh₂H)]Br [8] in 25 ml acetone. The suspension was stirred at room temperature for 10 min, during which it turned the characteristic deep red color of CpFe(CO)₂PPh₂. The acetone was then removed under vacuum and the residue was extracted with benzene (2 × 20 ml). The combined benzene extracts were filtered and titrated with a 0.1 *M* solution of AlR₃ (R = Me, Br) in benzene until the carbonyl bands of CpFe(CO)₂PPh₂ [9] were absent in the IR spectrum of the solution.

The adducts were also prepared by titrating the benzene solution of CpFe(CO)₂PPh₂ with a 1.0 *M* solution of L:AlR₃ (L = PPh₃ and PBu₃; R = Me and Br). The adducts CpFe(CO)₂PPh₂(AlMe₃) (IIA) and CpFe(CO)₂PPh₂(AlBr₃) (IIC) were used as prepared and not isolated.

Preparation of adducts of CpFe(CO)₂SO₂Ph

Solid AlBr₃ (0.85 g, 3.2 mmol) was added to a solution of CpFe(CO)₂SO₂Ph (1.0 g, 3.2 mmol) in 25 ml of CH₂Cl₂. The reaction mixture turned dark but remained homogeneous. An IR spectrum of the mixture at this point indicated the carbonyl bands for III had shifted to higher frequency as expected for formation of CpFe(CO)₂SO₂Ph(AlBr₃) (IIIC). A nucleophile was then added to this solution to test the reactivity of the adduct or alternatively the adduct IIIC could be isolated as an air sensitive, golden yellow solid by precipitating it from the CH₂Cl₂ solution with hexane.

Reactions of adducts with nucleophiles

Each of the adducts IA–IC, prepared as above, was combined in CH₂Cl₂ with one equivalent of nucleophile L (L = PPh₃, PBu₃, P(OEt)₃, or C₆H₁₀ (cyclohexene)). After stirring at room temperature for 24 h, the solvent was removed under vacuum and the residue was hydrolyzed with H₂O (35 ml). Filtration and addition of two equivalents of NH₄PF₆ to the filtrate precipitated the species [CpFe(CO)₂(L)]PF₆. CpFe(CO)(L)SPh and unreacted I were left on the filter, extracted into CH₂Cl₂ (20 ml), and separated on an alumina column using ether/CH₂Cl₂ mixtures as the eluant. The ¹H NMR and/or IR spectra of the various species isolated were then compared to literature values [10].

The adducts of IVA, IVC, and VA–VC were prepared as above and combined with one equivalent of the nucleophiles PPh₃ or PBu₃ in CH₂Cl₂. After stirring 24 h at room temperature the mixture was worked up in the same manner as were the adducts of IA–IC. After the reaction mixture was tested for cationic products using NH₄PF₆, the starting materials were isolated and purified by column chromatography using alumina and ether/CH₂Cl₂ as the eluent.

For the phosphide complex II, one equivalent of PPh_3 or PBu_3 was added to a solution of the adduct IIA or IIC prepared as above. When IIA or IIC was prepared using the phosphine adduct of the Lewis acid $\text{LA}:\text{PR}_3$, the solution was used as it was prepared. The mixture of adduct and nucleophile was stirred at room temperature for 24 h and then hydrolyzed with H_2O (35 ml). After separation of the organic and water phases, NH_4PF_6 was added to the aqueous layer to precipitate any ionic products. The amount of unreacted phosphide complex was determined by addition of two equivalents of MeI to the benzene layer and stirring the mixture at room temperature for 1 h. The solvent was then removed under vacuum and H_2O (35 ml) was added to the residue. Filtration and addition of two equivalents of NH_4PF_6 to the filtrate precipitated the cation as $[\text{CpFe}(\text{CO})_2(\text{PPh}_2\text{Me})]\text{PF}_6$ [8].

Results and discussion

The adducts IA, IB, and IC readily undergo substitution reactions with nucleophiles (L) at room temperature. With the nucleophiles PBu_3 , PPh_3 , $\text{P}(\text{OEt})_3$ and cyclohexene, the thiolate ligand is displaced and ionic products of the type $[\text{CpFe}(\text{CO})_2(\text{L})]^+$ are isolated, after hydrolysis, as PF_6^- salts. Varying amounts of unreacted compound I and $\text{CpFe}(\text{CO})(\text{L})\text{SPh}$ were also isolated with yields dependent on the nucleophile used but relatively independent of the Lewis acid used (Table 2). Addition of NEt_3 to the adducts IA, IB, and IC in CH_2Cl_2 , resulted in reversal of adduct formation but no substitution as evidenced by the IR spectrum of the mixture which shows carbonyl stretching frequencies only for compound I. Similar reactivity has been observed by Treichel [10b] who has shown that amine nucleophiles do not readily undergo substitution reactions with complexes of the general type $\text{CpFe}(\text{CO})_2\text{X}$. The total yield of the ionic and carbonyl substituted

TABLE 2
PRODUCT DISTRIBUTION FROM $\text{CpFe}(\text{CO})_2\text{SPh}(\text{AIR}_3) + \text{L} \rightarrow$

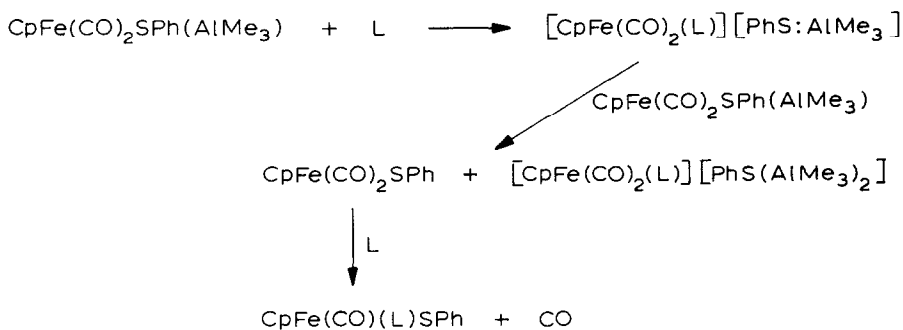
Starting compound	(L)	Product yields (%)		
		$\text{CpFe}(\text{CO})_2\text{SPh}$	$\text{CpFe}(\text{CO})(\text{L})\text{SPh}$	$[\text{CpFe}(\text{CO})_2(\text{L})]^+$
I	PBu_3	60	40	0
	PPh_3	80	20	0
	$\text{P}(\text{OEt})_3$	85	15	0
	C_6H_{10}	100	0	0
IA	PBu_3	10	35	50
	PPh_3	35	25	40
	$\text{P}(\text{OEt})_3$	55	15	30
	C_6H_{10}	> 95	0	< 5
IB	PBu_3	10	35	40
	PPh_3	45	15	35
	C_6H_{10}	> 95	0	< 5
IC	PBu_3	15	30	45
	PPh_3	40	10	35
	C_6H_{10}	> 95	0	< 5
IV	PBu_3	100	0	0
IVA	PPh_3	100	0	0
	PBu_3	> 95	0	< 5
IVB	PBu_3	> 95	0	< 5

species is thus dependent on the nature of the incoming ligand and is greatest for the more nucleophilic phosphines [11].

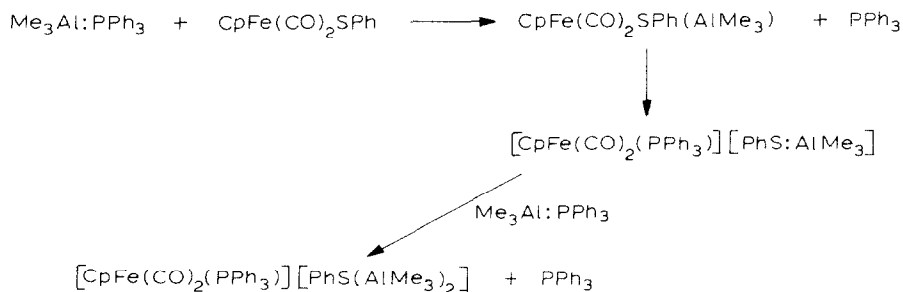
In the absence of Lewis acid, complex I slowly reacts with the same phosphine nucleophiles to yield carbonyl substituted species V, $\text{CpFe}(\text{CO})(\text{PBU}_3)\text{SPh}$ (VI), and $\text{CpFe}(\text{CO})(\text{P}(\text{OEt})_3)\text{SPh}$ (VII). With cyclohexene, unreacted compound I is the only species isolated from the reaction mixture. Ionic products are not isolated on workup and are not observed to form on monitoring the reaction by IR when Lewis acid is not present.

When the course of the reaction of PPh_3 with IA was followed by monitoring the IR spectrum of the mixture, a rapid formation of $[\text{CpFe}(\text{CO})_2(\text{L})]^+$ and I was detected. After this initial rapid phase of the reaction, which was typically complete in 1 h, the carbonyl bands for I slowly disappeared over a period of 24 h as the one for V increased in intensity. The slow rate of growth of the peak for V in the IR is consistent with that observed for the reaction of I with PPh_3 in the absence of added Lewis acid. Ionic products were not isolated in the reaction of I with phosphine nucleophiles indicating that the Lewis acid plays a significant role in the displacement of the mercaptide ligand.

The generation of compound I in the reaction mixture suggests cation formation is accompanied by formation of the anion $[\text{PhS}(\text{AlMe}_3)_2]^-$ (VIII'). Apparently this 2/1 anionic adduct is formed with consumption of AlMe_3 from $\text{CpFe}(\text{CO})_2\text{SPh}(\text{AlMe}_3)$ producing $\text{CpFe}(\text{CO})_2\text{SPh}$ which then slowly undergoes carbonyl substitution at room temperature with PPh_3 (Scheme 1). Independent synthesis of the anion VIII' supports the proposal that the anion PhS^- does form a 2/1 adduct with AlMe_3 in this reaction. It also appears the sulfur in VIII' acts as a stronger Lewis base than that in compound I as addition of VIII' to I does not result in formation of the adduct IA. The formulation of the anion as a 2/1 adduct is also consistent with the work of Atwood [12] who prepared similar adducts with anions of Group VI elements. The carbonyl stretching frequencies of the cationic product, having VIII' as the counterion, are clearly distinguishable and do not vary significantly from those found when PF_6^- is the anion. The stoichiometry of the reaction shown in Scheme 1 leads to the expectation that the theoretical yield of the cationic product can be no greater than 50% based on the starting complex. This is consistent with our observations that reactions involving IA with PBU_3 gave an actual yield of 50% whereas the less nucleophilic phosphines gave 35–40% yields and cyclohexene gave less than a 5% yield.



SCHEME 1



SCHEME 2

When two equivalents of the phosphine adduct, $\text{Ph}_3\text{P}:\text{AlMe}_3$, were added to the thiolate complex the only product detected or isolated after hydrolysis was the cation $[\text{CpFe}(\text{CO})_2(\text{PPh}_3)]^+$. When the reaction was monitored by IR, we observed immediate formation of the Lewis acid adduct of the thiolate complex, IA. This was followed by rapid, quantitative formation of the cationic product. At no time were carbonyl bands observed for compounds I or V. In this case (Scheme 2), it appears the phosphine adduct, rather than the adduct of the thiolate complex, as in Scheme 1, supplies the second equivalent of Lewis acid for formation of the anion VIII'. The observation of quantitative formation of the ionic product under these conditions is consistent with the stoichiometry proposed by Scheme 2.

The course of the reaction could not be followed by ^1H NMR as the methyl resonances appear as singlets in all cases apparently due to rapid exchange of AlMe_3 between the various species present in the reaction mixture. The chemical shifts of the phenyl protons for the starting materials and products are nearly the same and thus were not useful in monitoring the reaction (Table 1). The Cp resonances could not be observed due to interference from the resonance of the solvent, CH_2Cl_2 . Thus IR appeared to be the best method for monitoring the course of the reaction.

The Lewis acid adducts of IV, also react with nucleophiles with displacement of the mercaptide ligand. The reaction is limited, however, in that measurable amounts of the ionic product $[\text{Cp}'\text{Fe}(\text{CO})_2(\text{L})]^+$, are formed only with PBU_3 , the most nucleophilic phosphine used in the study. Other examples where permethylation of the cyclopentadienyl ring hinders substitution reactions are also known [13].

The complexes $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}(\text{AlMe}_2\text{Cl})$ (VB) and $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{-SPh}(\text{AlBr}_3)$ (VC), yield the halide complexes $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{X}$ ($\text{X} = \text{Cl}$ and Br respectively) on reaction with PPh_3 . The halide complexes are obtained in low yield, < 30%, and the remainder of the isolated material is unreacted V. The chloride complex, as reported by Treichel [10b], is unstable and was not isolated but was present in the reaction mixture as determined by IR. The formation of the halides was not detected by IR when the adducts were stirred alone in CH_2Cl_2 for 24 h. The AlMe_3 adduct $\text{CpFe}(\text{CO})(\text{PPh}_3)\text{SPh}(\text{AlMe}_3)$ (VA) was unreactive with PPh_3 as complete recovery of V was observed on hydrolysis and workup of the mixture. The addition of NEt_3 to VA, VB, and VC resulted only in reversal of adduct formation as determined by IR. Apparently NEt_3 reverses adduct formation much more rapidly than it participates in a reaction similar to that of PPh_3 with VB and VC.

The only carbonyl substitution reaction, reported for the phosphide complex II, is formation of the phosphide bridged dimer $[\text{CpFe}(\text{CO})\text{PPh}_2]_2$ [14]. The AlMe_3 or

AlBr_3 adducts of II appear to be unreactive toward phosphine nucleophiles even on heating the mixture to 80°C for 24 h. Although these conditions cause the free phosphide complex to form a dimer [14], substitution products of the adducts were neither detected in the reaction mixture nor isolated from the mixture on workup. Quantitative yields of the unreacted phosphide complex, in the form of $[\text{CpFe}(\text{CO})_2(\text{PPh}_2\text{Me})]\text{PF}_6$, were recovered by addition of MeI followed by precipitation with NH_4PF_6 . Formation of the adducts IIA and IIC was totally reversible on addition of NEt_3 as indicated by the IR spectrum.

Carbonyl substitution reactions and adduct formation with BF_3 have also been reported for sulfonyl complexes [15]. In this case the sulfonyl group is bound to the iron through the sulfur as in the thiolate complexes, while adduct formation occurs at an oxygen of the sulfonyl group to form a two atom bridge between the iron and the Lewis acid. Among the Lewis acids used in this study AlBr_3 gave the largest increase in the carbonyl stretching frequencies on adduct formation (Table 1). Thus it might be expected to show the greatest effect on the substitution reactions. The AlBr_3 adduct was prepared to determine if this type of coordination would cause displacement of the sulfonyl on reaction with nucleophiles as was observed with the mercaptide ligand. The IR spectrum of the adduct $\text{CpFe}(\text{CO})_2\text{SO}_2\text{Ph}(\text{AlBr}_3)$ (IIIC), indicates that AlBr_3 is bound at the oxygen of the sulfonyl as expected (Table 1). Addition of a phosphorus nucleophile to the adduct results in formation of free sulfonyl complex as determined by the appearance of the carbonyl bands of compound III in the IR spectrum. Substitution products were not isolated in any case even on refluxing the mixture for 24 h. Apparently the Lewis basicity of the sulfonyl oxygen is too low to compete with the phosphine nucleophile for the AlBr_3 .

These observations lead to the conclusion that Lewis acid coordination to a ligand Y, on $\text{CpFe}(\text{CO})_2\text{Y}$, has a pronounced effect on the course of substitution reactions occurring at the metal center. This is most evident with the thiolate complexes, $\text{Y} = \text{SPh}$, in which the mercaptide ligand, upon adduct formation, has its donor ability decreased enough that it, rather than a carbonyl, is displaced on reaction with nucleophiles. This behavior is also characteristic of the halide complexes, $\text{CpFe}(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{and I}$), where displacement of the halide occurs on reaction with nucleophiles in the presence of Lewis acid [10b,16]. However in these complexes the X group may also be displaced in the absence of the acid to form the ionic products. With the thiolate derivatives ionic products are detected only in the presence of the Lewis acids.

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