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CHELATING PHOSPHINES ON SILICA GEL

I. CARBONYL COMPLEXES AS A MEAN TO PROBE CHELATING LIGAND SITES

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Summary

Two methods for the preparation of the silica-bound chelating phosphine ligand bis(diphenylphosphino)maleimide have been studied. In the first a silica surface with bound amine groups is treated with bis(diphenylphosphino)maleic acid anhydride. By use of different Group VI carbonyl complexes $M(CO)_6$, $M(CO)_4L$ (M = Cr, Mo, W; L = norbornadiene) and $M(CO)_5Cl^-$ as IR probes it is shown that this method yields two different types of metal-binding sites on the gel, involving amine groups and bidentate phosphine groups, respectively.

In the second method bis(diphenylphosphino)maleic acid anhydride is treated with 3-aminopropyltriethoxysilane and the imide formed by this reaction is, without isolation, further condensed on the silica surface. Use of the same type of IR probes as in the first route shows that the silica gel in this case contains the bidentate phosphine group as the sole metal-binding site.

The preparations of new metal tetracarbonyl complexes for Cr, Mo and W bound to silica via bidentate phosphino groups are described.

Introduction

Chemical modification of surfaces of various supports has attracted much interest in recent years. The technique has found applications in several fields, e.g. matrix-binding of enzymes and co-factors [1], provision of stationary phases for gas and liquid chromatographic purposes [2,3], modification of electrodes [4], and the immobilization of homogeneous metal complex catalysts [5–12]. For catalytic applications two types of supports have been most frequently used, viz. polystyrene [5] and silica gel [13,14]. At present a number of synthetic procedures are known by which phosphines can be linked to polystyrene supports [5,15,16], and oxide supports can be phosphinated by the use of phosphine substituted silanes, e.g.

$R_2P(CH_2)_nSiX_3$ (X = alkoxy, chloro). The studies have mainly involved monodentate phosphine ligands.

Recent studies on catalytic reactions by metal complexes linked to solid supports

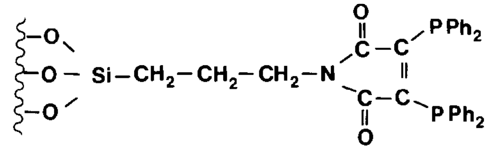


Fig. 1. The silica-bound bidentate phosphine ligand.

via monodentate phosphines have revealed that in many cases these catalysts are unstable with respect to reduction [17–19] and metal leaching [20,21]. This instability is not surprising, since in many examples of catalytic cycles involving metal complexes a metal–ligand dissociation reaction is a key step in creating a vacant coordination site. To improve catalyst stability the use of chelating ligands seems to offer a useful approach. This idea has been put forward by Marquardt [22] and Neuberg [23]. A summary of recent literature reports on bidentate phosphine ligands bound to solid supports can be found in Neuberg's thesis [23], in which the preparation of an active and stable cationic rhodium catalyst bound to silica via a chelating phosphine viz. $NBDRhL_2^+$ (L_2 = bis(diphenylphosphino)maleimide (Fig. 1)) is also reported. We have previously studied the use of cationic phosphinerhodium complexes viz. $[RhNBDL_2]^+ [ClO_4]^-$ for the catalytic hydrogenation of fatty oils [24]. In a further study of the cationic rhodium catalysts, we have tried to use the same ligand bound to silica. Our experience so far, however, has been disappointing; our silica bound complexes are usually stable in respect to metal particle formation (no colour change is observed), but unfortunately are also inactive. An obvious reason for the lack of activity is the presence of undesired ligands on the gel such as free amine groups, amidic acids and free surface hydroxyls. These groups, formed during the preparation of the gel, can act as catalyst poisons by blocking vacant coordination sites.

The present study had two aims. Firstly we sought a route by which undesired ligand sites on the surface can be avoided or minimized. Secondly we sought ways of proving the existence of potential ligand sites on the silica surface, which is not an easy task. Because of the very low concentration of such sites on the surface normal analytical and spectroscopic techniques are often not very informative [25], and so we used various IR probes. By treating metal carbonyl complexes with the functionalized gels, the nature of the ligand sites can be inferred from the infrared spectra of the resulting gels. This method has been frequently used in the past [26–29]. The bound metal carbonyl complexes are of interest in themselves besides being valuable infrared probes; Bailey and Langer [12] mentioned no Group VI metal carbonyl complexes containing bidentate ligands bound to silica and so the complexes prepared in the present study may have some novelty value.

Experimental

Materials

Analytical grade solvents were used throughout this work without further purification. The metal carbonyls were purchased from Alfa Ventron Chemicals. 3-Aminopropyltriethoxysilane (AMEO) (a gift from Dynamit Nobel, West Germany), was vacuum distilled before use. The silica gel used (Kieselgel 200) was purchased from Merck and purified by repeated washings with concentrated HCl followed by thorough washings with distilled water and finally drying in vacuum at 135°C.

Bis(diphenylphosphino)maleic acid anhydride (BDMA) was synthesized as described by Fenske et al. [30]. $Mo(CO)_4NDB$ [31], $M(CO)_4(Pyridine)_2$ [32] and $[M(CO)_5Cl]PPh_4$ [33] ($M = Cr$, Mo, W) were prepared by published methods. All syntheses and other manipulations were carried out under dry argon. UV irradiations were carried out with an 150W Hanau high-pressure mercury lamp equipped with a quarz cooling jacket.

Infrared spectra

Infrared spectra were recorded with a Perkin–Elmer 580 infrared spectrometer equipped with a PE data station. The phosphinated silica gel was examined as KBr pellets and the immobilized metal carbonyls as Nujol mulls.

Analyses

C, H, N elementary analyses were carried out at the Microanalytical laboratory, University of Lund. The phosphorus content was determined as described by Hershcovitz et al. [34]. For confirmatory determinations we used the iodine method of Bartholin et al. [19] except that the excess iodine was determined spectrophotochemically. The analytical results for the phosphinated silica gels are listed in Table 1.

Preparation of phosphinated silica gels

Route 1. The aminated silica was prepared as described by Allum et al. [13]. 10 g aminosilica was suspended in 150 ml toluene. 5.1 g bis(diphenylphosphino)maleic acid anhydride and 100 µl pyridine where then added. The suspension was stirred at 60°C overnight. The reaction vessel was then equipped with a Dean–Stark apparatus and heated under reflux for 8 h then the suspension was filtered. The isolated solid was extracted with toluene for 12 h in a Soxhlet apparatus and finally dried in vacuo. This gel is subsequently referred to as P2I(1).

Route 2. 0.56 g bis(diphenylphosphino)maleic acid anhydride was dissolved in 100 ml degassed THF. To this solution 0.17 ml freshly distilled 3-aminopropyltriethoxylsilane was added. The colour then changed from dark red-orange to yellow-orange. After 2 h stirring at room temperature 1.2 g dry silica gel 200 was added and the slurry was stirred for 12 h, during which the colour changed to dark

TABLE 1

ANALYTICAL DATA

	P(%)	N(%)	$\frac{\text{mmol bisphosphine}}{\text{mmol N}}$
P2I(1)	0.64	0.34	0.42
P2I(2)	1.75	0.40	0.98
Aminosilica	–	0.46	–

red. 100 ml toluene was added and the reaction vessel was equipped with a Dean–Stark apparatus and heated under reflux for 8 h, after which the mixture was filtered. The isolated orange gel was washed with several portions of THF, toluene, acetone and finally dried in vacuum at 30°C. This phosphinated silica gel is referred to as P2I(2). Analytical results are given in Table 1. IR(Nujol): 1703 cm^{-1} (s, $\nu(C{=}O)$).

Preparation of immobilized metal carbonyls

A. Photochemical reaction. About 1 mmol of the metal carbonyl ($M(CO)_6$) was dissolved in 50 ml degassed THF. After careful purging with argon the solution was irradiated for 1 h, then 0.2 g of P2I(2) (0.056 mmol ligand) was added and the resulting suspension was irradiated for 2 h. The gel was filtered off and washed several times with THF and toluene and finally dried in a stream of argon.

B. Thermal reactions. A suspension of 0.2 g P2I(2) and 0.5 g $W(CO)_6$ in 75 ml *o*-xylene was refluxed for 2 h. After cooling the solid was filtered off and washed several times with *o*-xylene and toluene.

C. Ligand exchange reactions. 0.3 g P2I(2) and an excess of $M(CO)_5ClPPh_4$ or $M(CO)_4L_2$ was equilibrated in acetone or THF for 2–4 hours. The mixture was filtered and the product washed several times with acetone.

Results and discussion

Preparation of the silica supported phosphine ligands

Reactions of hydroxyl groups on oxide surfaces with silylating agents, e.g. alkoxysilanes ($(RO)_3$–Si–R′) or halosilanes (X_3–Si–R′), do not fully remove all the hydroxyl groups on the surface [2,3]. Moreover the location of these hydroxyl groups is such that some unreacted alkoxy groups will remain [4] (Fig. 2). These unreacted hydroxy and alkoxy groups probably show little tendency to interact with a metal complex, but on treatment with aminoalkyltriethoxysilanes the hydroxyl groups might cause complications. Hydrogen bonding between surface bonded amine groups and hydroxyl groups [4] or between adjacent amine groups [35] will influence the likelihood of further reactions of the amine group (Scheme 1); even weak hydrogen bonding will make some of the amine groups inaccessible. The surface topology might increase this effect. Thus, as determined by ESCA [4]) only 6–27% of a propylamine modified SnO_2 surface could be brought into reaction with 3,5-nitrobenzoyl chloride to yield the desired surface bonded amide. Other investigators [36] have found, that only 20–50% conversion of bound amine groups can be achieved on silica gel surfaces.

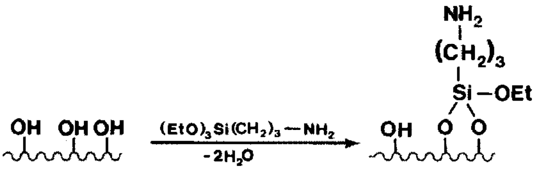
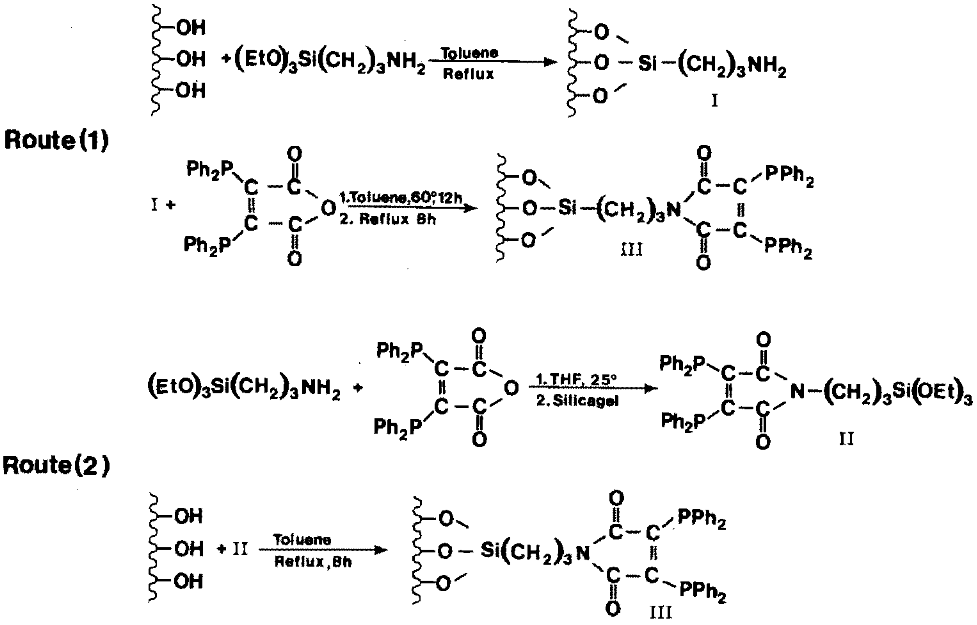


Fig. 2. Reaction of 3-aminopropyltriethoxysilane with surface hydroxyls on silica gel. Unreacted hydroxyls present on the surface.



SCHEME 1. Reaction sequences and conditions for the two preparative methods studied.

In Scheme 1 two different routes for the preparation of the silica-bound chelating ligand bis(diphenylphosphino)maleimide are outlined. Route 1 uses the traditional way of modifying silica surfaces, but in the present study only 42% (Table 1) of the surface bonded amine groups could be brought into reaction by this method; this is the highest figure we have reached and close to that observed by Neuberg (43–46%) [23], and in accord with the results in the similiar systems discussed above. The resulting silica gel thus contains two different ligand sites, viz. bidentate phosphine groups and amine groups.

In contrast, route 2 leaves almost no amine groups on the resulting gel. The principal difference between the two routes (Scheme 1) is the reaction sequence. To avoid reaction between the anhydride and the amine on the silica surface, this condensation was instead carried out in solution, where all the reactants are fully mobile and accessible for reaction. The imide II was then, without isolation, condensed on to the silica surface. To shift the equilibrium towards the imide site (II, Scheme 1) we used a 50% excess of the anhydride and carefully dried silica gel as the dehydrating agent. To avoid reactions of the ethoxy group on the 3-aminopropyltriethoxysilane it is important even at this stage to work under rigorously anhydrous conditions and to use freshly distilled organosilane, otherwise small primary particles of polymerized silane may form and they may contain amine groups inaccessible for further reaction with the anhydride. In the next step of the reaction (Scheme 1) this prepolymer can be condensed onto the silica surface. Provided that these careful steps are taken the preparation according to route 2 leads to a functionalized silica gel with only very small amounts of unreacted amine groups on the surface. This is shown by the ratio bisphosphine/nitrogen for the two preparations in Table 1. The increased incorporation of the phosphinomaleic unit in

TABLE 2

INFRARED STRETCHING FREQUENCIES IN THE ν(C–O) REGION FOR PREPARED SILICA-BOUND COMPLEXES AND REFERENCE COMPOUNDS

Metal	Preparation [a] method	Ligand [b]	ν(CO) frequencies (cm^{-1})					Medium	Ref.
Cr	1	P2I(1)	2063(w)	2015(m)	1981(m)	1937(s)	1895(s)	Nujol	This work
Mo	1,3	P2I(1)	2072(w)	2025(m)	1985(m)	1944(s)	1907(s)	Nujol	This work
W	1	P2I(1)	2067(w)	2020(m)	1979(m)	1930(s)	1900(s)	Nujol	This work
Cr	1,3	P2I(2)	2015(m)	1934(s)	1900(vs)			Nujol	This work
Mo	1,2,3	P2I(2)	2027(m)	1939(s)	1909(vs)			Nujol	This work
W	1,2,3	P2I(2)	2023(m)	1932(s)	1902(vs)			Nujol	This work
Cr	2	CHA	2067	1980	1935	1890		$CHCl_3$	32
Cr	2	BPE	2018	1932	1907			CS_2	40
Cr	1	BDMA	2021(m)	1937(m)	1910(s)			CCl_4	30
Mo	2	CHA	2072	1983	1938	1895		$CHCl_3$	32
Mo	2	BPE	2028	1937	1915			CS_2	40
Mo	3	BDMA	2031(m)	1947(m)	1924(s)			CCl_4	30
Mo	3	BDMM	2026	1922	1910	1890		$CDCl_3$	41
W	2	CHA	2071	1974	1929	1894		$CHCl_3$	32
W	2	BPE	2024	1930	1907			CS_2	40
W	1	BDMA	2028(m)	1940(m)	1916(s)			CCl_4	30

[a] 1 = photochemical, 2 = thermal, 3 = ligand exchange. [b] CHA = cyclohexylamine, BPE = bis(diphenylphosphino)ethylene, BDMA = bis(diphenylphosphino)maleic acid anhydride, BDMM = bis(diphenylphosphino)maleimide.

P2I(2) at the same amine loading as in P2I(1) is also apperent from the IR absorption intensities of the C=O stretching vibration of the imide (II, Scheme 1) at 1703 cm^{-1}.

As discussed above one possible reason for the low conversion of amine groups on a silica surface is hydrogen bonding. Moses et al. raised the question whether the metal ions are effective in disrupting such hydrogen-bonded amine structures [4], but found no answer in their study. However, if metal ions can coordinate to hydrogen-bonded amine sites, a gel functionalized according to route 1 (Scheme 1) will most probably seriously effect the chemical behaviour of metal complexes bound to it. It is thus important to assay potential metal interacting groups. To do this we used metal carbonyls as the reacting metal species.

Reactions of the silica supported ligands with metal carbonyl complexes

Group VI e.g. Cr, Mo, W hexacarbonyl complexes are known to react with many Lewis bases such as amines [32] or phosphines [30] to yield the corresponding $M(CO)_{6-x}L_x$ complexes. The reaction can be carried out in different ways, e.g. thermally, photolytically (eq. 1) or via the replacement of a less strongly bonded ligand (eq. 2). If such reactions are used to assay potential ligands on a solid surface, the product formed should be independent of the method of preparation and, above all, it should depend on the type of ligands present.

eq.1 $$M(CO)_6 + L \xrightarrow[\text{or heat}]{h\nu} M(CO)_{6-x}L_x + xCO$$

eq.2 $$M(CO)_{6-x}Y_x + L \longrightarrow M(CO)_{6-z}L_z + xY$$

eq.3 $$M(CO)_5X^- \xrightarrow[K_1]{L} M(CO)_4LX^- + CO \xrightarrow[K_2]{L} M(CO)_4L_2 + X^-$$

eq.4 $$M(CO)_5X^- \xrightarrow[K_3]{L} M(CO)_5L + X^-$$

The photolytic reaction (eq. 1), is a rather specific reaction and the amine groups which take part in this reaction may not react under other conditions. Thus we have supplemented the photolytic reaction by using the very mild ligand-substitution route of equation 2 (Y = norbornadiene). The observed formation of a $Mo(CO)_5$-amine complex (Table 2) for both reactions shows the existence of amine groups on P2I(1) which although inaccessible for further reaction with anhydride can coordinate metal atoms.

One other feature of the reaction of P2I(1) with $Mo(CO)_4NBD$ should be noted. The dissociation of the NBD ligand will leave two vacant coordination sites on the metal atom, and so the bidentate phosphine might easily form a *cis*-chelating bisphosphine complex. Such a complex is actually observed (Table 2). An isolated amine group on the gel, on the other hand, could lead to one of the hypothetical tetracarbonyl complexes in Fig. 3, but no such products were observed (Table 2). Instead we found the pentacarbonylamine complex, and evidently the vacant metal site is filled by a CO ligand. As no extra CO was added in the preparation, the CO incorporated is probably derived from some kind of decomposition of the neighbouring carbonyl complexes. Similar decompositions have been observed in other studies concerning carbonyl complexes on solid carriers [38,39], but no mechanism for the reaction has been suggested.

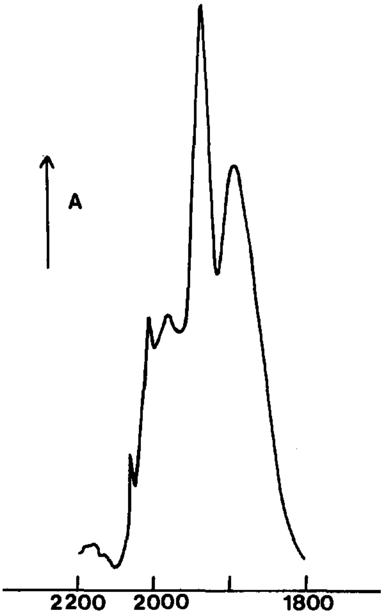
Fig. 3. Two possible substitution products from reaction of $Mo(CO)_4NBD$ with surface bound amine groups.

In Table 2 we list the infrared CO frequencies of the species we have prepared together with those for some selected reference compounds. For all our preparations from the P2I(1) gel the general spectral pattern observed (Fig. 4) is the same. It is rather complex but can be analysed in terms of two superimposed spectra of the two species present viz. the pentacarbonylamine complex and the tetracarbonylbischelating-phosphine complex. The bands of highest diagnostic value [37] are the $M(CO)_5$-amine A_1 mode at ≈ 2070 cm^{-1} (w), and the $M(CO)_4(P2I)$ A_1 mode at ≈ 2020 cm^{-1} (m). Many bands below 2000 cm^{-1} tend to coincide, but all the bands can nevertheless be seen more or less clearly.

For comparison we treated the molybdenum carbonyl with an aminated silica gel (not further treated with BDMA). The spectrum obtained for this preparation is in excellent agreement with our assignment of the pentacarbonylmonoamine bands in the other preparations viz. 2072 cm^{-1} (w), 1985 cm^{-1} (m), 1941 cm^{-1} (s), 1910 cm^{-1} (w,sh).

It is evident that the P2I(1) gel contains two different potential ligand groups. Both of these ligands can undoubtedly bind metal ions. The assumed hydrogen bonding of the amine groups does not prevent them taking part in metal coordination. The IR spectra of the product gels made from P2I(2) are clean and simple, showing only the pattern characteristic of a *cis*-$M(CO)_4L_2$ complex (Fig. 5). No trace of aminepentacarbonyl species are found. The positions of the bands are also in very good agreement with those found for similar soluble complexes (Table 2). Hence route 2 in Scheme 1 makes it possible to prepare a silica gel bearing the desired chelating bisphosphine as the sole metal binding group.

In addition to the two methods used to bring P2I(1) into reaction with carbonyl complexes, photochemical reaction with $M(CO)_6$ and reaction with $M(CO)_4NBD$, we have for P2I(2) also used thermal reaction with $M(CO)_6$ and treatment with the anionic pentacarbonyl halide complex $M(CO)_5Cl^- \; PPh_4^+$ ($M = Cr$, Mo, W); complexes of this latter type are known to react with donor ligands such as isonitriles [42], amines [43] and phosphines [44,45]. A number of different possible substitution products i.e. $M(CO)_5L$, $(M(CO)_4XL)^-$ and $M(CO)_4L_2$ complexes can be obtained depending on donor ligand, halide and solvent. Allen and Barret [45] report $K_1 \gg K_3$ for monodentate phosphines in the case of $M = Cr$, Mo and $X = Cl$, but $K_1 \approx K_3$ for $M = W$, $X = Cl$ (eq. 3 and eq. 4). In our preparations, regardless of



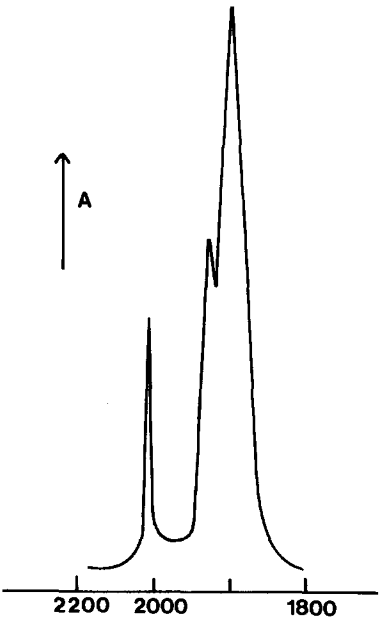


Fig. 4. IR spectrum in the CO stretching region of P2I(1) treated with $Cr(CO)_6$.

Fig. 5. IR spectrum in the CO stretching region of P2I(2) treated with $Cr(CO)_6$.

metal, we have found no evidence for any monosubstituted products, i.e. no $M(CO)_4XL^-$ complex or $M(CO)_5L$ (Table 2). For Cr and Mo this can be explained in terms of the reported rate constants [45] and the strong chelate effect of the phosphine used in our study. Once the kinetically favoured $M(CO)_4XL^-$ complex is formed it will react to form the observed bisphosphine complex because of the close proximity of the other phosphine group on the ligand. For W, on the other hand, on the basis of the same kinetic evidence [45] a mixture of the two complexes viz. $W(CO)_4LX^-$ and $W(CO)_5L$ would be expected, but the chelate effect will probably result in the formation of the bisphosphine complex from both these complexes. A product pattern in agreement with that expected on kinetic grounds i.e. $M(CO)_5L$ and $M(CO)_4L_2$ for Cr and Mo and for W also $W(CO)_4ClL^-$ was observed by Menzel et al. [38] in their study of polystyrene bound isonitrile ligands. This can be taken as a support for our assumption above that the reaction rates K_1, K_2, and K_3 (eq. 3 and 4) are not greatly altered by the use of matrix bound ligands, and thus the product pattern we have found is mainly due to the strong chelating effect of our ligand.

In the present study we have investigated potential ligand sites on silica gel by using carbonyl complexes as IR probes. Provided that the reacting complexes are carefully choosen much information can be gained this way. We are at present continuing our study with the aim of using silica systems as carriers for labile (i.e., catalytically active) as well as stable metal complexes.

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